39. *The Union of Gaseous Oxygen with Methyl Oleate at 20° and 120°*

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Oxygen was agitated with methyl oleate at 20° and 120° and the products obtained were partially separated by adsorption on silica gel. Portions of the separated products were oxidised in acetone solution with potassium permanganate, and the amount and nature of the mono- and di-carboxylic acid scission products examined.

The oxidised ester from the experiment at 20° yielded substantial proportions of suberic and octoic, as well as of azelaic and nonoic, acids, thus proving that to a large extent (although not necessarily exclusively) peroxidation had occurred at the $-CH_2-$ groups adjacent to the ethenoid bond (cf. Farmer *et al.*, *Trans. Faraday Soc.*, 1942, **38**, 134, 348, 356; J., 1943, 119).

The oxidised esters from the experiment at 120° gave much smaller yields of these mono- and di-carboxylic acids; the latter, moreover, contained only traces of suberic acid, and octoic acid could not be detected, nonoic and azelaic acids alone being obtained in quantity. At the higher temperature oxygen therefore appears to combine directly with the ethenoid bond, and in addition further changes of a more complex character probably take place, leading to oxidation at other points of the carbon chain.

Farmer and co-workers (J., 1943, 119) have recently shown that photochemical autoxidation of methyl oleate at 35° involves conversion of a $-CH_2-$ group adjacent to the ethenoid bond into a hydroperoxide $-CH(O\cdot OH)\cdot CH{:}CH-$. Other investigators (*e.g.*, Morrell *et al.*, *J. Oil Col. Chem. Assoc.*, 1929, **12**, 183; 1936, **10**, 264, 359; *Trans. Faraday Soc.*, 1942, **38**, 262), studying the autoxidation of conjugated systems (elæostearic derivatives), have demonstrated that with these compounds a peroxide is produced at the double bond itself, which may undergo rearrangement into a ketol, $-CO\cdot CH(OH)-$. The explanation of the variant observations may be connected with the temperature at which the action of oxygen on the unsaturated fatty derivative takes place, or on the nature of the latter (monoethenoid, non-conjugated multi-ethenoid, or conjugated multi-ethenoid). It appeared that the method of disruptive oxidation by means of powdered permanganate in acetone solution (Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44** 43T) which has proved useful in determining the position of ethenoid linkings in unsaturated long-chain acids, might throw further light on the course of autoxidation of these compounds under different conditions. Whilst union of oxygen with the ethenoid bond itself would be expected to afford an oxidised product which would give the same scission products (azelaic and nonoic acids) as the unoxidised compound, the mechanism suggested by Farmer *et al.* should involve the appearance of suberic and octoic acids in addition, on further oxidation of an autoxidised oleic derivative.

We have examined the autoxidised products obtained from methyl oleate at 20° and 120° in the manner outlined above, and have found that the course of the action is very different according to the temperature employed. Other experiments on similar lines are in progress in which the products of autoxidation of methyl linoleate, linolenate and elæostearate will be similarly examined.

Autoxidation of Methyl Oleate by Oxygen at 20°.—Methyl oleate (containing a small proportion of methyl linoleate) was stirred with oxygen in bright daylight at room temperature (*ca.* 20°) over a prolonged period amounting in all to 34·5 days (*i.e.*, 24-hour periods). At the end of this time its peroxide value was 920 (calc. for complete conversion into peroxide, 3050) and its iodine value 72·7. This fall in iodine value is greater than that demanded by the exclusive formation of hydroperoxide, but only about half of that which would occur if the peroxide were wholly that produced by union of oxygen with the double bond. Moreover, as the following figures show, this relationship persisted throughout the autoxidation :

Time of exposure (days).	Peroxide value.	Peroxide,[1] %.	Iodine value.		
				Drop in I.V.	
			Observed.	Observed.	Calc.[2]
0	0	—	89·8	—	—
9·5	323	10·6	85·2	4·6	9·1
14	497	16·3	83·2	6·6	14·0
20·5	646	21·2	78·6	11·2	18·2
27	840	27·5	75·7	14·1	24·6
34·5	920	30·2	72·7	17·1	27·1

[1] Calculated from the theoretical full peroxide value of 3050.

[2] Calculated on the assumption that the peroxide is formed at the double bond, and its iodine value nil.

