

The Oxidation of Methyl Oleate

I. The Preparation, Properties and Reactions of Methyl Hydroperoxido Oleate¹

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Introduction

THE reactions by which fats are oxidized with molecular oxygen have been extensively investigated for many years. While numerous theories have been advanced to explain the mechanisms involved in the reactions none of these theories has found universal acceptance among fat and oil chemists. Inadequate knowledge concerning the structure of the primary products of oxidation has constituted the chief barrier to the development of a universally acceptable theory of autoxidation and to the solution of innumerable practical problems involving this phenomenon. Of particular significance, therefore, is the recent proposal by Farmer and Sundralingam (1) that the primary oxidation product of simple olefins is a hydroperoxide formed at carbons adjacent to olefinic linkages as the result of dissociation (probably of free radical nature) of hydrogens promoted presumably by electronic displacements in the double bond systems. In support of this theory previous work was cited in which it had been proved that the oxidation products of cyclohexene and related compounds were hydroperoxides (1, 2). Subsequently, Farmer and Sutton (3) presented evidence that the initial attack of oxygen on methyl oleate results in the oxidation of the methylene group ($-\text{CH}_2-$) at either the 8th or 11th carbon atom to form a hydroperoxide. They also suggested that methyl hydroperoxido oleate may contain hydroperoxides of *iso*-oleic acids (4). More recently, Atherton and Hilditch (5) investigated the oxidation of methyl oleate and reported that oxidation at 20° C. yielded a peroxide which formed to a large extent, though not necessarily exclusively, in the manner described by Farmer *et al.* and also that oxygen combined directly with the double bonds at 120° C. The last mentioned work was primarily concerned with the location of the hydroperoxide group through identification of the products of oxidative fission with potassium permanganate. The specimen of oxidized methyl oleate which they investigated contained *ca.* 55 percent of nonperoxidic impurities. No evidence was presented to indicate that the product obtained by oxidation at 120° C. was actually a primary product of oxidation.

Since a thorough knowledge of the constitution of the peroxide formed as the primary product of oxidation of methyl oleate was believed to be prerequisite to the investigation of the concurrent and subsequent reactions occurring in the oxidation system, efforts were made to verify the results reported by Farmer *et al.* and by Atherton and Hilditch. This work was extended to include an investigation of the method of

preparation, properties, reactions, and decomposition products of methyl hydroperoxido oleate. The present report includes a discussion of the work of Farmer *et al.* and of Atherton and Hilditch, as well as a description of an efficient method for preparing methyl hydroperoxido oleate, and some of the properties and reactions of this oxidation product.

Experimental

Hydroxyl numbers (mg. of potassium hydroxide per gm. of sample) were determined with acetic anhydride-pyridine reagent by the method of West, Hoagland, and Curtis (6); carbonyl values [mg. of carbonyl group (CO) per gm. of sample] by the method of Leithe (7); peroxide values [milliequivalents of peroxide oxygen (O_2) per kg.] by the method of Wheeler (8) except that a reaction time of three minutes was used; and iodine values by the Wijs method with a reaction time of 30 minutes. The absorption spectra were determined in 95 percent ethyl alcoholic solutions by means of a Beckman quartz spectrophotometer.

Preparation of Methyl Oleate and Methyl Hydroperoxido Oleate: Methyl oleate, iodine value, 85.0, $n_D^{25} = 1.4500$, was prepared from U.S.P. olive oil by the method of Wheeler and Riemenschneider (9).

Methyl oleate was partially oxidized with oxygen at *ca.* 35° C., while the sample was irradiated with ultraviolet light. The aeration apparatus consisted of a Pyrex flask mounted on a shaker and attached to a large gas burette. The ultraviolet irradiation was supplied by a Hanovia ultraviolet quartz lamp fitted with a type L burner which was placed about 20 inches from the reaction flask. In the procedure used, samples of 300 to 800 grams of methyl oleate were placed in the reaction flask and the gas burette and reaction flask were filled with oxygen equivalent to 3 to 4 times the quantity required for oxidation. Vigorous mechanical shaking was maintained throughout the period of oxidation which was continued until a peroxide value of about 300 was obtained, which required about 30 hours. Under these conditions approximately 90 percent of the oxygen absorbed was utilized in the formation of peroxides.

