350. *The Oxidation of Monoethenoid Fatty Acids and Esters. Union of Gaseous Oxygen with Elaidic Acid, and Methyl and* n-*Propyl Elaidate.*

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The catalytic autoxidation, at various temperatures, of highly purified elaidic acid and methyl and *n*-propyl elaidate has been studied, and the course of the complex changes occurring has been investigated. Dimerisation occurs at high temperatures (120°) on prolonged oxidation, but at lower temperatures elaidic acid and its simple esters behave during controlled oxidations in much the same way as oleic acid. The results of the autoxidations at various temperatures up to 120° are illustrated graphically, and the nature of the curves shows that peroxide formation and subsequent decomposition are a characteristic feature of these autoxidations. The composition of the products depends to a considerable extent on the conditions. The presence of terminal alkyl groups apparently favours the entry of oxygen into the monoethenoid molecule.

OXIDATION of monoethenoid systems by gaseous oxygen has been extensively studied for a large range of compounds, but comparatively little work has been devoted to *trans*-oleic acid. Hilditch (*J.*, 1926, 1828) prepared methyl elaidate and subjected it to oxidation in acetic acid with hydrogen peroxide. Ellis (*Biochem. J.*, 1932, **26**, 2315) autoxidized elaidic acid in the presence of its cobalt salt, following this later (*ibid.*, 1936, **30**, 753) by work on the oxido-acid. King (*J.*, 1939, 974) and Dorée and Pepper (*J.*, 1942, 477) oxidized the acid with hydrogen peroxide in acetic acid; Sutton (*J.*, 1944, 242) oxidized the methyl ester at 35° in the presence of ultraviolet light and showed that the primary product is apparently a hydroperoxidic ester.

Little work has been done on the catalytic autoxidation of elaidic acid and its esters at varying temperatures, and our object was to ascertain whether the course of oxidation was similar to that of oleic acid (Atherton and Hilditch, *J.*, 1944, 195; Gunstone and Hilditch, *J.*, 1945, 836) and whether such course was influenced by the nature of the terminal groups of the esters. Skellon (*J.*, 1948, 343) investigated the course of thermal catalytic oxidation of methyl oleate as an extension of previous work on the acid (*J. Soc. Chem. Ind.*, 1931, **50**, 382T) and this work, together with that cited above, gives a fair background for comparison.

Pure oleic acid was prepared as formerly described (Skellon, *loc. cit.*, p. 131T), converted into elaidic acid by nitrous fumes, and crystallised from aqueous alcohol. Although later work (Smith, *J.*, 1939, 974) has shown that low-temperature crystallisation from acetone is at least as good as, if not superior to, the lithium-salt method, the product obtained by the latter method was of very satisfactory purity.

The conditions of oxidation were arranged to give high interim peroxide formation with a minimum of fission or polymerisation of the carbon chain, and the results obtained have yielded useful data for comparison with the work of Gunstone and Hilditch (*loc. cit.*). At 55° there was a definite induction period before peroxide formation; this period was far less marked, but definite, at 85°, whilst at 120° no such phenomenon was observed. In contrast, Gunstone and Hilditch (*loc. cit.*) observed a definite induction during oxidation of methyl oleate at 120°. The rapid increase of peroxidation, followed by a very similar rate of decrease (Fig. 2), at the higher temperatures was similar to that observed by Gunstone and Hilditch, and it was apparent that at higher temperatures the onset of peroxidation was considerably favoured.

The highest peroxide values were obtained at 85°, *viz.*, 1·71% for methyl elaidate at 85° (this work) and 1·95% for methyl oleate at 80° (Gunstone and Hilditch, *loc. cit.*) (peroxide values are expressed as % of active oxygen). The observed peroxidic oxygen content was below the theoretical maximum (calc. for methyl esters, 4·88%), and the peroxides were apparently unstable to heat, decomposing rapidly into secondary oxidation products. At the higher temperatures, catalytic oxidation of the esters resulted in ultimate formation of carbonyl compounds; however, at lower temperatures and in catalytic oxidations of the parent acid, the amount of such compounds appeared to be small.

