

84. *The Mechanism of Oxidation of Monoethenoid Fatty Acids and Esters. The Course of Thermal Catalytic Oxidation of Methyl Oleate.*

By J. H. SKELLON.

Highly purified methyl oleate was oxidised at 120° by gaseous oxygen in the presence of a vanadium catalyst, under conditions which resulted in little or no disruption or dimerisation of the carbon chain.

The initial attack by oxygen appears to take place mainly at the ethenoid linkage but the hydroperoxide undergoes rapid transition at this temperature and the final oxidation products are more complex.

The neutral non-disrupted oxidation products were separated and examined directly, without study of the scission products. They consisted chiefly of an oily monomeric complex of approximate composition $C_{18}H_{34}O_6$, in which one molecular proportion of oxygen is considered to be present as an irreducible peroxide, and a smaller proportion of a compound identifiable with isomeric hydroxy-keto-stearates.

The structure of the complex is discussed and a mechanism is advanced to account for the changes occurring during gaseous oxidation of monoethenoid fatty acids and esters.

ATHERTON and HILDITCH (*J.*, 1944, 105) showed that during autoxidation of methyl oleate at 20° and 120°, attack by oxygen at the methylene groups adjacent to the ethenoid bond was much less at 120° than at 20°. At the higher temperature, Gunstone and Hilditch (*J.*, 1945, 836) observed that peroxidation occurred mainly at the ethenoid group. Swern, Scanlan, and Ault (*J. Amer. Chem. Soc.*, 1945, 67, 1132), as a result of prolonged oxidation at 65°, separated an oxidation product of methyl oleate consisting partly of methyl monohydroxy-esters of one or more monomeric unsaturated acids in which the ethenoid linkage had apparently migrated from the 9 : 10-position.

These investigations indicate that in thermal oxidation of methyl oleate, oxygen attack may take place additively and substitutively in varying degree. At moderate temperatures (below 35°) such reactions may be similar to the photochemical oxidations of methyl oleate carried out first by Farmer and Sutton (*J.*, 1943, 119) and later by Swift, Dollar, and O'Connor (*Oil and Soap*, 1946, 23, 355), from which it is suggested that the primary oxidation product is a mixture of 8- and 11-hydroperoxido-octadecenoic acids.

It has become increasingly doubtful whether a mechanism involving oxygen attack at a methylene group adjacent to the ethenoid linkage is applicable to thermal oxidations; the experimental work to be described lends support to the view, recently expressed by Gunstone and Hilditch (*J.*, 1946, 1023) and Hilditch (*J. Oil Col. Chem. Assoc.*, 1947, 30, 1), that original entry of oxygen into the unsaturated system must be at the double bond.

Although it seems conclusive that the initial oxidation product is a hydroperoxide as opposed to a cyclic peroxide, it is by no means certain whether the isomeric forms are either (a) 10-hydroperoxido-octadec-8-enoate and 9-hydroperoxido-octadec-10-enoate or (b) 11-hydroperoxido-octadec-9-enoate and 8-hydroperoxido-octadec-9-enoate.

Thermal oxidation results in the disappearance of peroxidic oxygen, but little is known concerning the exact nature of the hydroperoxide transition product and the structure of the non-disrupted oxidised carbon chain.

In the present investigation, changes occurring at various stages of oxidation in the C_{18} chain before disruption have been studied, and a mechanism is advanced to account for such changes. Highly purified methyl oleate was oxidised by gaseous oxygen at 120° in the presence of a vanadium or cobalt catalyst, under conditions adjusted to give a maximum oxidation without rupture of the carbon chain. After 6 hours, the peroxide oxygen content reached a maximum at only 16% of the theoretical value (Calc. for $C_{18}H_{36}O_4$: 4.88% active oxygen), thereafter decreasing steadily. Extensive thermal catalytic oxidations of the ester and the parent acid have shown that, under such conditions, the initial peroxides rapidly undergo changes into secondary oxidation products.

During the transition phase (marked by peroxide decomposition) there was little evidence of abnormal changes in the rate of decrease of unsaturation, that in the first 6 and in the last 4 hours being 9.6 and 7.8 units per hour, respectively. The observed fall in iodine value was considerably greater than that required for exclusive formation of peroxide at the ethenoid linkage, and it was evident that the secondary reactions prevailing at 120° preclude any simple relationship between the observed iodine value and that calculated on the above assumption. The increase in free acidity was comparatively small up to 10 hours.

