853. *The Rôle of Peroxides in the Autoxidation of Elaidic Acid and Oleic Esters.*

By George King.

The effect of heat on autoxidised elaidic acid, and methyl and ethyl oleates, has been studied in order to elucidate the secondary changes resulting from the decomposition of hydroperoxides. Fractions enriched in peroxides have been prepared by the urea method.[1,2]

The decomposition of the peroxides at 80—90° appears to give rise invariably to hydroxy-compounds and, in the early stages of autoxidation, αβ-unsaturated ketones, but not to epoxides. Thermal decomposition of peroxide-enriched fractions from oleic esters yields also other carbonyl compounds, in which the carbonyl group is not vicinal to the double bond. Autoxidised elaidic acid similarly gives significant amounts of ketols and of unsaturated compounds of undetermined constitution, which may be oxygen-bonded but contain no other functional group. Chain scission at the double bond during this process is inextensive.

The epoxide in autoxidised methyl oleate has been established by isolation of the epoxy-acid as mainly, if not entirely, the *trans*-form.

Considerable importance is attached to the rôle of peroxides in the autoxidation of olefins. The active peroxides which are formed at an early stage in the autoxidation of oleic and elaidic acids and their alkyl esters appear to be mainly hydroperoxides of the type $R\cdot CH(O\cdot OH)\cdot CH{:}CH\cdot R'$, in which the double bond remains intact, although perhaps partly displaced from its original position.[3,4,5] These are commonly thought to give rise by thermal decomposition, or reaction with unchanged olefin, to 8- and 11-oxo-derivatives [(I) and (II) respectively] and epoxides:[6,2,5,7]

$$\text{(I)}\ CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot CO\cdot[CH_2]_6\cdot CO_2R \qquad CH_3\cdot[CH_2]_6\cdot CO\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2R\ \text{(II)}$$

The rearrangement of hydroperoxides to ketols has also been postulated.[8] However, much uncertainty remains concerning the sequence of changes and mechanisms involved in the autoxidation process,[9,10] and further work in this field was felt to be desirable.

Although substantially pure hydroperoxide fractions have been prepared from

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[1] Coleman, Knight, and Swern, *J. Amer. Chem. Soc.*, 1952, **74**, 4886.
[2] Coleman, Knight, and Swern, *J. Amer. Oil Chemists' Soc.*, 1955, **32**, 135.
[3] Waters, *Ann. Reports*, 1945, **42**, 130.
[4] Swern, Coleman, Knight, Ricciuti, Willits, and Eddy, *J. Amer. Chem. Soc.*, 1953, **75**, 3135.
[5] Swern and Coleman, *J. Amer. Oil Chemists' Soc.*, 1955, **32**, 700.
[6] Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348; Swift and Dollear, *J. Amer. Oil Chemists' Soc.*, 1948, **25**, 52.
[7] King, *J.*, 1954, 2114; 1956, 587.
[8] Skellon, *J.*, 1948, 343; Swern, Scanlan, and Knight, *J. Amer. Oil Chemists' Soc.*, 1948, **25**, 193.
[9] Cf. Szent-Györgyi, *Biochem. Z.*, 1924, **146**, 246; Farmer and Sundralingam, *J.*, 1942, 121.
[10] Ellis, *Biochem. J.*, 1950, **46**, 129.

autoxidised methyl oleate,[11,2,12] relatively little is known about their subsequent decomposition. Thermal decomposition of these hydroperoxides gives rise at 100° to hydroxy-compounds,[12] at 150—260° to αβ-unsaturated carbonyl compounds, including 2-undecenal,[13] and at 210° to dimeric products.[14] Swift and Dollear [6] failed to isolate either epoxy- or dihydroxy-compounds when the hydroperoxides were heated alone under nitrogen, but when heated with oleic acid at 90° small yields of *threo*-9,10-dihydroxystearic acid and oleic acid epoxide were isolated from the acidic fraction. O'Neill [15] heated methyl oleate hydroperoxide with methyl oleate and obtained mainly oxygen-bonded products.