Evolution of carbon dioxide commenced some hours before maximum peroxide formation, but the small amount evolved indicated little or no major fission of the molecule. The increased molecular weights at higher temperature (120°) indicated that when oxidation was prolonged for more than 20 hours some form of polymerisation commenced. At lower temperatures, carbon dioxide evolution was very small and there was little change in peroxide and iodine values (Figs. 2 and 3). In the case of the esters, there was a marked increase in saponification value together with an irregular decrease in iodine value (Fig. 3); the observed form of the

FIG. 1.

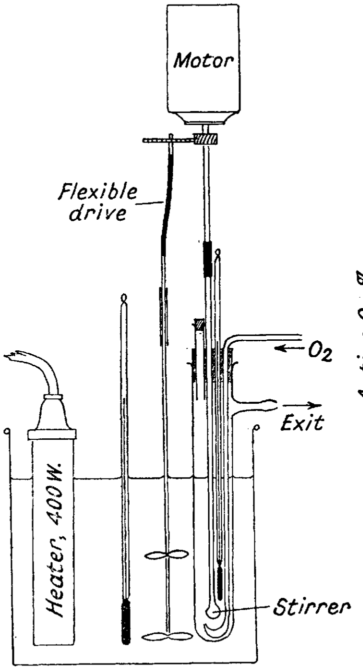


FIG. 2.

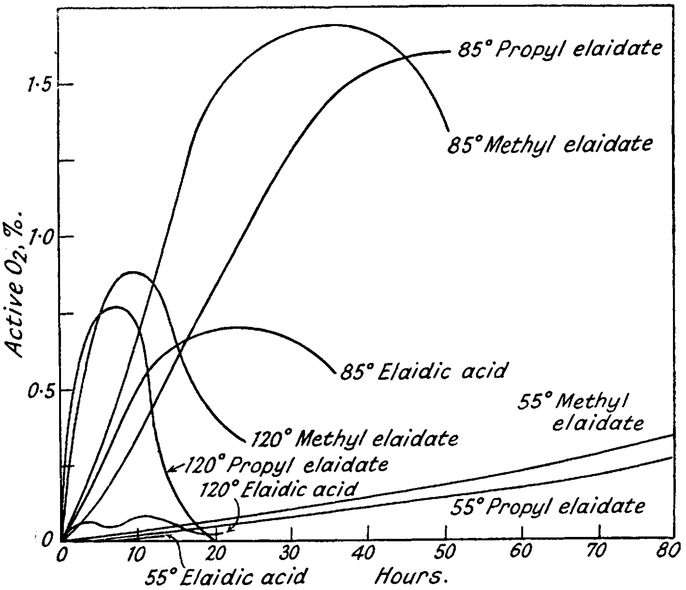
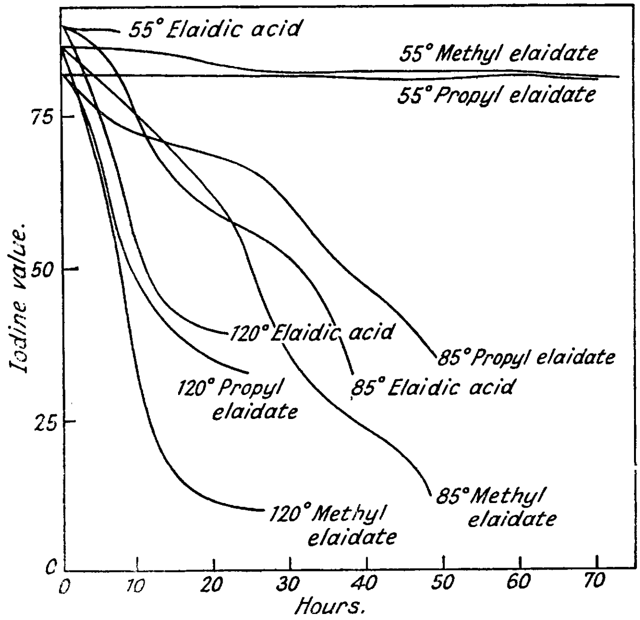


FIG. 3.