A slower, but otherwise satisfactory method of preparing methyl hydroperoxido oleate comprised reaction of methyl oleate in a flask immersed in a constant temperature bath held at 60° C. Air was rapidly passed through a sintered glass dispersion tube placed in the bottom of the reaction flask which acted to supply both oxygen and simultaneous agitation of the sample. In this method the aeration was discontinued when a peroxide value of 100 to 150 was obtained, which required 100 to 150 hours.

Separation of the Hydroperoxide: Two methods were employed to separate the hydroperoxide from

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unoxidized methyl oleate. In earlier work fractional molecular distillation was used, but later low temperature crystallization from acetone was employed.

Separation by molecular distillation was conducted in a cyclic, falling-film type of still having a total capacity of one kilogram. Usually a charge of about 500 gm. of partially oxidized methyl oleate was used for fractionation. Methyl oleate distilled at an average rate of 17 gm. per hour at *ca.* 50° C., and methyl hydroperoxido oleate distilled at an average rate of one to two grams per hour at *ca.* 90° C. The pressures, measured with a Pirani gauge near the distilling surface were 11 to 17 microns. The best fraction of peroxidized ester contained approximately 75 percent of methyl hydroperoxido oleate and 25 percent of some other product having the same oxygen content as the hydroperoxide. The concentrated methyl hydroperoxido oleate represented about 20 percent of the total peroxide which was present in the oxidized methyl oleate. The total yield of the various hydroperoxide fractions of reasonably high purity amounted to approximately 40 percent of the hydroperoxide present in the original oxidized methyl oleate.

Separation of methyl hydroperoxido oleate by low temperature crystallization was accomplished by dissolving the oxidized methyl oleate in five volumes of acetone and cooling the solution overnight at -80° C. The crystalline, unoxidized methyl oleate was removed by filtration at -80° C. and the soluble methyl hydroperoxido oleate was recovered on removing the solvent from the filtrate under vacuum. The fraction containing the concentrated hydroperoxide was dissolved in 2.5 to 3 volumes of acetone and cooled for 48 hours at -80° C. The solid and liquid phases were separated by filtration at -80° C. and the methyl hydroperoxido oleate was recovered from the filtrate by removal of the solvent under vacuum. The product consisted of 85 to 90 percent methyl hydroperoxido oleate, based on the observed peroxide value. This yield represents about 60 percent of all the hydroperoxide which was present in the original partially oxidized methyl oleate. A flow sheet of operations and yield obtained in a typical preparation of methyl hydroperoxido oleate, based on weights and peroxide values of the fractions, is given in Figure 1.

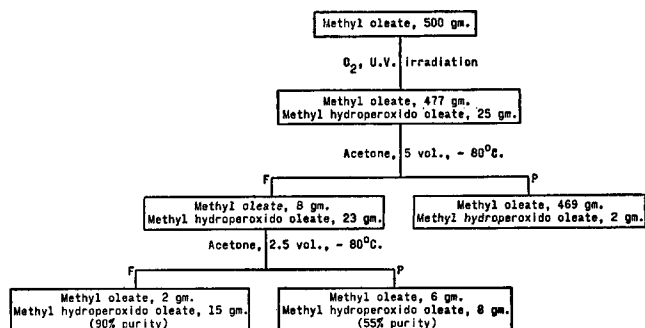


Fig. 1. Flow sheet of operations and yields in preparation of methyl hydroperoxido oleate.