Preliminary observations on the effect of heat on autoxidised elaidic acid have already been reported.[16] The urea-complex method,[1,2] by which most of the epoxides and unchanged acid (or ester) are removed as inclusion compounds, has now afforded a convenient means of preparing suitable fractions containing 25—40% or more of peroxides from elaidic acid or oleic esters, following mild autoxidation at 50° or 82—83°. When these fractions are heated without a catalyst at about 85° under nitrogen for 2 days, the active peroxides are largely destroyed, and a marked rise in the total carbonyl and αβ-unsaturated-ketone content occurs (Tables 1—8, columns B). The observed increase in the latter rarely exceeds 25% of that calculated for the simple dehydration $\cdot\mathrm{CH(O\cdot OH)\cdot CH{:}CH}\cdot \longrightarrow \cdot\mathrm{CO\cdot CH{:}CH}\cdot$, or 50% for the intermolecular oxidation $2\,\cdot\mathrm{CH(O\cdot OH)\cdot CH{:}CH}\cdot + \cdot\mathrm{CH_2\cdot CH{:}CH}\cdot \longrightarrow 2\,\cdot\mathrm{CH(OH)\cdot CH{:}CH}\cdot + \cdot\mathrm{CO\cdot CH{:}CH}\cdot + H_2O$, but there may be some

TABLE 1.

Effect of heat on the products obtained by autoxidising elaidic acid at 50° for 23 days: (A) whole product; (B) fraction not forming urea complex; (C) fraction forming urea complex. (i) Before, (ii) after being heated under N_2 at 85° for 24 hr.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Physical condition	Mainly crystalline	Slightly yellow, oily crystals	Oil	Pale yellow, thick oil	Slightly oily crystals	Slightly yellow, semi-solid
Reduction of Fehling's soln.	Slight	Slight	Slight	Slight	None	Trace
Equivalent weight	300	320	342	324	299	317
Iodine value	61	62	56	57	67	68
$E^{1\%}_{1\,\mathrm{cm.}}$ at 224 mμ	36·7	40·3	32·0	56·9	38·3	33·5
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	2·51	1·18	5·15	2·67	0·31	0·24
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distn. with 0·5N-NaOH (%)	3·09	3·08	3·46	4·50	3·42	2·92
Nonanal on distn. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	3·21	5·85	5·18	5·31	1·56	3·64
Saponification value	46	53	88	78	15	23
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·16	1·19	0·51	1·47	0·12	0·26
Carbonyl (%)	1·06	1·52	0·93	2·13	0·81	0·84
Oxiran-O (%)	0·64	0·26	0·01	0·00	1·08	0·77
Active O (%)	0·52	0·01	1·22	0·15	0·06	0·02
OH value (corrected for hydroperoxide and epoxide)	42	55	78	92	0	17
Steam-volatile acids, mequiv. (%)	48	43	62	70	18	33
Non-volatile, water-soluble acids, mequiv. (%)	43	32	51	42	4	3

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[11] Farmer and Sutton, *J.*, 1943, 119; Swift, Dollear, and O'Connor, *Oil and Soap*, 1946, **23**, 355.
[12] Holman, Nickell, and Privett, *J. Amer. Oil Chemists' Soc.*, 1958, **35**, 422.
[13] Swift, Dollear, Brown, and O'Connor, *J. Amer. Oil Chemists' Soc.*, 1948, **25**, 39.
[14] Frankel, Evans, and Cowan, *J. Amer. Oil Chemists' Soc.*, 1960, **37**, 418.
[15] O'Neill, *Chem. and Ind.*, 1954, 384.
[16] King, *J.*, 1958, 1485.

TABLE 2.

