27. *The Oxidation of Monoethenoid Fatty Acids and Esters. Catalytic Oxidation of Elaidic Acid, Methyl Elaidate, and* n-*Propyl Elaidate. The Oxidation Products.*

By J. H. SKELLON and M. N. THRUSTON.

The products of oxidation of highly purified elaidic acid and its methyl and *n*-propyl esters by gaseous oxygen have been semi-quantitatively resolved. Whilst dimerisation may occur on prolonged oxidation at 120°, in short, controlled catalytic oxidations pure elaidic acid and its esters behave similarly to the *cis*-acid. The primary reaction is a chain-reaction involving the formation of isomeric hydroperoxides, and is followed by secondary breakdown to unsaturated ketones, acidic fission compounds, and neutral saturated substances. The production of carbon dioxide and water are due to this secondary breakdown, which at 120° commences at an early stage. At 98°, only small amounts of elaidic acid epoxides were isolated, and there was little or no evidence to indicate that such compounds are formed in the initial stages of autoxidation.

The mechanism of catalytic oxidation of monoethenoid fatty acids and esters is discussed.

SKELLON and THRUSTON (*J.*, 1949, 1626) showed that at 85—120° maximum peroxidation of elaidic acid and its methyl and *n*-propyl esters occurred with little or no dimerisation. Investigation of the numerous products of controlled autoxidations at a stage where minimum secondary degradation occurs is now described.

Farmer (*J.*, 1942, 121) put forward a radical chain reaction, later extended (*Trans. Faraday Soc.*, 1946, **42**, 233) to postulate universal initial attack by oxygen at the ethylenic linkage, but only to an extent sufficient to initiate the chain reaction. Gunstone and Hilditch (*J.*, 1946, 1022) suggested primary entry of oxygen at the ethylenic linkage with subsequent migration of the ethenoid bond owing to induced polar effects. Ross, Gebhardt, and Gerecht (*J. Amer. Chem. Soc.*, 1949, **71**, 282), from a study of autoxidations of methyl oleate at 35° in the presence of ultra-violet light, suggested that the initial point of entry of oxygen was at the α-methylene group. According to Ellis (*Biochem. J.*, 1950, **46**, 129) autoxidation may involve initial formation of olefinic keto-acids with secondary degradation to hydroperoxides. Modern views have been reviewed by Hilditch (*Nature*, 1950, **166**, 558) who stressed the necessity for purity of initial starting materials : thus, linoleate containing the pentadiene system will catalyse oxidation of mono-ethenoid fatty acids. Below 50°, it is probable that attack occurs at the α-methylene group and at higher temperatures direct union between oxygen and the double bond proceeds rapidly.

The highly purified oleic acid used in the present work was isolated from saponified high-grade olive oil by low-temperature crystallisation from acetone. Although in our previous work a pure acid was obtained by the lead–lithium salt method (Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 130T) it was considered that low-temperature separation might afford less likelihood of premature oxidation. After elaidinisation and esterification, the pure compounds were catalytically oxidised with uranium elaidate as catalyst (Skellon and Spence, *ibid.*, 1948, **67**, 365) and high oxygen dispersion in order to achieve rapid peroxidation with the minimum of secondary breakdown. It was apparent that such secondary decomposition occurrred more readily at high temperature. During oxidation of elaidic acid, carbon dioxide was not observed until after 5 hours, when peroxidation had reached 0·5%, whilst water formed amounted to one mole per mole of acid. The degree of fission, however, amounted to only approx. 0·1 carbon atom per molecule. There was no evidence that the small yield of epoxide obtained was a *primary* product of oxidation. The nature of some of the low-temperature products indicated occurrence of slight dimerisation above 100°. Strong alkaline hydrolysis destroyed peroxide, yielding unsaturated resinous complexes of low ketone content together with dihydroxystearic acid, the latter not being present in the original oxidised acid.