These figures therefore suggest that the autoxidation at 20° did not follow exclusively either of the supposed mechanisms, unless all the reduction in iodine value could be accounted for by secondary interaction of hydroperoxide with methyl oleate.

The final product was dissolved in light petroleum and separated into fractions by passage through a column of powdered silica gel, and subsequent development of the adsorbate with fresh light petroleum. About half of the ester passed through into the filtrates; this portion had I.V. 81 and a peroxide value of 170 (for details see Experimental, p. 107) and thus consisted very largely of unoxidised methyl oleate. The mean iodine and peroxide values calculated from those of the fractions separated by adsorption were 76·3 and 734, *i.e.*, respectively higher and lower than those (72·7 and 920) of the original oxidised ester. This is ascribed to some loss of oxygen and restoration of unsaturation during heating under reduced pressure (in order to remove the last traces of solvent), a feature previously noted by Hilditch and Lea (J., 1928, 1577). It may be observed that an increase of 3·6 units of iodine value is accompanied by a fall of 180 units in peroxide value, figures which are consistent with loss of oxygen from an ethenoid peroxide and equally inconsistent with loss of oxygen from a hydroperoxide (in which case an increase of 3·6 in iodine value corresponds with a fall of about 1300 in peroxide value).

The material left on the silica gel (40% of the whole) was eluted with acetone in six portions, which had iodine values of 51—63 and peroxide values of 1200—1350. These were re-assembled into two fractions, representing the adsorbates on the upper and the lower part of the column, for oxidation in acetone with permanganate. The yields of mono- and di-carboxylic acids obtained in this way were as follows:

	Fraction oxidised, g.	Unoxidised residue, g.	Acidic products.		Combined yield of acids on material oxidised, %.
			Monobasic, g.	Dibasic, g.	
Upper adsorbate	8·45	1·34	2·35	3·06	76
Lower ,, ...	8·95	1·50	3·21	3·14	85

In each case the dicarboxylic acids were found to consist of a mixture of suberic and azelaic acids. The approximate amounts isolated were 0·7 g. of suberic and 1·0 g. of azelaic acid from the upper adsorbate, and 0·8 g. of suberic and 1·6 g. of azelaic acid from the lower adsorbate.

The monocarboxylic acids from the two permanganate–acetone oxdiations were combined and fractionated; fractions were then obtained with equivalents (148·3 and 150·7) intermediate between those of octoic and nonoic acids (144 and 158).

These results confirm Farmer's view that autoxidation of methyl oleate at the ordinary temperature involves conversion of the methylene group at carbon atom 8 or 11 of the acyl chain into hydroperoxide. The 8-hydroperoxido-oleic ester furnishes suberic and nonoic acids on oxidative scission, azelaic and octoic acids resulting similarly from 11-hydroperoxido-oleic ester. Since there is no evidence at present regarding the relative proportions in which the 8- and 11-hydroperoxides may be formed, it is not possible to judge, from the comparative yields of the four acids, whether production of hydroperoxide is the sole mechanism operative under these conditions. As already mentioned, however, the observed alterations in iodine value during autoxidation at 20°, and during recovery of the eluted products (cf. above), were considerably greater than would have been the case if hydroperoxide formation had been exclusive, and we consider that the results indicate that, whilst the latter may well preponderate at 20°, an appreciable proportion of the autoxidation product must be formed by union of oxygen with ethenoid groups.

Autoxidation of Methyl Oleate by Oxygen at 120°.—After stirring in presence of a current of oxygen at 120° for 6 hours, the iodine value of the methyl oleate was reduced to 14·4, and the product was a viscous reddish-yellow oil, of which 22% (fraction A, iodine value 17·4) was insoluble in light petroleum. The portion soluble in light petroleum was adsorbed, as in the previous experiment, on a column of silica gel, the adsorbate being developed with light petroleum. The filtrates (30%, fraction C) had iodine values of 22—37, whilst the portions left adsorbed on the silica gel (48%, fraction B) had iodine values of 12—16. No unaltered oleate appeared to be present, but the products of autoxidation seemed to consist of three main groups differing somewhat in iodine value and, respectively, insoluble in light petroleum, soluble in the latter but unadsorbed by silica gel, and soluble in light petroleum but adsorbed from solution by silica gel. Each group was oxidised with permanganate, fractions A and B in acetone solution, and fraction C (which resisted oxidation in acetone) in glacial acetic acid solution. The yields of mono- and di-carboxylic acids obtained were as follows:

	Fraction oxidised, g.	Unoxidised residue, g.	Acidic products.		Combined yield of acids on material oxidised, %.
			Monobasic, g.	Dibasic, g.	
A (insoluble in light petroleum)	9·1	1·2	1·53	1·97	44
B (adsorbed on silica gel)	20·0	3·4	1·36	3·90	32
C (filtrates from silica gel)	12·1	0·8	3(?)	3·18	55

The weights of acids recovered, expressed as a percentage of the materials oxidised, were very much lower than those in the preceding experiment, which in turn were somewhat lower than those normally obtained from a fresh, unoxidised specimen of methyl oleate (90—95%; cf. Armstrong and Hilditch, *loc. cit.*). It is inferred that a considerable proportion of the scission products must have been acids of low molecular weight, which owing to their volatility or high solubility in water escaped isolation by the procedure employed. This suggests that, during autoxidation at 120°, points in the acyl chain other than the unsaturated centre are attacked by oxygen subsequently to the initial action at or adjacent to the ethenoid group.

Examination of each group of dicarboxylic acids showed that they consisted for the most part of azelaic acid. Only small amounts of suberic acid were isolated, the weights of crude suberic acid obtained from the dibasic acids (1·97 g., 3·90 g., and 3·18 g.) from fractions A, B, and C being respectively 0·10, 0·32, and 0·13 g. The crude monocarboxylic acids from permanganate–acetone oxidations of A, B, and C were fractionally distilled, fractions with equivalents of 158·6 and 166·4 being obtained; no indication of the presence of octoic acid was detected in this case.

The results of autoxidation of methyl oleate at 120° thus point to almost complete absence of hydroperoxide at the 8th or 11th carbon atom of the acyl chain. The action which takes place at this temperature appears to proceed exclusively at the ethenoid group itself, and is probably followed by secondary action at other points in the acyl chain; it is extremely rapid in comparison with that of the formation of hydroperoxides.

EXPERIMENTAL.

The methyl oleate employed had been distilled under 0·1 mm. pressure through a fractionating column in order to eliminate minor amounts of palmitic or lower saturated esters. Its iodine value, 89·8, showed that it contained a small proportion (4·5%) of methyl linoleate.

The autoxidations were carried out in a 250 c.c. three-necked flask, fitted with mechanical stirrer (*ca.* 300 r.p.m.), thermometer, inlet and outlet tubes. A current of oxygen was passed through the ester throughout the experiments.

Autoxidation of Methyl Oleate at 20°.—The ester (55·4 g.) was stirred with oxygen during daylight for a total period of 828 hours (equivalent to 34·5 days). The alterations in peroxide and iodine value during this period have been illustrated on p. 105. The pale yellow liquid product (48·6 g.) was dissolved in light petroleum (250 c.c., b. p. 40—60°), filtered from slight turbidity, and passed down a 14″ column of activated dried silica gel. No clearly visible bands of colour were observed. The adsorbate was developed by passage of further light petroleum (450 c.c.), the filtrates being collected in three portions. The column was drained and cut into six portions, each of which was eluted with acetone. The peroxide and iodine values of the esters recovered from each portion, and from the filtrates, were as follows :

	Wt., g.	Peroxide value.	Iodine value.
Column, top ½ inch	0·51	1231	56·9
,, ,, ½—2½ inches	1·96	1214	50·6
,, ,, 2½—4½ ,,	2·48	1350	54·3
,, ,, 4½—7¾ ,,	4·08	1016	56·7
,, ,, 7¾—11 ,,	5·84	1278	60·9
,, bottom 3 inches	3·42	1270	63·4
Filtrate, third (200 c.c.)	3·36	432	79·1
,, second (200 c.c.)	21·64	170	81·4
,, first (250 c.c.)	1·83	nil	76·1

The upper four portions (9·03 g.) and the lower two portions (9·26 g.) of oxidised esters from the column were respectively combined, and each was further oxidised in acetone solution with powdered potassium permanganate.