The conditions of oxidation resulted in little or no dimerisation, whilst the small percentage

of carbon destroyed (considerably less than 1 atom per mol. of ester) indicated no extensive disruption of the carbon chain. The amount of oxygen ultimately consumed was greater than that required for a hydroperoxide or isomeric derivative. Such changes were invariably observed during numerous catalytic oxidations of the ester and of oleic acid, the stage at which peroxidic oxygen formation was at a maximum being dependent on the conditions of oxidation. These observations partly afford an explanation of the apparently anomalous results noted by many workers during the atmospheric oxidation of glycerides and fats at various temperatures.

The detailed oxidation data are given in Table I. Peroxide values are expressed as % of active oxygen [Calc. for $C_{19}H_{36}O_4$: 4.88% active oxygen = 9.76% total peroxidic oxygen (Farmer and Sutton) = 3050 ml. of 0.002N-thiosulphate per g. (Atherton and Hilditch) = 6100 milli-equivs. per kg. (Swift, Dollar, and O'Connor, *loc. cit.*)].

From data available, comparative peroxide values obtained during oxidations by various authors are expressed in terms of active oxygen :

| (i). | (ii). | (iii). | (iv). |
|---|---|--|---|
| Farmer and Sutton <i>(loc. cit.)</i> . | Gunstone and Hilditch <i>(J., 1945, 836)</i> . | Author. | Swift, Dollar, and O'Connor <i>(loc. cit.)</i> . |
| 0.64% (photochemical, 4 hrs.). | 120° (4 hrs.). 1.17% (max.). 0.77% (7 hrs., decreasing). | 120° (4 hrs., catalytic). 0.56% (increasing). 0.54% (7 hrs., decreasing). | 0.24% (photochemical, 30 hrs.). |

The Oxidation Products.—The yellowish-red oily oxidation product at 6 hours, containing the maximum peroxidic oxygen attained, gave *M*, 333 (Calc. for $C_{19}H_{36}O_4$: *M*, 328). After 10 hours, it contained little free peroxidic oxygen (0.2% active oxygen), and was almost saturated. Qualitative tests indicated the presence of ketonic derivatives. The neutral product (85%) was separated and examined in order to ascertain the precise nature of the peroxide transition.

Successive treatment with large volumes of light petroleum at low temperature resulted in recovery of a semi-crystalline product (25%), completely saturated and containing no appreciable amount of peroxidic oxygen. Analysis showed that it contained one carbonyl group per mol., and was apparently identical with a mixture of isomeric 9-hydroxy-10-keto- and 10-hydroxy-9-keto-stearates. Comparative analysis of specimens of such isomeric hydroxyketostearic acids, prepared from oleic acid by the method of King (*J.*, 1936, 1788), confirmed the nature of the product.

Catalytic thermal oxidation of methyl oleate appears to result in partial transition of the hydroperoxide grouping to the grouping $-CO-CH(OH)-$ but the comparatively low yield of this oxidation product indicated either that concurrent changes occur or that the neutral ketol in turn undergoes further transition. The main oxidation product was therefore examined for presence of neutral monoxides or dihydroxy-derivatives. Methyl oxido-oleate and oxido-elaidate were not found in the product of thermal catalytic oxidation at 120°; under these conditions there seem to be little grounds for the supposition that epoxy-compounds of this nature result from interaction between peroxide and ethenoid linkage. Ellis (*Biochem. J.*, 1936, 30, 753) isolated oxido-oleic and -elaidic acids from the autoxidation products of elaidic and oleic acids at moderate temperature (60–70°), and Dorée and Pepper (*J.*, 1942, 477) obtained oxido-brassicic acid during catalytic oxidation of erucic acid at 70° and 120°.

This isolation of oxido-acids from the products of catalytic oxidation of three mono-ethenoid acids at temperatures between 60° and 120° is significant, as it has a direct bearing on the mechanism of autoxidation. It is possible that neutral oxido-derivatives if formed are less easy to isolate; on the other hand, it is difficult to reconcile this with modern views that epoxy-compounds are not formed in the oxidation and polymerisation of the parent oils.

The absence of appreciable amounts of neutral dihydroxy-derivatives was also confirmed; the non-disrupted oxidised product consisted largely of an oily complex together with a minor proportion of the neutral ketone.

The Complex Oxidation Product.—The residual dark brown oil (60%) was almost saturated and contained only a small percentage of peroxidic oxygen capable of liberating iodine from potassium iodide. On strong heating in a vacuum, this peroxidic oxygen disappeared and there was some evidence of disruption. Analysis indicated a main monomeric constituent of approximate composition, $C_{19}H_{36}O_6$, very resistant to the action of boiling alcoholic potash; it appeared to be a neutral analogue of the complex obtained during catalytic oxidation of oleic acid (see Skellon, *J. Soc. Chem. Ind.*, 1931, 50, 382r).