In autoxidation of the esters, two temperatures were used. At 120°, carbon dioxide was evolved at once, whereas at 98° no carbon dioxide was evolved for 10 hours. As with elaidic acid, unchanged ester was detected at the lower temperature, though not at 120°. Similarly 9 : 10-dihydroxystearic acid, m. p. 132°, was produced only after hydrolysis. Infra-red analysis of oxidation products (freed from acidic degradation substances) indicated an increase in asymmetry due possibly to migration of the ethylenic linkage.

The presence of dihydroxystearic acid, invariably resulting from strong alkaline hydrolysis of the oxidation products, appeared to indicate that the main reactive centres are seated at $C_{(9)}$ and $C_{(10)}$; the acid would be produced on decomposition of hydroperoxides, on breakdown of dimeric complexes, or on hydrolysis of an epoxide, although the epoxides are fairly resistant to hydrolysis.

The degree of peroxidation was 33% for methyl elaidate at 98° and 10—15% for the elaidic acid at 98° and for propyl elaidate at 120° but, as the oxidations were arrested soon after the stage of maximum peroxidation, pronounced fission was not to be expected (10—15% was found). The acids produced were: azelaic and suberic (from elaidic acid); azelaic, nonanoic, and decanoic (from methyl elaidate); and azelaic and decanoic (from *n*-propyl elaidate). It therefore seemed likely that attack was initiated at one of the forms:

$CH_3\cdot[CH_2]_8\cdot CH{:}CH\cdot[CH_2]_6\cdot CO_2R$ $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2R$ $CH_3\cdot[CH_2]_6\cdot CH{:}CH\cdot[CH_2]_8\cdot CO_2R$

Hydroperoxidation could therefore occur at $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, and $C_{(11)}$, with production of following degradation products: (*a*) at $C_{(9, 8)}$: decanoic, heptanoic, nonanoic, and suberic acid; (*b*) at $C_{(11, 10)}$: sebacic, octanoic, heptanoic, and azelaic acid. Both oxidised esters yielded comparatively large amounts of decanoic acid. These results indicated that the primary reaction involves hydroperoxide formation which may occur at $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, or $C_{(11)}$; secondary fission products are then formed together with long-chain unsaturated ketonic compounds.

Mild hydrolysis of the oxidised esters, followed by isolation of a volatile oil as described by Ellis (*Biochem. J.*, 1950, **46**, 129), was carried out, but no positive evidence was obtained indicative of the presence of α- or β-unsaturated keto-acids. During autoxidations of oleic and elaidic acid at about 65° Ellis (*loc. cit.*) suggested that the α- and β-unsaturated keto-acids (I) and (II) were formed in significant amount. Mild hydrolysis of (I) yields azelaic semialdehyde and heptyl methyl ketone, and (II) gives nonaldehyde and 8-oxo-octane-1-carboxylic acid, products which afford evidence of the presence of the original unsaturated keto-acids.

(I) $CH_3\cdot[CH_2]_6\cdot CO\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot CO\cdot[CH_2]_6\cdot CO_2H$ (II)

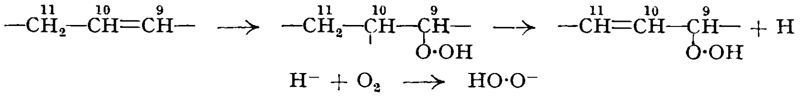
The volatile oils recovered from autoxidised elaidic esters at 85—120° were neutral and in the case of the *n*-propyl derivative yielded a ketone with an approximate molecular weight of 240 and a CO content of 9·3%.

Infra-red spectra of some of the products (see p. 142) appeared to substantiate the experimental evidence already adduced. Symmetry of the molecule about the double bond was apparently disturbed by oxidation, as shown by the appearance of a band near 6·1 μ, which was rather more pronounced in the oils *before* subjection to attempted ketone removal by Ellis's method (*loc. cit.*). The disturbance of symmetry might well indicate bond shift in peroxidation such as would take place on a direct attack at the unsaturated centres.

The *trans*-configuration of the compounds as a whole was apparently unaffected, as the characteristic band at 10·37 μ was clearly visible (Cross, Richards, and Willis, Faraday Soc. Symposium, Sept., 1945).