Properties of Methyl Hydroperoxido Oleate: Some of the characteristics of the methyl hydroperoxido oleate prepared by the above methods are shown in Table 1, along with the corresponding calculated values. The hydroperoxide is a colorless, practically

TABLE 1
Characteristics of Methyl Hydroperoxido Oleate

	Prepared by molecular distillation	Prepared by low temperature crystallization	Calculated
Peroxide value.....	4,500	5,600	6,100
Iodine value.....	71.9	71.3	77.4
Hydrogen absorption ml./g. ¹	125.1	130.0	130.0
Specific gravity, 24°/4°.....	0.950	0.951
Refractive index, N _D ²⁰	1.4628	1.4610
Molecular refractivity.....	95.0	94.7	95.1 ²
Carbon, percent.....	69.5	69.1	69.5
Hydrogen, percent.....	11.0	10.9	11.05
Oxygen, percent (by difference)...	19.5	20.0	19.45

¹ Platinum oxide catalyst.

² Hoch's [Hoch, H., and Lang, S., *Ber.*, 75, 300-313 (1942)] value of 4.10 was used as the refraction equivalent of the hydroperoxide group.

odorless, mobile liquid, which is readily soluble in ordinary organic solvents. Storage for a month or more at 0° C. produced no discernible changes in the product. When kept in an open beaker at 25°-28° C. and exposed to daylight passing through window glass, the peroxide content decreased about 13 and 30 percent in 30 and 60 days, respectively. At temperatures of 120° C., or higher, the hydroperoxide decomposed rapidly and at 150° C. complete decomposition occurred in 15 minutes. The ultraviolet absorption spectrum of a typical specimen of methyl hydroperoxido oleate is shown in Figure 2. On comparing the ultraviolet absorption spectra of several specimens of

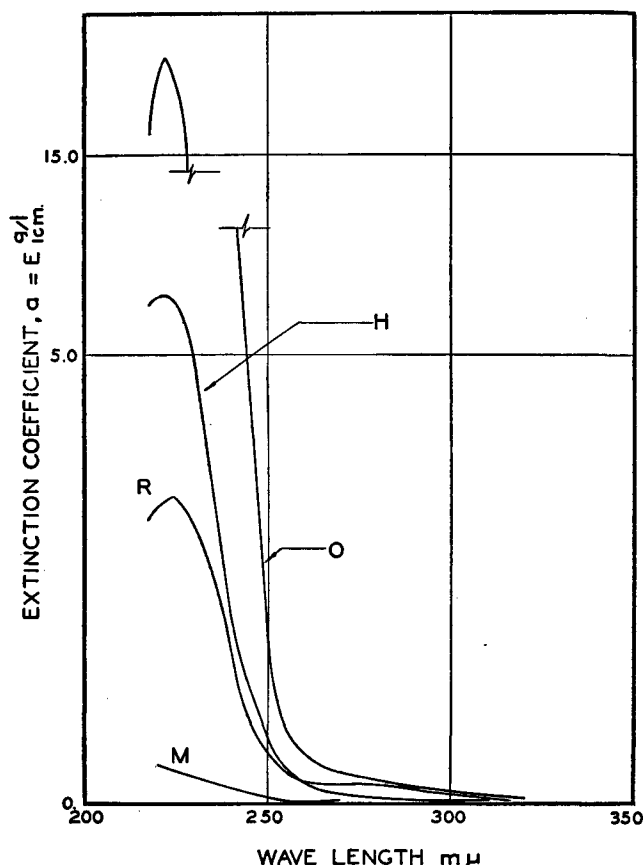


Fig. 2. Ultraviolet spectral absorption of methyl oleate, hydroperoxide of methyl oleate and products derived from the hydroperoxide.

O—Hydroperoxide oxidized with lead tetraacetate.
H—Hydroperoxide of methyl oleate.
R—Hydroperoxide reduced with hydrogen iodide.
M—Methyl oleate.

the hydroperoxide only insignificant differences were found, principally consisting in small variations in the intensity of the maximum absorption at 222 μ .