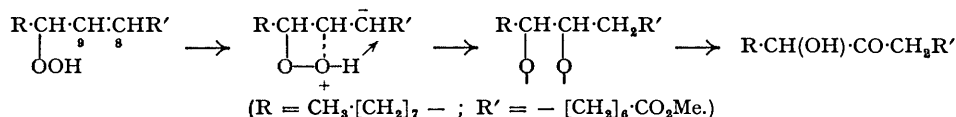
Further examination of the products obtained by oxidising oleic acid at 120° with various

catalysts has confirmed that breakdown into cleavage products is not extensive up to 7 hours. No free dihydroxystearic, oxido-oleic, or oxido-elaidic acids were found, but there was evidence of the presence of minor proportions of ketones in the material separated from light petroleum at low temperature. The complexes were partly broken down by alcoholic potash, affording small quantities of dihydroxystearic acid, m. p. 132°, and acids of high equivalent weight similar to those formerly described (Skellon, *loc. cit.*).

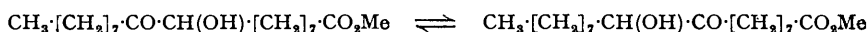
The oily complex is invariably obtained during autoxidation of monoethenoid acids and esters; similar products have also been observed during atmospheric oxidation of fats at high temperature. It is considered that at least one type may be formed as the result of enolisation of a $^{-}\text{CO}\cdot\text{CH}(\text{OH})^{-}$ group at temperatures above 100° with subsequent further entry of oxygen; ultimate dimerisation or polymerisation may be due to cross linkage between such molecules, and is not due to formation of epoxides.

A Mechanism of Gaseous Oxidation of Methyl Oleate applicable to Monoethenoid Fatty Acids and Esters.—The course of catalytic oxidation of methyl oleate is considered to take place as follows: (1) Initial attack by oxygen at the ethenoid bond, with formation of the 9-hydroperoxido-octadec-10-enoic and 10-hydroperoxido-octadec-8-enoic esters suggested by Gunstone and Hilditch (*J.*, 1946, 1023).

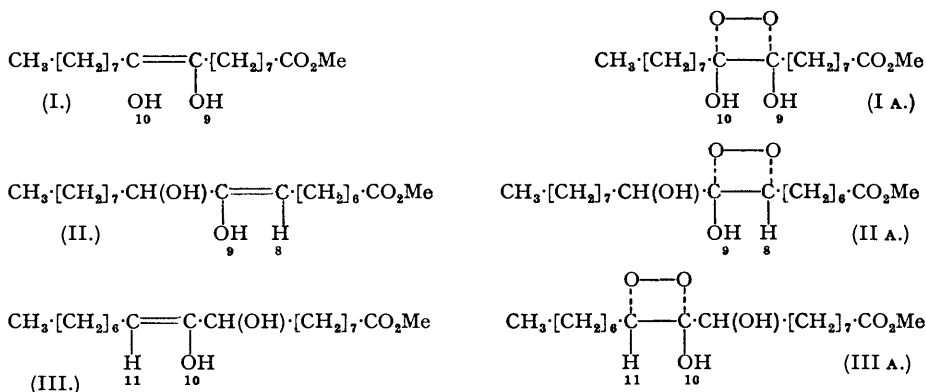
(2) Intermediate transition of the hydroperoxides to isomeric hydroxyketostearates, with consequent diminution in peroxidic oxygen content:



(3) The isomeric ketol carboxylic esters enolise or rearrange in thermal oxidations, and further entry of oxygen results in formation of a monomeric complex containing "bound" peroxidic oxygen not reducible by interaction with potassium iodide:



may thus give rise to (I), (II), or (III). The further entry of oxygen thus results in complexes ($\text{C}_{19}\text{H}_{36}\text{O}_6$) which may have the possible structures (IA), (IIA), or (IIIA). The mode of



attachment of the "bound" peroxidic groups (shown by dotted lines) may or may not involve a cyclic structure. Subsequent oxidation of (IIA) and (IIIA) would result in formation of a carbonyl group at the 10 and the 9 position respectively, giving a product, $\text{C}_{19}\text{H}_{34}\text{O}_6$.