The oil (V) recovered from oxidised propyl oleate after cold alcoholic treatment of the neutral product gave a prominent band at 9·55 μ (which might possibly be due to a hydroxy-group), and another about 11·4 μ. The infra-red curves for oxidised propyl elaidate gave no positive evidence of presence of epoxides; the results of chemical analysis had also given no yield of epoxide in oxidised propyl oleate, but from oxidised elaidic acid and methyl elaidate 3—5% of epoxides had been recovered.

These results generally confirmed chemical evidence supporting the view that migration of the ethylenic linkage occurs, and that at temperatures above 100° initial attack by oxygen at the α-methylenic groups seems unlikely. Thermal catalytic oxidation of elaidic acid and its esters appears, therefore, to take the following course : (1) The oxidations are probably chain reactions initiated by $^-O\cdot OH$ (Gibson, *J.*, 1948, 2275) with direct attack at, and subsequent displacement of, the ethylenic linkage :



$$-\overset{11}{CH_2}-\overset{10}{CH}=\overset{9}{CH}- \longrightarrow -\overset{11}{CH_2}-\overset{10}{CH}-\underset{O\cdot OH}{\overset{9}{CH}}- \longrightarrow -\overset{11}{CH}=\overset{10}{CH}-\underset{O\cdot OH}{\overset{9}{CH}}- + H$$

$$H^- + O_2 \longrightarrow HO\cdot O^-$$

The resulting hydroperoxides would be identical with those obtained either by assumption of initial loose complex formation, as suggested by Bergstrom (*Nature*, 1945, **156**, 717) or on the alternative theory of initial attack at an α-methylenic group (Farmer, *loc. cit.*). The presence of terminal alkyl groups undoubtedly favours hydroperoxide formation. (2) Decomposition of the hydroperoxide occurs at a rate depending on the external conditions, with formation of three main types of secondary oxidation products, in varying quantity : (*a*) Monomeric oily complexes (40—60% yield) containing ketonic groups, one possible structure for which was formerly suggested by Skellon (*J.*, 1948, 343). There is little or no evidence of dimerisation in catalytic oxidations below 100°. (*b*) Other secondary oxidation products formed without rupture of the carbon chain, *viz.*, epoxides (from elaidic acid and the lower esters) and volatile ketonic esters. Dihydroxystearic acid, however, is only recovered after powerful alkaline hydrolysis. (*c*) Scission products (monobasic and dibasic acids) which may result from hydroperoxide fission or from breakdown of the oily complexes.

EXPERIMENTAL

Preparation of Elaidic Acid by Low-temperature Crystallisation.—High-grade olive oil (500 g.) was saponified for 3 hours with potassium hydroxide (100 g.) in 95% alcohol (1 l.) and water (200 ml.). After removal of excess of alcohol and acidification the separated acids were washed six times with hot water (yield, 481 g.). These (250 g.) were dissolved in acetone (2500 ml.), cooled (½ hour) to −25° in solid carbon dioxide with stirring, and kept at −25° to −20° in a 1-gallon Dewar vessel for 4½ hours. The precipitate was filtered off at −15° to −18° and the filtrate cooled to −60° and filtered, after a few hours, at the pump (Smith, *J.*, 1939, 974). The insoluble material was dissolved in acetone (1500 ml.), and the whole cooled at −40° for 4 hours and filtered. The colourless solid was redissolved in acetone (1500 ml.), again cooled to −40°, and treated as before. The solid thus obtained (largely oleic acid, plus some saturated acids) was treated with alcohol (500 ml.) containing lead acetate (6 g.) and acetic acid (1—2 ml.). After boiling and cooling rapidly in nitrogen a small crop of lead salts was removed, and the filtrate freed from residual acetone *in vacuo*. After acidification, ether-extraction, and removal of traces of lead chloride, pure oleic acid was recovered by vacuum-distillation in nitrogen. It was converted into elaidic acid (*J.*, 1949, 1626), which, dried over ignited alumina *in vacuo* (1 week), had m. p. 43·7° ± 0·1° (Found : I.V., 88·7. Calc. for $C_{18}H_{34}O_2$: I.V., 90·1).