Approximate composition (%), calculated from Table 1, of the products obtained by autoxidising elaidic acid at 50° for 23 days.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
8- and 11-Oxoelaidic acids, $C_{18}H_{32}O_3$ deduced from (a) $E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	6·8	7·5	6·0	10·5	7·1	6·2
(b) hydrolysis	7·3	7·3	8·3	10·2	8·0	7·0
9,10-Ketol-acids, as $C_{18}H_{34}O_4$	0·9	6·6	2·8	8·2	0·6	1·5
Other oxo-acids, as $C_{18}H_{32}O_3$	0·0	0·0	0·0	0·0	0·2	0·8
9,10-Epoxystearic acid	11·9	4·8	0·3	0·0	20·1	14·4
Hydroperoxyelaidic acids	10·2	0·2	24·0	2·9	1·1	0·3
9,10-Dihydroxystearic acid (combined)	5·6	10·2	11·6	9·7	1·0	6·3
Hydroxyelaidic acids	16·0	13·4	27·9	32·0	0·0	1·9
Other unsaturated products and unchanged elaidic acid, as $C_{18}H_{34}O_2$	36·8	49·3	8·2	20·7	66·6	67·3
Steam-volatile acids, as nonanoic	7·7	6·8	9·9	11·1	2·8	5·3
Non-volatile, water-soluble acids, as azelaic	4·1	3·0	4·8	4·0	0·4	0·3
Neutral, steam-volatile oil	2·5	1·2	5·1	2·7	0·3	0·2

TABLE 3.

Effect of heat on the products obtained by autoxidising elaidic acid at 82° for 24 hr.: (A) whole product; (B) fraction not forming urea complex; (C) fraction forming urea complex. (i) Before, (ii) after being heated under N_2 at 83° for 2 days.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Physical condition	Oily crystals	Slightly yellow oily crystals	Viscous oil	Dark thick oil	Oily crystal-line	Oily crystal-line
Reduction of Fehling's soln.	None	Slight	None	Slight	Trace	Trace
Equiv. wt.	294	318	347	350	289	308
Iodine value	71	69	61	61	74	76
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	19	22	30	57	12	11
Neutral, steam-volatile oil (mainly nonanal and nonan-2-one) (%)	0·5	0·4	1·2	1·8	0·2	0·3
Volatile oil (nonanal and nonanone) resulting from hydrolysis on distn. with 0·5N-NaOH (%)	1·25	2·0	3·69	4·72	1·05	1·03
Nonanal on distn. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	2·09	3·85	3·4	3·8	1·03	4·24
Saponification value	40	56	72	72	16	33
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·00	0·95	0·70	1·50	0·28	0·80
Carbonyl (%)	0·38	0·70	0·40	2·17	0·13	0·48
Oxiran-O (%)	0·56	0·27	0·03	0·00	0·59	0·19
Active O (%)	0·46	0·01	1·31	0·01	0·03	0·002
OH value (corrected for hydroperoxide and epoxide)	41	57	76	101	21	31
Steam-volatile acids, mequiv. (%)	29	25	37	38	10	13
Non-volatile, water-soluble acids, mequiv. (%)	56	41	26	27	1·0	1·3

concurrent decomposition. The former process, which is typical of the catalysed decomposition of cyclic hydroperoxides,[3] should lead to unsaturated ketones in which the *trans*-configuration predominates, since the hydroperoxides themselves, even when derived from oleate, appear to be mainly the *trans*-forms.[17,4,5,12] Ketones of this type are normally isolable without difficulty,[18,16] yet neither (I) nor (II) has been satisfactorily separated from the complex mixtures resulting from autoxidation. The latter process, on the other hand, is in harmony with the observed rise in the hydroxyl value (Tables 1, 3, 5, and 7), as found by the acetic anhydride–pyridine method.[19a] Thus, although it is highly probable

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[17] Knight, Eddy, and Swern, *J. Amer. Oil Chemists' Soc.*, 1951, **28**, 188.

[18] Ellis, *J.*, 1950, 9; King, *J.*, 1951, 1980.

[19] O'Neill, " The Autoxidation of Drying Oils, II " (Technical Paper No. 155, The Research Assocn. of British Paint, Colour, & Varnish Manufacturers), 1948, (*a*) p. 19, (*b*) p. 37.

TABLE 4.