Upper portions of adsorbate. The four mixed fractions (8·45 g.) were dissolved in acetone (85 c.c.), and the solution kept at the boiling point during gradual addition of powdered potassium permanganate (35 g.); the action proceeded smoothly. The solvent was removed, and the product reduced with bisulphite and taken up in ether. The ethereal solution was washed with potassium carbonate solution until all acidic products were removed, and incompletely oxidised ester (1·34 g.) was recovered from the ether. The aqueous carbonate washings were made strongly alkaline with caustic potash (5 g.) and evaporated on the steam-bath to a small volume, the semi-ester of the dicarboxylic acids formed during the oxidation being concurrently hydrolysed. The concentrated solution was made acid and distilled in steam until 2 l. of aqueous distillate were collected; on extraction with ether these yielded 2·35 g. of monocarboxylic acids. The residue from the steam distillation was thoroughly extracted with ether, which removed 3·06 g. of solid dicarboxylic acids.

The dicarboxylic acids were first crystallised from chloroform, which deposited crude suberic acid (0·68 g., m. p. 130—135°); after several crystallisations from ethyl acetate the acid melted at 138—141° (unchanged when mixed with authentic suberic acid, m. p. 140—142°). The acids left in solution in the chloroform were recovered and crystallised from ethyl acetate, impure azelaic acid (0·65 g., m. p. 94—99°, unchanged when mixed with pure azelaic acid, m. p. 104°) being deposited. The ethyl acetate mother-liquors still contained acids which, on crystallisation from water, gave further small quantities (0·34 g. in all) of crude azelaic acid.

Lower portions of adsorbate. The two mixed fractions (8·95 g.) were oxidised in acetone (90 c.c.) with permanganate (36 g.), and the product worked up as in the preceding case. The initial action with permanganate was much more vigorous than in the former case. The products obtained were incompletely oxidised ester (1·50 g.), monocarboxylic acids (3·21 g.), and dicarboxylic acids (3·14 g.).

The dicarboxylic acids, on crystallisation from chloroform at 20°, gave crude suberic acid (0·79 g., m. p. 130—135°), which after recrystallisation melted at 135—140° (138—140° when mixed with suberic acid, m. p. 140—142°). The chloroform mother-liquors were cooled at 0° and then deposited crude azelaic acid (1·13 g.), which on crystallisation from water gave a product, m. p. 92—100° (unchanged when mixed with pure azelaic acid). The acids left in solution in chloroform at 0° were recovered and crystallised from water, further quantities (0·46 g.) of crude azelaic acid being isolated.

The monocarboxylic acids from both portions of the oxidised adsorbates (2·35 g. and 3·21 g.) were combined and distilled at 15 mm. pressure through a long electrically-heated and packed fractionating column; two fractions (0·40 g. and 1·89 g.) were obtained with equivalents of 148·3 and 150·7 respectively (Calc. for $C_8H_{16}O_2$, 144; for $C_9H_{18}O_2$, 158). The acids (0·67 g.) recovered from a fraction which preceded these and which also contained small proportions of aldehydic or ketonic compounds had an equivalent of 121, corresponding with a mixture of octoic and hexoic acids; the latter probably resulted from oxidation of the small proportion of linoleate present in the original ester.

Autoxidation of Methyl Oleate at 120°.—The ester (39·7 g.) was maintained at 120° whilst it was stirred with oxygen. The fall in iodine value was very rapid compared with the previously-described experiment at 20° :

Time (hours)	0	0·5	1·5	2·5	3·5	4·5	6·0
Iodine value	89·8	84·9	63·4	39·8	27·7	19·5	14·4

The product (a reddish-yellow oil) was taken up in light petroleum (b. p. 40—60°, 150 c.c.); an insoluble portion then separated, which was extracted twice with further portions (75 c.c.) of the solvent. The light petroleum solutions were united and passed down a 14″ column of activated dried silica gel, the adsorbate being further developed by washing with three successive portions (200 c.c. each) of light petroleum. No clearly visible bands of colour appeared on the column of silica gel, which, after draining, was cut into five portions, each being then eluted with acetone. In all, the following fractions were thus obtained :

	Wt., g.	Iodine value.	Colour and consistency.
Insoluble in light petroleum	9·30	17·4	Dark, viscous.
Column top fifth	3·97	12·0	Light yellow, mobile.
,, second fifth	6·16	12·6	,, ,, ,,
,, third fifth	3·56	13·3	,, ,, ,,
,, fourth fifth	3·25	16·2	,, ,, ,,
,, bottom fifth	2·96	15·4	,, ,, ,,
Filtrate fourth (200 c.c.)	0·50	27·1	Almost colourless.
,, third (200 c.c.)	1·00	26·5	Very pale yellow.
,, second (200 c.c.)	8·43	22·0	Light red-yellow.
,, first (250 c.c.)	2·80	37·4	Red-yellow.