Catalytic Oxidations. General.—Pure dry oxygen at a known pressure was passed into the molten acid or ester contained in a round-bottomed Pyrex tube (5 × 1½″) fitted with a stopper through which passed a sintered-glass bubbler (for oxygen), a thermometer, a stoppered tube (for a sampling pipette), and an exit tube. The apparatus was immersed in a thermostatically controlled oil-bath, and exit gases were passed through a glass-stoppered weighed U tube and through saturated barium hydroxide solution. All oxidations were carried out in the presence of 0·05% of uranium as " uranium elaidate."

Elaidic Acid at 98°.—A stream of oxygen at 20 mm. pressure was passed into the acid (I.V., 88·2; acid val., 197; m. p. 43·6°; 30 g.) for 11 hours. Volatile product were first observed at 5 hours as a condensate (1·884 g.) in the U tube; after 5 hours 1·95 g. of barium carbonate were formed. Peroxide contents were :

Time (hr.)	1	2	3	5	7	10	11
Active O, %	0·140	0·217	0·256	0·508	0·678	0·648	0·625

The oxidised product [I.V., 39·6; acid val., 180; *M* (Rast), 324] (10 g.) was dissolved in acetone (100 ml.) and cooled overnight at −80°. After recrystallisation of the precipitate, the bulked filtrates were subjected to vacuum-distillation at low temperature, yielding a yellow oil (active O, 0·607%) (8·05 g.) and a white solid (A) [I.V., 54·5; *M* (Rast), 269; acid val., 190] (1·43 g.). The oil (7·75 g.) was further fractionated in acetone (40 ml.) at −20° (4 hours), giving a solid (active O, 0·285%; I.V., 43·0; acid val., 196) (0·127 g.). The filtrate at −40° gave a semi-solid material (1·70 g.) [active O, 0·313%; I.V., 33·1; *M* (Rast), 424; acid val., 170] and then at −80° gave a solid (0·616 g.) melting at room temperature [active O, 0·370%; I.V., 24·1; *M* (Rast), 352; acid val., 178]. The final filtrate gave a yellow oil (4·45 g.), n_D^{20} 1·4642 (active O, 0·689%; I.V., 36·3; *M* (Rast), 306; acid val., 157].

Solid A, when kept in aqueous alcohol overnight at 0°, afforded elaidic acid (0·57 g.; m. p. 43·8°) and there was recovered 0·57 g. of a solid, equiv. 285, after recrystallisation. The soluble material, when twice recrystallised from *n*-hexane, gave elaidic acid epoxide, m. p. 54·5° (lit., 55·5°) (Found: equiv., 301. Calc. for $C_{18}H_{34}O_3$: equiv., 298). The residue consisted of oily keto-derivatives. The original oxidised end-product contained no epoxide (Ellis's method, *Biochem. J.*, 1936, **30**, 753), but yielded small amounts of azelaic, m. p. 107° (Found: equiv., 98), and suberic acid, m. p. 140° (Found: equiv., 86·2. Calc. for $C_8H_{14}O_4$: equiv., 87·1).

Saponification of the original oxidation product (6·7 g.), acidification, and ether-extraction afforded insoluble dihydroxystearic acid (1·1 g.), m. p. 131° (lit., m. p. 132°) (Found: equiv., 316·4. Calc. for $C_{18}H_{36}O_4$: equiv., 316). From the ether-extract was recovered brown solid (4·9 g.), whence hot light petroleum (150 ml.; b. p. 40—60°) left an insoluble brown residue, which crystallised from benzene; recrystallisation of the resultant solid gave 0·05 g. of solid, having m. p. 100—103° (0·05 g.) and reducing Fehling's solution (Found: equiv., 298). The benzene filtrates yielded an orange viscous oil (1 g.) (Found: equiv., 217; I.V., 34·4; CO, 1·9%). The light petroleum filtrate at 0° gave a very small amount of dihydroxystearic acid and then, on evaporation to dryness and recrystallisation of the residue from aqueous alcohol (at 0°), a solid (B) (1·2 g.) which, after crystallisation from *n*-hexane, was identified as elaidic acid; the aqueous alcoholic filtrates from B contained a yellow oil (Found: CO, 1·4%).