Approximate composition (%), calculated from Table 3, of the products obtained by autoxidising elaidic acid at 82° for 24 hr.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
8- and 11-Oxoelaidic acids, $C_{18}H_{32}O_3$, deduced from (a) $E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	3·4	4·1	5·6	10·6	2·1	2·0
8- and 11-Oxoelaidic acids, $C_{18}H_{32}O_3$, deduced from (b) hydrolysis	3·3	5·1	8·5	10·7	2·8	2·7
9,10-Ketol acids, as $C_{18}H_{34}O_4$	0·0	5·2	3·8	8·3	1·6	4·5
Other oxo-acids, as $C_{18}H_{32}O_3$	0·0	0·0	0·0	0·8	0·0	0·0
9,10-Epoxystearic acid	10·4	5·0	0·5	0·0	11·1	3·6
Hydroperoxyelaidic acids	9·1	0·2	25·7	0·2	0·6	0·04
9,10-Dihydroxystearic acid (combined)	3·7	5·7	6·8	6·1	0·2	7·5
Hydroxyelaidic acids	18·3	20·0	30·4	40·1	9·5	5·1
Other unsaturated products and unchanged elaidic acid, as $C_{18}H_{34}O_2$	50·3	53·7	10·7	18·8	70·8	77·8
Steam-volatile acids as nonanoic	4·6	4·0	5·8	6·0	1·5	2·0
Non-volatile, water-soluble acids, as azelaic	5·3	3·9	2·4	2·5	0·1	0·1
Neutral, steam-volatile oil, as $C_9H_{18}O$	0·5	0·4	1·2	1·8	0·2	0·3

TABLE 5.

Effect of heat on the products obtained by autoxidising methyl oleate at 50° for 12 days: (A) whole product; (B) fraction not forming urea complex; (C) fraction forming urea complex. (i) Before, (ii) after being heated under N_2 at 88° for 53 hr.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Physical condition of oil	Colour-less, mobile	Very pale yellow	Pale yellow	Yellow, less mobile	Colour-less	Very pale yellow
Reduction of Fehling's soln.	Slight	Trace	Slight	Moderate	None	None
Acid value (mg. KOH/g.)	12	21	18	52	1	1
Iodine value	63	61	58	62	65	64
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	25	38	39	63	19	21
Neutral, steam-volatile oil (%)	1·1	1·1	1·2	2·4	1·1	1·1
Volatile oil (mainly nonanal and nonanone) resulting from hydrolysis on distn. with 0·5N-NaOH (%)	2·3	3·1	4·6	4·8	2·0	1·9
Nonanal on distn. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·6	1·0	1·2	1·6	0·5	0·4
Saponification value	220	208	254	220	200	199
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·1	0·0	0·0	0·0	0·1	0·0
Carbonyl (%)	0·39	0·97	0·54	2·91	0·28	0·41
Oxiran-O (%)	0·08	0·14	0·00	0·00	0·24	0·29
Active O (%)	0·93	0·20	2·01	0·07	0·14	0·01
OH value (corrected for hydroperoxide and epoxide)	10	24	22	74	6	0
Steam-volatile acids, mequiv. (%)	25	26	52	75	8	10
Non-volatile, water-soluble acids, mequiv. (%)	10	12	16	25	1	1

that in the early stages of autoxidation the greater part of the αβ-unsaturated ketones originates from hydroperoxides by one or other of these routes, other pathways cannot be excluded. Spectroscopic and other evidence seems to suggest that, in the more advanced stages of autoxidation, peroxide decomposition gives a much smaller yield of αβ-unsaturated ketones (Table 9; cf. ref. 16). This may be connected with the heterogeneity of the peroxides, some part of which is thought to consist of monoxides of the Staudinger type,[4] but could also be due to progressive cyclisation to 1,2-dioxolans, which are known to give the usual iodide and titanium tests.[20]

In general, the total concentrations of (I) and (II), deduced from their neutral volatile hydrolysis products (nonanal and nonan-2-one), agree reasonably with those found by the

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[20] See Criegee and Paulig, *Chem. Ber.*, 1955, **88**, 712.

TABLE 6.