Breakdown of these complexes at the 9: 10-, 8: 9-, and 10: 11-positions would account for the various scission products obtained by different authors: (a) nonoic and azelaic acids from (IA), (b) suberic and ketodecoic acids from (IIA), (c) octoic and oxalic acids from (IIIA). The reported presence of irreducible peroxides in fats submitted to atmospheric oxidation at high temperature may be accounted for by formation of complexes of a similar character.

It is noteworthy that application of the mechanism to the alternative attack by oxygen at methylene groups adjacent to the ethenoid linkage could result in formation of 8:9- and 10:11-ketol carboxylic esters, eventually giving rise to complexes not very dissimilar in structure, but more resistant to further attack by oxygen. The possibility of both reactions

proceeding concurrently under certain conditions cannot be excluded in the light of present knowledge.

EXPERIMENTAL.

Methyl Oleate.—The ester used was prepared from oleic acid (purified as described by Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 131r), the amount recovered being 88%; b. p. 165–166°/3–5 mm. (Found: equiv., 296; I.V., 87.3. Calc. for $C_{19}H_{38}O_2$: equiv., 295; I.V., 85.8). Samples not sealed under an inert gas absorbed atmospheric oxygen slowly at room temperature (Found, after 24 hrs., 6 months, and 12 months: I.V., 77.5, 70.1, 68.8, respectively). The last specimen then contained 1% of peroxidic oxygen expressed as active oxygen.

Catalytic Oxidations.—The oxidation apparatus consisted of a wide-mouthed glass container fitted with a Bakelite cover, through which passed a bell-shaped perforated stirrer, together with an inlet tube for oxygen terminating as a jet inside the hollow dome. Constant temperature was maintained by use of the usual thermostatic temperature control in an oil-bath. The delivery of a slow stream of dry oxygen at the jet with rotation of the special stirrer at high speed ejected a fine spray of oil and gas bubbles through the perforations, thus ensuring intimate mixing. Carbon dioxide evolved was absorbed in baryta solution. The purified freshly distilled ester (48 g.) containing sufficient vanadium oleate to provide 0.02% of vanadium was oxidised at 120° for 10 hours. A similar oxidation was carried out using 0.03% of cobalt (as oleate) as catalyst. The results are given in Table I (Calc. for $C_{19}H_{38}O_4$: active oxygen, 4.88%). Peroxide values were determined iodometrically; control determinations were carried out simultaneously on pure benzoyl peroxide.

TABLE I.

Catalytic oxidation of methyl oleate at 120°.

| Time (hours). | 1. | 4. | 6. | 10. | | | | | | |
|---|-------|-------|-------|-------|------|------|------|----|------|------|
| (Catalyst, 0.02% V as oleate.) | | | | | | | | | | |
| Iodine value (Wijs) | 71.9 | 52.7 | 29.3 | 8.6 | | | | | | |
| Fall in iodine value | 15.4 | 34.6 | 58.0 | 78.6 | | | | | | |
| Rate of fall (units per hour) | 15.4 | 8.5 | 9.6 | 7.8 | | | | | | |
| Acid value | — | 10.5 | 19.7 | 35 | | | | | | |
| Sap. value | 215.6 | 221.1 | 228.0 | 292.0 | | | | | | |
| Peroxide value (% active oxygen) | — | — | — | 0.3 | | | | | | |
| (Catalyst, 0.03% Co as oleate.) | | | | | | | | | | |
| Peroxide value | 0.42 | 0.57 | 0.76 | 0.40 | | | | | | |
| Peroxide value (as % of theoretical) | 8.7 | 11.6 | 15.5 | 8.3 | | | | | | |
| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
| Peroxide values taken at hourly intervals | 0.42 | 0.48 | — | 0.57 | 0.63 | 0.76 | 0.54 | — | 0.41 | 0.40 |

In order to verify the general trend of peroxide changes, a series of gaseous oxidations was carried out with pure oleic acid, the peroxidic oxygen content being determined at regular intervals. Typical data were:

Catalytic oxidation of oleic acid at 120°.

| Time (hours). | 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|----------------------------|---|------|------|------|------|------|------|
| Catalyst | (0.05% of metal as oleate or naphthenate) | | | | | | |
| | Peroxide-oxygen, % active oxygen. | | | | | | |
| Vanadium | 0.22 | 0.33 | 0.38 | 0.40 | 0.57 | 0.34 | 0.20 |
| Cobalt (naphthenate) | — | 0.51 | — | — | 0.60 | 0.78 | 0.26 |
| Barium | — | 0.86 | — | — | 0.92 | — | 0.35 |

Examination of Oxidation Products.—The oxidised ester (6 hours, 120°, 0.02% V) was a yellowish-red oil soluble in alcohol, chloroform, carbon tetrachloride and warm light petroleum [Found: acid value, 19.7; sap. value, 228; I.V., 19.7; peroxide value, 0.28%; *M* (Menzies-Wright), ebullioscopic in chloroform, 333; in carbon tetrachloride, 308. Calc. for $C_{19}H_{38}O_4$: *M*, 328]. At 10 hours the same specimen was darker and more viscous (Found: I.V., 8.6; acid value, 35; sap. value, 292; peroxide value, 0.2%).