Permanganate–acetone oxidations were conducted on the portion insoluble in light petroleum, the combined extracts from the silica gel, and the combined material from the filtrate.

Material insoluble in light petroleum. This (9·1 g.) was dissolved in actone (200 c.c.) and oxidised with permanganate (100 g.). The action proceeded normally except that, as in some other instances during these studies, a certain amount of gel formation occurred transiently in the early stages of the action; this behaviour has not been observed in oxidations of pure unsaturated fatty esters. After working up the products as described earlier, there were obtained incompletely oxidised ester (1·19 g.), monocarboxylic (1·53 g.), and dicarboxylic (1·97 g.) acids. As in the other two oxidations about to be described, the yield of oxidation products recovered was much below that normally observed. The dicarboxylic acids were completely soluble in chloroform at 0°, and on crystallisation from water yielded successive crops which consisted substantially of azelaic acid (m. p. 94—98°). The final aqueous mother-liquors contained acids, from an ethyl acetate solution of which 0·1 g. of very impure suberic acid (m. p. 120—129°, mixed m. p. with suberic acid, 125—130°) was isolated.

Material adsorbed by the silica gel. This (20·0 g.) was dissolved in acetone (250 c.c.) and oxidised with permanganate (125 g.). The products obtained were incompletely oxidised ester (3·39 g.), monocarboxylic (1·36 g.) and dicarboxylic (3.90 g.) acids. The latter deposited on prolonged standing in chloroform at 20° a small amount (0·19 g.) of crystals, m. p. 122—127°, which on recrystallisation from ethyl acetate melted at 129—130° (mixed m. p. with 9 : 10-dihydroxystearic acid, 130°). The 9 : 10-dihydroxystearic acid of m. p. 130° was not observed in any of the other oxidations carried out during this work. The remaining acids present proved to be almost entirely azelaic acid, with the exception of a small amount (0·32 g.) of very impure suberic acid, m. p. 126—138° (mixed m. p. with suberic acid, 129—136°), which was obtained when the acids from aqueous mother-liquors were dissolved in ethyl acetate and kept at 0° for several days.

Material in the light petroleum filtrates. This (12·1 g.) was dissolved in acetone (240 c.c.) and oxidised with permanganate (120 g.). The oxidation was unexpectedly difficult and there were obtained incompletely oxidised ester (5·36 g.), monocarboxylic (2·23 g.) and dicarboxylic (1·60 g.) acids. The latter consisted almost wholly of azelaic acid, but a very small amount (0·05 g.) of impure suberic acid was eventually isolated (m. p. 125—130°, unchanged when mixed with suberic acid).

The incompletely oxidised ester (5·36 g.) resisted further attack by permanganate in acetone solution; on solution in glacial acetic acid (60 c.c.) and gradual addition of permanganate (45 g.) no action took place in the cold but on gradual warming a very vigorous action set in which subsided when the mixture was cooled. Subsequently the action was maintained smoothly on the steam-bath for 2 hours; then a further, almost explosive, action set in. The products finally obtained were incompletely oxidised residue (0·79 g.), monocarboxylic acids (5·81 g., mainly acetic which had escaped complete removal) and dicarboxylic acids (1·58 g.) from which a further 0·08 g. of impure suberic acid (m. p. 124—133°, mixed m. p. 126—136°) was eventually isolated, the remainder being azelaic acid.

The monocarboxylic acids recovered from the three preceding permanganate–acetone oxidations (1·53, 1·36 and 2·23 g.) were united and fractionally distilled at 15 mm. pressure. Two fractions (0·74 g. and 1·67 g.) were obtained which had equivalents of 158·6 and 166·4 respectively, so that no evidence was forthcoming of the presence of any octoic acid.

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