Methyl Elaidate at 98°.—The ester (Skellon and Thruston, *loc. cit.*) was oxidised for 20 hours. Carbon dioxide was observed after 10 hours (1·38 g. of barium carbonate). 0·503 G. of volatile material was collected, from which 0·10 ml. of aldehydic or ketonic oil was isolated. Changes in peroxide oxygen content were:

Time (hr.)	3	8	13	19
Active O, %	0·439	1·08	1·31	1·46

n-*Propyl Elaidate at* 120°.—The ester (30 g.), n_D^{20} 1·4481 (Found: sap. val., 175·5. Calc. for $C_{20}H_{38}O_2$: sap. val., 173), was oxidised for 11 hours (2·05 g. of barium carbonate; 0·5417 g. of volatile product giving 0·10 ml. of aldehydic or ketonic oil). Changes in peroxide oxygen content were:

Time (hr.)	5	6	9	11
Active O, %	0·454	0·445	0·508	0·407

Detailed Analysis of the Oxidised Esters.—(a) *Resolution into acidic and neutral fractions.* The oxidation products of methyl elaidate (termed Me below) (10 g.) and propyl elaidate (termed Pr below) (15 g.) in ether (40 ml.) were extracted thrice with 20% sodium carbonate solution. After being washed with ether, the alkaline extracts were refluxed with 30% aqueous potassium hydroxide (50 ml.), and then recovered with ether. Me gave 1·40 g. (Found: I.V., 15·6; equiv., 167), and Pr 1·70 g. (Found: I.V., 20·6; equiv., 189) of brown acids. Recovery of the neutral oxidation products yielded pale oils (Me, 7·6; Pr, 11·6 g.).

(b) *Separation of the acidic products.* The acids were refluxed four times with light petroleum (b. p. 40—60°), and the concentrated extracts cooled at 0° overnight, yielding from Me an acid, m. p. 108° (0·05 g.) (Found: equiv., 98), and, from Pr, azelaic acid (0·04 g.), m. p. 102° (from benzene) (Found: equiv., 93. Calc. for $C_9H_{16}O_4$: equiv., 94). The light petroleum mother-liquors afforded, on evaporation, sharp-smelling, lemon-yellow oils [from Me, 0·40 g., equiv., 176; alkaline hydrolysis gave decanoic acid, m. p. 31·5° (lit., 31·5°) (Found: equiv., 174. Calc. for $C_{10}H_{20}O_2$: equiv., 172); from Pr, equiv., 176 (hydrolysis gave an acid of equiv. wt., 179].

The acids insoluble in hot light petroleum were treated with absolute alcohol, concentrated, and cooled to 0°. The acids from Me yielded a trace of solid, m. p. 58—61° (Found: equiv., 300). The acids soluble in light petroleum, recovered and extracted with warm *cyclo*hexane, formed pasty waxes: from Me, nonanoic acid (0·05 g.), m. p. 10—12° (Found: equiv. 159.

Calc. for $C_9H_{18}O_2$: equiv., 158); from Pr, an acid (0·12 g.), m. p. 23° (Found: equiv., 189). Materials insoluble in *cyclo*hexane were similar pasty waxes. This Me wax (0·07 g.) (Found: equiv., 147) was dissolved in hot alcohol and diluted with water until a faint emulsion was obtained: cooling to 0° afforded a flocculent colourless solid (0·03 g.) (Found: equiv., 200), and a brown wax (0·03 g.), m. p. 30° (Found: equiv., 170. Calc. for decanoic acid, $C_{10}H_{20}O_2$: equiv., 172). The last wax (from Pr) (0·08 g.) yielded from chloroform–light petroleum at 0° a lemon-yellow solid (0·05 g.) (Found: equiv., 120).