The Neutral Oxidation Product.—The oxidised ester (10 hours, 120°, 0.02% V) was washed with a 20% solution of sodium carbonate, the alkaline liquors being repeatedly extracted with ether; 25.1 g. (84%) of a neutral product were recovered (Found: I.V., 8.3; sap. value, 267; peroxide value 0.2%). It gave qualitative tests for ketols.

10 G. were dissolved in 100 ml. of chloroform and cooled below 0° for 24 hours. No dihydroxystearate separated. The chloroform was removed, and the residue warmed with 400 ml. of light petroleum and cooled well below 0° for 36 hours. After filtration of the ice-cold petroleum, there remained 0.3–0.4 g. (3%) of a white crystalline deposit on the sides of the vessel, and 2.5 g. (25%) of a semi-solid product. The former was identified as methyl dihydroxystearate not previously separated by use of chloroform; m. p. 68° [Found: *M* (Rast), 325. Calc. for $C_{19}H_{38}O_4$, methyl dihydroxystearate: *M*, 330]. The m. p. of methyl dihydroxystearate is 71°. The semi-solid product melted at a lower temperature and gave qualitative tests for a ketone. It was again treated with light petroleum at 0° and attempts were

made to crystallise it from dilute alcohol. Analysis gave the following results: Found: I.V., 3.5; peroxide value, 0.1%; C, 69.65; H, 10.86; >CO, 10.4; *M* (Menzies-Wright), ebullioscopic in chloroform, 330. Calc. for $C_{18}H_{34}O_4$: C, 69.50; H, 10.97%; *M*, 328; 1 >CO per mol., 8.5%; 2 >CO per mol., 17.1%.

Control determinations of carbonyl content were carried out simultaneously on a specimen of isomeric 9-hydroxy-10-keto- and 10-hydroxy-9-keto-stearic acids prepared from oleic acid by King's method (*J.*, 1936, 1788) (Found: >CO, 8.8%; peroxide value, 0; *M*, by titration, 312. Calc. for $C_{18}H_{34}O_4$: *M*, 314; 1 >CO, 8.9%). The m. p. was 64–65°.

Specimens (10 g.) of the neutral product were examined for the presence of neutral oxido-oleates or oxido-elaidates, by adaptation of Ellis's method (*loc. cit.*) for isolation of the parent oxido-acids during autoxidation of elaidic acid. No neutral oxido-derivatives were isolated.

The neutral product was further examined for presence of methyl dihydroxystearate. 5 G. were dissolved in acetone and left below 0° for 72 hours, but no crystalline material separated. On repetition of the process with minimal amounts of solvent, 0.3 g. of semi-crystalline material was recovered and hydrolysed (Found: I.V., 0; equiv., 359). The 0.3 g. of semi-crystalline material was therefore not methyl dihydroxystearate, which would give a dihydroxystearic acid of m. p. 132° or 95°.

The Complex Neutral Oxidation Product.—The bulk light petroleum mother-liquors after separation of the ketol carboxylic ester from 10 g. of oxidised methyl oleate (10 hours, 120°, 0.02% V) were evaporated down, affording 6 g. (60%) of a yellowish-brown oil (Found: acid value, 17; I.V., 8.2; sap. value, 280; peroxide oxygen content, 0.5%). On strong heating in a vacuum, the small peroxidic oxygen content disappeared and there was an odour of aldehydic products. The oil saponified with difficulty on prolonged boiling with alcoholic potash, giving sap. equiv., 201, indicating only partial disruption.