Hydrogenation: Methyl hydroperoxido oleate (6.06 gm.) was hydrogenated in the presence of platinum oxide as catalyst during which process 792 ml. of hydrogen was absorbed. After saponification and acidification of the hydrogenated product, 5.28 gm. or 86.7 percent of crude mixed monohydroxystearic acids, m.p. 54°-59° C., was recovered. Analysis of this product gave carbon, 72.5 percent; hydrogen, 11.8 percent; neutralization equivalent, 300; compared with calculated values, carbon, 72.0 percent; hydrogen, 12.0 percent; neutralization equivalent, 300. On recrystallization from acetone the melting point of the product was raised to 62°-63° C. A relatively insoluble product (0.5 gm.; m.p., 68.5° C.) was separated and identified as stearic acid on the basis of carbon, hydrogen, and molecular weight determinations.

Oxidation With Potassium Permanganate: The products of fission of the hydroperoxide with potassium permanganate were determined essentially by the method described by Atherton and Hilditch (5). Methyl hydroperoxido oleate (9.8 gm.) was dissolved in acetone (100 ml.), and oxidized by the addition, in small portions of potassium permanganate (39 gm.).

The mixed acids recovered from the oxidation product were separated by steam distillation into fractions consisting essentially of mono- and dicarboxylic acids. The monocarboxylic acids were distilled through an efficient column to give two further fractions having neutralization equivalents of 142 and 154, respectively, from which were prepared *p*-toluidides melting at 58°-60° C. and 72°-74° C., respectively. It is apparent that the original monocarboxylic acids consisted of a difficultly separable mixture from which no single pure acid could be unequivocally identified but which probably contained both caprylic and pelargonic acids (theoretical neutralization equivalents of acids 144 and 158, literature m.p. of *p*-toluidides, 66° C. and 80°-81° C., respectively).

The dicarboxylic acid fraction was further separated by crystallization from chloroform into two additional fractions as follows: 1.1 grams of a product melting at 139°-141° C., neutralization equivalent 89.5; 1.1 grams of a second product, melting at 92°-97° C., neutralization equivalent 93. The latter product after recrystallization from ethyl acetate melted at 102° C. The original mixture of dicarboxylic acids therefore may be considered to have consisted of suberic acid (m.p. 141° C., neutralization equivalent 87.0; and azelaic acid, m.p. 106° C.; neutralization equivalent 94).

Reduction With Hydrogen Iodide: To a solution of methyl hydroperoxido oleate (6.3 gm.) in 250 ml. of chloroform-glacial acetic acid (2:3) 15 ml. of a saturated solution of potassium iodide was added. After 5 minutes 200 ml. of distilled water was added and the iodine in the solution was reduced by the addition of a solution of sodium thiosulfate. The chloroform layer containing the reaction product was separated from the aqueous layer and washed several times with water. The chloroform solution was dried with anhydrous sodium sulfate and the solvent removed under vacuum. On analysis the reaction product gave carbon, 71.5 percent; hydrogen, 11.3 percent;

iodine, 0.76 percent; iodine value, 74.2; hydroxyl number, 154. Its ultraviolet absorption spectrum is included in Figure 2. The product appeared to consist essentially of methyl monohydroxy oleate which requires carbon, 73.1 percent; hydrogen, 11.6 percent; iodine value, 81.3; hydroxyl number, 179. The product was hydrogenated in the presence of a platinum oxide catalyst, saponified, and the crude acids were recovered. By fractionally crystallizing these acids, mixed monohydroxy stearic acids (m.p. 58°-60° C.) were separated in *ca.* 70 percent yield.

Reaction With Alkali: A solution of 6 gm. of the hydroperoxide and 12 gm. of potassium hydroxide in 125 ml. of 95 percent ethanol was heated under reflux for two hours. On diluting the solution with water, acidifying, extracting with ethyl ether and evaporating the solvent, an oil was obtained which had the following characteristics: peroxide value, 0; iodine value, 71.6; carbonyl value, 7.0; hydroxyl number, 161.0. The product was identified on the basis of these characteristics as consisting principally of monohydroxyoleic acid.