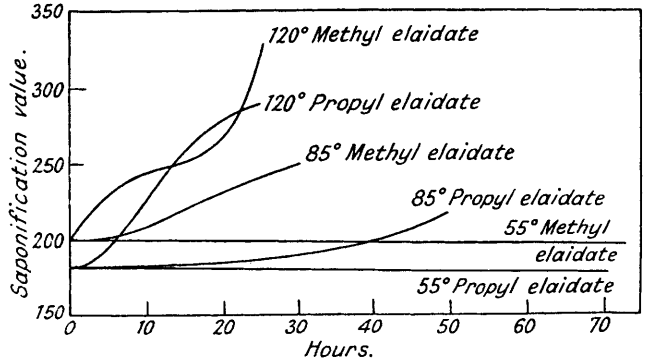


decreases at 85° differed somewhat from that at higher temperatures, and oxygen absorption at 85° apparently occurs in stages.

These observations appear to indicate possible differences in the nature of thermal oxidations taking place at high and moderate temperature.

The course of catalytic oxidation of elaidic acid and its esters, as indicated by changes in acid value, iodine value, and peroxide oxygen content, appeared generally to be similar to that of oleic acid and methyl oleate for the same metallic catalysts; there was, however, some evidence in the case of the acids that configuration of the molecule may affect the initial formation and decomposition of peroxides in thermal oxidations, for the peroxidic-oxygen content during oxidations of elaidic acid was generally much lower than the values obtained in similar oxidations of the *cis*-acid (cf. Skellon and Spence, *J. Soc. Chem. Ind.*, 1948, **67**, 365T). Further exhaustive investigation of the catalytic oxidation of *cis*- and *trans*-monoethenoid fatty acids will be necessary before this can be decided with certainty. The necessity for identical conditions in comparing the course of oxidation of oleic and elaidic acids and their esters is illustrated in Table IV, from which it may be noted that greatly increased rates of flow of oxygen, together with the presence of different metallic catalysts, affect peroxide formation and decomposition to an extreme degree.

FIG. 4.



Finally, the lower value for the peroxide maxima obtained for the acid, as compared with the esters, indicated that esterification influences the entry of oxygen into the molecule. There was also evidence that the nature of the alkyl group in esters of either acid exerts a specific influence; the fall in iodine value, at 120° and 85° over 24 and 48 hours, respectively, was considerably greater for the methyl than for the propyl ester.

The results of a detailed systematic investigation of the numerous and varied products of catalytic oxidation at all stages will form the subject of further communications.

EXPERIMENTAL.

Elaidic Acid.—Pure oleic acid (90 g.) was prepared from high-grade olive oil (500 g.) by a method described earlier (*J. Soc. Chem. Ind.*, 1931, **50**, 130T) and isomerised with nitrous fumes. The product was recrystallised three times from aqueous alcohol, and the pure white crystals were dried over sulphuric acid; m. p. 43·6° (Found: I V., 88·4. Calc. for $C_{18}H_{34}O_2$: I V., 90·1).

Catalytic Oxidations.—The substance (15 g.) was mixed with uranium elaidate (0·0246 g.), prepared as described by Skellon and Spence (*J. Soc. Chem. Ind.*, 1948, **67**, 365T; Found: U, 30·5. Calc.: U, 28·6%). This concentration of catalyst (U, 0·05%) was used throughout the subsequent oxidations. The mixture was transferred to a test-tube (6 × 1 in.), having a side-arm and fitted as shown in Fig. 1 into an electrically-heated (400 w.) oil-bath with a " Sunvic Simmerstat " as control. As the oil temperature (" Castrolite " lubricating oil was satisfactory) was always above the m. p. of the acid, the reaction mixture was liquid, which enabled a slow fine stream of oxygen to be passed in through a thin tube drawn out into a jet. Stirring was maintained by a flattened glass rod connected to an electric motor which, by means of two " Meccano " gears, simultaneously stirred the oil-bath. The maximum temperature variation was ±1°. Samples were withdrawn with a 1-ml. pipette at suitable intervals. The exit vapours were passed through a saturated solution of barium hydroxide to indicate the commencement and rate of evolution of carbon dioxide. The oxygen rate was, arbitrarily, 50 ml. per minute, and the gas appeared as a fine stream of bubbles in the reaction vessel.