Approximate composition (%), calculated from Table 5, of the products obtained by autoxidising methyl oleate at 50° for 12 days.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Methyl 8- and 11-oxo-oleates, $C_{19}H_{34}O_3$, deduced from (a) $E^{1\%}_{1\,\text{cm.}}$ at 224 mμ ...	4·8	7·3	7·5	12·2	3·8	4·0
Methyl 8- and 11-oxo-oleates, $C_{19}H_{34}O_3$, deduced from (b) hydrolysis	6·0	7·7	11·7	12·0	5·2	5·1
9,10-Ketol-esters, $C_{19}H_{36}O_4$	0·6	0·0	0·0	0·0	0·4	0·1
Other oxo-esters, as $C_{19}H_{34}O_3$	0·0	1·3	0·0	15·4	0·0	0·0
Methyl 9,10-epoxystearate	1·5	2·7	0·0	0·0	4·7	5·6
Hydroperoxy-esters, as $C_{19}H_{36}O_4$	19·1	4·1	41·3	1·4	2·8	0·3
9,10-Dihydroxy-esters, as $C_{19}H_{38}O_4$	0·5	1·6	3·3	4·4	0·0	0·0
Hydroxyoleate esters, $C_{19}H_{36}O_3$	4·8	11·8	9·4	36·9	3·0	0·1
Other unsaturated products and unchanged methyl oleate, as $C_{19}H_{36}O_2$	46·9	47·8	14·6	10·2	66·7	70·9
Steam-volatile acids, as nonanoic	4·0	4·1	8·2	11·9	1·3	1·6
Non-volatile, water-soluble acids, as monomethyl azelaate	2·0	2·4	3·3	5·0	0·1	0·1
Neutral, steam-volatile oil	1·1	1·1	1·2	2·4	1·1	1·1

TABLE 7.

Effect of heat on the products obtained by autoxidising methyl oleate at 83° for 24 hr.: (A) whole product; (B) fraction not forming urea complex; (C) fraction forming urea complex. (i) Before, (ii) after being heated under nitrogen at 85° for 2 days.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Physical condition of oil	Nearly colour-less	Very pale yellow	Very pale yellow	Pale yellow	Nearly colour-less	Nearly colour-less
Reduction of Fehling's soln.	Slight	Slight	Moderate	Moderate	None	None
Acid value (mg. KOH/g.)	24	30	33	63	3	4
Iodine value	48	48	49	53	50	50
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	37	44	39	68	32	33
Neutral, steam-volatile oil (%)	1·5	1·5	2·1	2·3	1·1	1·1
Volatile oil (mainly nonanal and nonan-2-one) resulting from hydrolysis on distn. with 0·5N-NaOH (%)................................	2·6	3·4	3·7	4·8	3·0	3·1
Nonanal on distn. of the residual solution from the above hydrolysis with KIO_4 at pH 8·0 (%)	0·9	2·0	1·7	2·0	1·1	1·1
Saponification value	218	211	250	213	197	197
Nonanal resulting from oxidn. with KIO_4 at pH 8·0 (%)	0·0	0·1	0·0	0·0	0·0	0·1
Carbonyl (%)	0·68	1·19	0·96	2·69	0·45	0·52
Oxiran-O (%)	0·61	0·47	0·0	0·0	1·09	1·06
Active O (%)	0·82	0·28	1·81	0·20	0·14	0·07
OH value (corrected for hydroperoxide and epoxide)	35	47	42	74	13	11
Steam-volatile acids, mequiv. (%)	32	39	63	77	9	10
Non-volatile, water-soluble acids, mequiv. (%)	18	18	22	28	1	1

spectrophotometric method.[7] The discrepancies observed in the case of peroxide-enriched fractions [Tables 2, 4, 6, and 8; columns B(i)] may be attributed to secondary oxidative changes during alkaline hydrolysis. The presence of appreciable concentrations of βγ-unsaturated ketones in these fractions appears to be ruled out by the virtual absence of "other oxo-acids" (or esters) as calculated from the carbonyl content. However, significant amounts of carbonyl compounds of unknown constitution, in which the carbonyl group is presumably more remote from the double bond, result from heating peroxide-enriched fractions from methyl oleate [Tables 6 and 8; columns B(ii)]. These resist hydrolysis, and may contain some di- or poly-meric material.[21,10,7]

[21] Swern, Knight, Scanlan, and Ault, *J. Amer. Chem. Soc.*, 1945, **67**, 1132.

TABLE 8.

Approximate composition (%), calculated from Table 7, of the products obtained by autoxidising methyl oleate at 83° for 24 hr.