Reaction With Hydroxylamine: Methyl hydroperoxido oleate (4.2 gm.) was heated under reflux for 20 minutes with 230 ml. of hydroxylamine solution prepared in the manner described by Leithe (7). An apparent carbonyl value of 114 was obtained by titrating an aliquot of the reaction mixture by the method described by Leithe. Distilled water was added to the main portion of the solution after which the solution was extracted with ethyl ether. The ethereal solution, after thorough washing with water, was dried with anhydrous sodium sulfate, and the soluble product recovered by removing the solvent under vacuum. This product consisted of an oil with the following characteristics: peroxide value, 0; hydroxyl number, 142; carbon, 68.4 percent; hydrogen, 10.5 percent; nitrogen, 2.6 percent. Efforts to crystallize the product were unsuccessful.

Oxidation With Lead Tetraacetate: The hydroperoxide (10 gm.) was dissolved in 90 ml. of glacial acetic acid and 20 gm. of lead oxide (Pb_3O_4) was added in small portions. A mildly exothermic reaction occurred and 185 ml. of gas was evolved. When the evolution of gas had ceased (after *ca.* 2 hours), 200 ml. of distilled water was added, and the product was extracted with ethyl ether. The ethereal solution of the product was washed several times with distilled water and then with an aqueous sodium bicarbonate solution to remove the last traces of acetic acid. The solution was washed free of sodium bicarbonate with several portions of distilled water and dried with anhydrous sodium sulfate after which the product was recovered by removing the solvent under vacuum. It consisted of an oil with the following characteristics: peroxide value, 0; iodine value, 37.5; carbonyl value, 79; hydroxyl number, 58; epoxy oxygen, 1.90 percent; carbon, 70.4 percent; hydrogen, 10.7 percent. The ultraviolet absorption spectrum is included in Figure 2.

Reaction of Methyl Hydroperoxido Oleate and α -Tocopherol: A mixture of methyl hydroperoxido oleate (0.3789 gm.) and α -tocopherol (0.1885 gm., Merck) was prepared and stored in an open microbeaker at room temperature in diffused daylight. The peroxide and tocopherol contents of the mixture were determined at intervals over a 55-day period. The results are presented graphically in Figure 3.

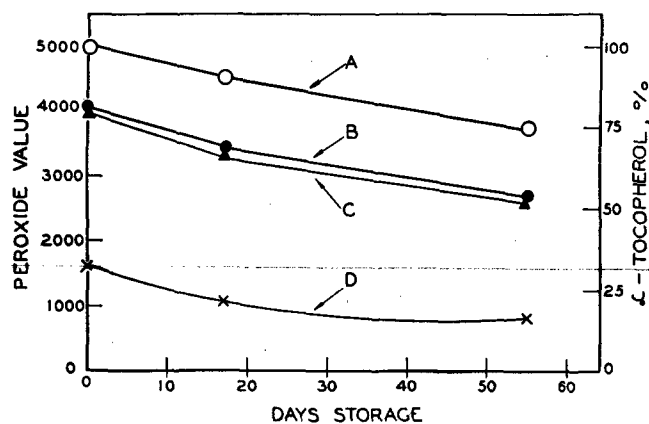


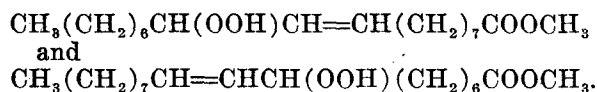
FIG. 3. Peroxide decomposition (curves A, B, and C) and α -tocopherol disappearance (curve D) in a mixture of 32.5 percent α -tocopherol and 67.5 percent methyl hydroperoxido oleate.

- A. ○ Peroxide decomposition of methyl hydroperoxido oleate.
 B. ● Peroxide decomposition of α -tocopherol-peroxide mixture (calculated from A).
 C. ▲ Peroxide decomposition of α -tocopherol-peroxide mixture.
 D. × α -tocopherol content of α -tocopherol-peroxide mixture.