The experiments were conducted at 55°, 85°, and 120°. Changes in acid value, peroxide value, and iodine value were investigated, together with molecular weight (Rast), refractive indices (for the esters only), and qualitative tests for reducing substances in the end-products. The results are set out in Tables I, II, and III, peroxide values being expressed as % of active oxygen as determined by the method of Skellon and Wills (*Analyst*, 1948, **73**, 78). The course of the various oxidations is illustrated in the curves in Figs. 2, 3, and 4.

Methyl Elaidate.—Elaidic acid (36 g.) was treated with "AnalaR" methyl alcohol (140 ml.) and conc. sulphuric acid (2 ml.), and after the mixture had been heated under reflux for 2 hours, the alcohol was distilled off, and the residue poured into water (*ca.* 200 ml.) and extracted with ether. The ethereal solutions were washed with dilute potassium carbonate solution and dried (Na_2SO_4). After filtration,

TABLE I.

Catalytic oxidation of elaidic acid at 120°.

Time (hours).	1	2	3	4	5	6	7	14	21
Iodine value (Wijs)	85·3	81·0	76·2	74·4	71·0	68·0	64·4	41·7	39·4
Acid value	197	185	178	175	170	166	161	149	137
Peroxide value (% active oxygen)	0·085	0·080	0·083	0·078	0·065	0·071	0·063	0·078	0·021
M (Rast)	—	—	—	—	—	—	—	—	549
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	—	—	—	Very slight

Catalytic oxidation of elaidic acid at 85°.

Time (hours).	2	4	6	10	14	18	23	29½	37
Iodine value (Wijs)	86·3	87·6	83·1	73·6	64·7	61·6	57·7	52·1	32·4
Acid value	196	196	196	192	185	184	181	176	176
Peroxide value	0·060	0·150	0·269	0·502	0·625	0·672	0·722	0·527	0·547
M (Rast)	—	—	—	—	—	—	—	—	332
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	—	—	—	Very slight

Catalytic oxidation of elaidic acid at 55°.

Time (hours).	1	2	3	4	5	6	7
Iodine value (Wijs)	88·4	87·7	87·3	87·5	88·4	87·9	86·4
Acid value	197	192	188	182	192	184	186
Peroxide value	0·014	0·016	0·016	0·020	0·022	0·024	0·027
M (Rast)	—	—	—	—	—	—	308
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	—	None

TABLE II.

Catalytic oxidation of methyl elaidate at 120°.

Time (hours).	6	12½	18½	24½
Iodine value (Wijs)	54·0	20·2	12·3	15·0
Sap. value	235	—	261	330
Peroxide value	0·805	0·575	0·394	0·276
M (Rast)	—	—	—	322
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	Rapid
$n_D^{20°}$	1·4563	1·4600	1·4621	1·4633

Catalytic oxidation of methyl elaidate at 85°.

Time (hours).	6	12	18	24	30	36	42	48
Iodine value (Wijs)	78·2	71·3	63·1	52·2	40·3	28·1	21·6	14·5
Sap. value	203	216	227	236	250	—	—	—
Peroxide value	0·42	0·93	1·38	1·63	1·71	1·66	1·52	1·33
M (Rast)	—	—	—	—	—	—	—	259
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	—	—	Slight
$n_D^{20°}$	1·4530	1·4548	—	—	—	1·4573	1·4569	1·4580

Catalytic oxidation of methyl elaidate at 55°.