(c) *Resolution of the neutral substances.* The neutral oils (7·6 g. from Me; 11·6 g. from Pr) strongly reduced Fehling's solution. Solutions in alcohol (7 pts. by wt.) at 0° were treated with water to a faint permanent cloudiness. After 120 hours at 0°, the precipitates were collected [from Me, very little; from Pr, 1·1 g. of a yellowish oil (room-temp.) (V, below]. The residual materials recovered by evaporation and ether-extraction gave no precipitates from acetone, chloroform, or light petroleum at 0°. They gave on analysis: sap. val., Me 284, Pr 261; I.V., Me 34·4, Pr 41·6; active O, Me 0·808, Pr, 0·465%; *M* (Rast), Me 301, Pr 364.

Further samples of neutral oils were hydrolysed for 1 hour with 50% alcohol containing 10% of potassium hydroxide, yielding dihydroxystearic acid [m. p. (lit.) 132°]: from Me (5·4 g.), 0·20 g., m. p. 130° (Found: equiv., 314); from Pr (7·8 g.), 0·30 g. (Found: equiv., 316·5). The ether-soluble filtrates from these acids yielded oils which were thrice extracted with light petroleum; these solutions at 0° gave, from Pr, a precipitate (0·03 g.), m. p. 95° (Found: equiv., 294). In this experiment, Me gave elaidic acid epoxide, m. p. 53° (0·30 g.) (Found: equiv., 296. Calc. for $C_{18}H_{34}O_3$: equiv., 298) [hydrolysed to dihydroxystearic acid, m. p. 128° (Found: equiv., 320)]. The light petroleum filtrate from Me yielded a yellow oil which in aqueous alcohol deposited a small amount of elaidic acid, m. p. 43° (Found: equiv., 283. Calc. for $C_{18}H_{34}O_2$: equiv., 282).

Some heterogeneous resinous mixtures were left from the light petroleum extractions, in the case of Me sufficient for further resolution. A white solid (0·03 g.), washed out with light petroleum and recrystallised from aqueous alcohol, was crude dihydroxystearic acid, m. p. 125° (Found: equiv., 310). The residual resin gave from benzene a precipitate, m. p. 105° (Found: equiv., 320); the resin reduced Fehling's solution and had equiv. 295, I.V. 16·6; it was a C_{18} ketonic product.

Examination of the original neutral oils by mild hydrolytic distillation. The oils (*ca.* 5 g.) were refluxed with 0·1N-sodium hydroxide (100 ml.) for 2 hours and the small yields of volatile oils were trapped in a sealed-in U tube. Both were of sharp odour and zero titre, and strongly reduced Fehling's solution {from 3·49 g. of Me, 0·0605 g.; from 7·80 g. of Pr, 0·124 g. [Found: I.V., 29·5; *M* (Rast), 240; CO (ketone), 9·3%]}. The non-volatile materials from Me and Pr had, respectively: *M* (Rast), 301, 364; active O, 0·56, 0·57%; sap. val., 252, 236; I.V., 26·1, 31·8; CO, 2·8, 2·6%.

Infra-red Analysis.—The following materials were examined by means of a recording double-beam infra-red spectrometer with a rock-salt prism: (I) The neutral oil isolated from the oxidation of methyl elaidate at 98° after removal of the small volatile fraction by the Ellis U-tube method for ketones. (II) As (I) but before removal of the volatile fraction. (III) The neutral oil from oxidation of *n*-propyl elaidate at 120°, after removal of the small volatile fraction as above. (IV) As (III), but before removal of the volatile fraction. (V) Precipitate from cold alcoholic treatment of neutral oil from oxidised *n*-propyl elaidate. (VI) The final oil obtained from the attempt at low-temperature separation of elaidic acid oxidised at 98°. A constant thickness of liquid was used.

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Acton Technical College, High Street,
Acton, London, W.3.

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