Discussion

The preparation of methyl hydroperoxido oleate of 85 to 90 percent purity was accomplished by partially oxidizing methyl oleate under conditions selected to effect maximum utilization of oxygen in the formation of hydroperoxides and separating the reaction product from unoxidized ester by either molecular distillation or low temperature fractional crystallization. The fractionation of the peroxide from the unoxidized ester by molecular distillation was not accomplished as satisfactorily as the fractionation reported by Farmer *et al.* (3) owing probably to differences in the type of stills used and to the fact that distillation in the present instance was carried out in large batches. Compared with the method of separating the peroxide by molecular distillation, the method of low temperature crystallization from acetone is advantageous because (a) decomposition of the peroxide during the separation is eliminated, (b) the method is rapid and results are readily reproducible, and (c) the scale of operation is optional within a broad range.

While the structure of the oxidation product obtained could not be rigorously proved, the experiments reported, including repetitions of some previously reported by Farmer *et al.* and by Atherton and Hilditch, support the proposal of Farmer *et al.* that the first product of oxidation of methyl oleate is methyl hydroperoxido oleate, *i.e.*, it is a mixture of the isomers



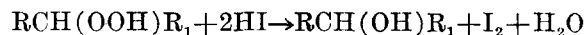
The evidence is summarized as follows: (a) the iodine value, 71.3, indicated that the oxidation product is unsaturated although the presence of a saturated impurity tends to lower the iodine value (71.3; 71.9) below the calculated iodine value, 77.4 (Table 1); (b) one mole of peroxide absorbs 2 moles of hydro-

gen to form methyl monohydroxy stearate; (c) oxidative fission yields caprylic, pelargonic, suberic, and azelaic acids which would be expected from the structures assumed for the product of oxidation⁴; (d) the molecular refractivity, 94.7, agrees well with the calculated value, 95.1 (Table 1); (e) reduction with hydrogen iodide yields mainly methyl hydroxy oleate as has previously been reported in the case of reduction with aluminum amalgam.

It was observed that the hydroperoxide was colorless, practically odorless, and hence not responsible *per se* for the organoleptic changes which are observed in oxidizing fats. The hydroperoxide proved to be relatively stable over a reasonably broad temperature range, a factor of prime importance in any theory that attempts to relate the formation of peroxides as intermediates in the production of subsequent products presumed to be responsible for the development of off-odors and flavors of deteriorated fats.

The ultraviolet absorption spectra of the hydroperoxide and the products produced from it by reduction or oxidation with hydrogen iodide and lead tetraacetate, respectively, are qualitatively similar. Since the peroxide content of the derived products was nil or negligibly low, the hydroperoxide group is not responsible for the characteristics of these products; *i.e.*, this group has no specific absorption in the ultraviolet region unless, as appears unlikely, the hydroperoxide, the reduced hydroperoxide containing a hydroxyl group, and the oxidized hydroperoxide containing a carbonyl group have absorption in the region of *ca.* 222 $m\mu$. The substance responsible for the absorption in the diene region (maximum at *ca.* 222 $m\mu$) is as yet unknown.

The reduction of hydroperoxide with hydrogen iodide, as used in ordinary peroxide determinations, has been assumed to release one mole of iodine per mole of hydroperoxide. According to the literature (10) the products produced by reaction between hydrogen iodide and cyclic peroxides are dihydroxy and epoxy compounds. However, present observations indicate that methyl hydroperoxido oleate reacts in molar proportions to produce methyl monohydroxy oleate with liberation of one mole of iodine as shown in the following equation:



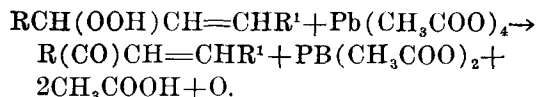
The action of strong alkali on the hydroperoxide was investigated to determine whether the reaction was similar to that which occurs on treating the hydroperoxides of cyclohexene and related compounds with this reagent (1). The results indicate that the reaction consists essentially of the conversion of the hydroperoxido group to a hydroxyl group, as is the case with the hydroperoxides of cyclohexene and related compounds.