Time (hours).	12	24	36	48	60	72
Iodine value (Wijs)	85·2	82·9	82·5	82·6	82·5	81·0
Sap. value	—	—	194	197	195	198
Peroxide value	0·065	0·089	0·130	0·159	0·256	0·334
M (Rast)	—	—	—	—	—	273
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	None
$n_D^{20°}$	—	—	—	—	—	1·4557

TABLE III.

Catalytic oxidation of n-*propyl elaidate at* 120°.

Time (hours).	3	6	12	18	24
Iodine value (Wijs)	73·5	54·2	—	36·3	28·6
Sap. value	187	209	240	275	292
Peroxide value	0·770	0·757	0·442	—	0·010
M (Rast)	—	—	—	—	375
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	Rapid
$n_D^{20°}$	1·4536	1·4547	1·4569	1·4629	1·4639

Catalytic oxidation of n-*propyl elaidate at* 85°.

Time (hours).	6	12	18	24	30	36	42	48
Iodine value (Wijs)	74·0	71·2	68·3	65·8	59·0	50·7	45·1	37·0
Sap. value	—	—	—	192	—	189	212	210
Peroxide value	0·214	0·478	0·801	1·04	1·39	1·50	1·59	1·59
M (Rast)	—	—	—	—	—	—	—	265
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	—	—	Very slight
$n_D^{20°}$	—	—	—	—	—	—	—	1·4563

Catalytic oxidation of n-*propyl elaidate at* 55°.

Time (hours).	12	24	36	48	60	70½
Iodine value (Wijs)	81·0	81·0	80·3	79·9	80·7	80·1
Sap. value	180	180	179	180	—	174
Peroxide value	0·074	0·133	0·156	0·201	0·224	0·268
M (Rast)	—	—	—	—	—	344
Reduction of Fehling's solution and ammoniacal silver nitrate	—	—	—	—	—	None

the ether was removed under reduced pressure. The product was then fractionated at 1—2 mm., in a Willstätter flask with a modified Perkin triangle: yield, 34·4 g.; m. p. 10·0°; b. p. 166—169°/1—2 mm.; n^{20} 1·4525 (Found: I V., 84·7. Calc. for $C_{19}H_{36}O_2$: I V., 85·8).

n-*Propyl Elaidate.*—50 G. of elaidic acid were treated with 200 ml. of *n*-propyl alcohol as above, and the final product fractionated: yield, 46·6 g.; b. p. 173—174°/1—2 mm.; n^{20} 1·4512 (Found: I V., 80·7. Calc. for $C_{20}H_{38}O_2$: I V., 81·7).

Barium Hydroxide Test.—Carbon dioxide evolved was absorbed in a saturated solution of barium hydroxide. At 55° only traces were detected with the esters and none with the acid. At 85° evolution occurred after 3—4 hours, whereas at 120° it occurred after only 15—30 minutes.

Increased-oxygen-rate Experiments.—These were initiated in order to observe (*a*) the effect of higher rates of oxygen flow on peroxide formation, and (*b*) the advantage or otherwise of a catalyst under these conditions. Three side-arm test-tubes (½ × 6 in.) were immersed in a boiling water-bath, each tube having a fine capillary (0·75-mm. bore) dipping into the reaction mixture (3·0 g. of elaidic acid with 0·05% of uranium or cobalt as catalyst; a control containing 3·0 g. of acid alone was included), through which a rapid stream of oxygen was passed. The results are tabulated in Table IV.

TABLE IV.

Catalytic oxidation of elaidic acid at 98°.

Time (hours).	2	4½	7
Peroxide value: (i) No catalyst	0·810	2·58	3·66
(ii) Uranium	1·37	2·99	3·99
(iii) Cobalt	0·231	0·361	0·670

One of us (M. N. T.) wishes to acknowledge a grant from the University of London Research Fund for assistance in this work.

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[*Received, December* 14*th*, 1948.]