A second specimen of these oily products was obtained from the neutral oxidation product obtained during a similar oxidation of methyl oleate, 0.03% of cobalt being used as catalyst. 7 G. of oxidised methyl oleate (10 hours, 120°, 0.03% Co) were dissolved in 50 ml. of chloroform and kept for 48 hours below 0°. As no solid separated, the chloroform was removed, and the residue dissolved in 200 ml. of light petroleum and cooled below 0° for 60 hours. 1.4 G. (20%) of semi-crystalline product were recovered (Found: I.V., 19.3; peroxide value, 0.59%; C, 69.49; H, 10.89. Calc. for $C_{18}H_{34}O_4$: C, 69.50; H, 10.97%). This product gave qualitative tests for ketols, and appeared to be similar to the keto-derivative obtained in the oxidation using 0.02% V as catalyst.

Evaporation of the light petroleum mother-liquors resulted in recovery of 4.5 g. (64%) of a yellowish-brown oily product (Found: I.V., 26.7; sap. equiv., 227.5; peroxide value, 0.5%; C, 60.01; H, 9.41. Calc. for $C_{18}H_{34}O_6$: C, 63.3; H, 10.0%).

Acidic Oxidation Products.—After removal of the neutral product from 30 g. of oxidised methyl oleate (10 hours, 120°, 0.02% V), the alkaline extracts were boiled with excess of alcoholic potash. On acidification and extraction with ether, 3 g. (10%) of mixed acidic products were recovered [Found: I.V., 15; equiv., 158. Calc. for $C_9H_{18}O_2$: equiv., 158. Calc. for $C_9H_{18}O_2 + C_9H_{18}O_4$ (monobasic and dibasic acid): mean equiv., 126].

Comparative Catalytic Oxidations of Oleic Acid.—A series of oxidations were carried out on the pure parent acid, using the same catalysts—vanadium and cobalt—and the same conditions of oxidation. Analytical data for the products at 7 hours, 120°, are given in Table II. These results indicated that the

TABLE II.

Catalytic oxidation of oleic acid (7 hours, 120°).

| Catalyst, % (oleate). | Acid value. | Analysis. | | | | | Calc. for: | C, %. | H, %. |
|---------------------------|----------------|-----------|--------------------|----------------|-------|-------|-------------------|-------|-------|
| | | I.V. | Peroxide value. | Sap. value. | C, %. | H, %. | | | |
| V, 0.04 | 172.4 | 50.7 | 0.20 | 243.6 | 68.0 | 10.29 | $C_{18}H_{34}O_4$ | 68.8 | 10.82 |
| V, 0.08 | 161.4 | 20.1 | 0.16 | 283.6 | 62.04 | 9.15 | $C_{18}H_{34}O_6$ | 62.43 | 9.83 |
| Co, 0.05 (naphthenate) | 170.6 | 47.9 | 0.26 | 245.2 | 68.69 | 8.83 | $C_{18}H_{34}O_4$ | 68.8 | 10.82 |
| Co, 0.05 | 169.7 | 38.3 | 0 | 260.0 | 62.32 | 9.20 | $C_{18}H_{34}O_6$ | 62.43 | 9.83 |
| Co, 0.05 | — | — | — | — | 61.66 | 9.41 | $C_{18}H_{34}O_6$ | 62.43 | 9.83 |

final products in the more efficient short gaseous oxidations of oleic acid had an approximate composition, $C_{18}H_{34}O_6$. Qualitative tests indicated the presence of small proportions of ketones. The products were saponified with difficulty, the ultimate products being dihydroxystearic acid, m. p. 132° (5–7%), and oxidised acids of high equivalent—indicating only partial disruption into scission products.

Oxidised oleic acid (0.05% Co as naphthenate), 7 hours 120°: no free dihydroxystearic acid was separable. 10 G. were dissolved in light petroleum; after standing at 0° for 24 hours, 2 g. (20%) of semicrystalline material were recovered (Found: acid value, 181; equiv., 347.3; I.V., 25.8). After evaporation of the light petroleum an oily residue (6–7 g.) was recovered (Found: mean equiv., 343. Calc. for $C_{18}H_{34}O_6$: 346).

Oxidised oleic acid (0.05% Co as oleate, 7 hours' oxidation at 120°): 6 g. were saponified on prolonged boiling with alcoholic potash. After removal of alcohol, acidification and extraction with light petroleum and ether, there were recovered: 2.5 g. (42%) of acids soluble in light petroleum (Found: mean equiv., 290), 2.4 g. (40%) of brown oily oxidised acids soluble in ether (Found: equiv., 306), and 0.3–0.4 g. (5%) of white solid acids, which were recrystallised from alcohol (Found: equiv., 314. Calc. for dihydroxystearic acid, $C_{18}H_{34}O_4$: equiv., 316); m. p. 131–132° (lit., 131–132°).