A completely reliable method for determining the carbonyl content of the oxidation products of methyl oleate is not available. The reaction between methyl hydroperoxido oleate and hydroxylamine was investi-

⁴ It should be pointed out that the same fission products would result from permanganate oxidation of a mixture of the methyl esters of 9-hydroperoxido-10-octadecenoic acid and 10-hydroperoxido-8-octadecenoic acid if these products were formed during oxidation of methyl oleate by a shift of the unsaturated linkage, a mechanism which has been shown to occur in the case of the oxidation of 1,2-dimethyl- Δ^1 -cyclohexene by E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 1946, 10-13.

gated because of the anomalous results obtained in attempts to estimate the carbonyl content of the hydroperoxide and of methyl oleate in various stages of oxidation. It was found that one mole of hydroperoxide reacts with 1.3 moles of hydroxylamine to produce a product with *ca.* 60 percent of the nitrogen required for the corresponding oxime. These results confirm those of Treibs that hydroperoxides react in a complex manner with hydroxylamine (11).

The behavior of methyl hydroperoxido oleate with lead tetraacetate is significant in view of Criegee's observation (2) that other hydroperoxides behave in a characteristic manner which may be represented by the equation:



This reaction is of further interest in view of the fact that the absorption spectrum of the reaction product exhibited a considerably increased absorption at 222 $m\mu$, $E_{1\text{cm}}^{2\%} = 16.1$, as compared with the absorption spectrum of the unoxidized hydroperoxide at 222 $m\mu$, $E_{1\text{cm}}^{2\%} = 4.7$ (Figure 2). The carbonyl value of the lead tetraacetate reaction product, 79.0, indicates that the hydroperoxide group was converted almost quantitatively to a carbonyl group. However, the results of the carbonyl value determination are not necessarily reliable. According to the above equation the product should be an α,β -unsaturated ketone. The absorption spectrum of the reaction product did not exhibit a maximum at 275 $m\mu$, which is the region in which ketones have been reported as absorbing strongly. However, this should be the case if the reaction product is assumed to be an α,β -unsaturated ketone, since absorption in the region 220-230 $m\mu$ has been cited by Woodward (12) as typical of singly substituted α,β -unsaturated ketones.

Combustion data indicated that the oxygen content of the lead tetraacetate reaction product was practically the same as the oxygen content (20.0 percent) of the hydroperoxide. This fact, plus the presence in the reaction product of appreciable hydroxyl and epoxy oxygen, indicates that side reactions occurred during reaction of the lead tetraacetate in which oxygen attacked the double bonds. Obviously the reaction observed in the present instance is more complex than that described by Criegee.

It has been suggested that at the end of the induction period in oxidizing fat systems, the tocopherols inhibiting oxidation have disappeared (13, 14) owing, presumably, to the fact that they have undergone oxidation by one or more of the products of prior fat oxidation. On mixing methyl hydroperoxido oleate with α -tocopherol no appreciable oxidation-reduction reaction occurred (Figure 3), indicating that substances with higher oxidation potential are apparently responsible for the oxidation of α -tocopherol in oxidizing fats.

Summary

Low temperature fractional crystallization from acetone has been applied to the separation of methyl hydroperoxido oleate in 85 to 90 percent purity from partially oxidized methyl oleate. The hydroperoxido ester was subjected to hydrogenation, oxidative fission, and reduction with hydrogen iodide. Certain characteristics of the original hydroperoxide and its reaction products have been described. The results obtained lend definite support to the view that the first oxidation product of methyl oleate is a mixture of 8- and 11-hydroperoxido octadecenoic acids, at least under the conditions employed, *i.e.*, oxidation under the influence of ultraviolet light or reaction temperatures up to 60° C.

The spectral absorption of methyl hydroperoxido oleate and some derived products was determined. The hydroperoxide group was shown to have no characteristic absorption in the ultraviolet region.

The reactions of the peroxide with alkali, hydroxylamine, lead tetraacetate, and α -tocopherol have been described and discussed.

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