	(A)		(B)		(C)	
	(i)	(ii)	(i)	(ii)	(i)	(ii)
Methyl 8- and 11-oxo-oleates, $C_{19}H_{34}O_3$, deduced from (a) $E_{1\,\text{cm.}}^{1\%}$ at 224 mμ ...	7·1	8·6	7·5	13·3	6·2	6·3
Methyl 8- and 11-oxo-oleates, $C_{19}H_{34}O_3$, deduced from (b) hydrolysis	6·6	8·3	9·0	11·5	7·5	7·6
9,10-Ketol-esters, $C_{19}H_{36}O_4$	0·0	0·6	0·0	0·0	0·0	0·3
Other oxo-esters, as $C_{19}H_{34}O_3$	0·0	1·1	0·0	12·1	0·0	0·0
Methyl 9,10-epoxystearate	12·0	9·2	0·0	0·0	21·3	20·8
Hydroperoxy-esters, as $C_{19}H_{36}O_4$	16·8	5·7	37·2	4·1	2·9	1·4
9,10-Dihydroxy-esters, as $C_{19}H_{38}O_4$	0·7	3·5	4·7	5·3	0·8	0·7
Hydroxyoleate esters, $C_{19}H_{36}O_3$	19·0	22·3	19·0	36·2	6·3	5·1
Other unsaturated products and unchanged methyl oleate, as $C_{19}H_{36}O_2$	16·0	21·0	0·0	0·0	44·0	46·0
Steam-volatile acids, as nonanoic	5·1	6·2	10·0	12·2	1·4	1·5
Non-volatile, water-soluble acids, as monomethyl azelaate	3·6	3·6	4·4	5·7	0·2	0·2
Neutral, steam-volatile oil	1·5	1·5	2·1	2·3	1·1	1·1

TABLE 9.

Effect of heat on peroxide-enriched fractions from methyl oleate after autoxidation at 80° for (a) 10 hr., (b) 60 hr. (i) Before, (ii) after being heated under N_2 at 80° for 2 days.

	(a)		(b)	
	(i)	(ii)	(i)	(ii)
Active O (%)	1·55	0·07	1·11	0·09
$E_{1\,\text{cm.}}^{1\%}$ at 224 mμ	50	77	38	42
8- and 11-Oxo-oleic esters (%)	9·7	14·9	7·4	8·1
Carbonyl (%)	1·19	2·42	1·26	1·98
Iodine value	62	64	27	35

Fractions enriched in peroxides by the urea-complex method contain little or no epoxide before or after being heated under nitrogen, while the whole products (columns A) usually suffer some reduction of epoxide content and increase of dihydroxystearic acid derivatives when heated (cf. refs. 22 and 10). The absence of any appreciable epoxide formation or double-bond scission during the heating process is supported by the relatively constant iodine value, the accuracy of which as determined by Wijs's method (1 hr.) does not appear to be seriously affected by the presence of moderate concentrations of peroxides.[23, 19b] In an independent experiment, no expoxide was found after methyl oleate had been heated with 50% t-butyl hydroperoxide in t-butyl alcohol at 85° for 2 days. The 9,10-epoxystearic acid in autoxidised oleic or elaidic acid is predominantly the *trans*-form,[24] and has also been separated from autoxidised n-propyl oleate following saponification.[25] This oxide, but not the *cis*-isomer, has now been isolated similarly from autoxidised methyl oleate. A free-radical mechanism has been suggested[17] to explain the formation of the *trans*-oxide from oleate by way of hydroperoxides, involving an inversion of configuration, but the present work suggests that this oxide is not a primary product of either hydroperoxide decomposition or the action of hydroperoxides on unchanged olefin.

The increase in the hydroxyl value when the autoxidation products of elaidic acid or oleic esters are heated is most marked with the peroxide-enriched fractions from methyl

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[22] Nicolet and Poulter, *J. Amer. Chem. Soc.*, 1930, **52**, 1186; Deatherage and Mattill, *Ind. Eng. Chem.*, 1939, **31**, 1425.

[23] Hamilton and Olcott, *Ind. Eng. Chem.*, 1937, **29**, 217; Farmer and Sutton, ref. 11; cf. Coleman, Knight, and Swern, ref. 2.

[24] Ellis, *Biochem. J.*, 1936, **30**, 753.

[25] Feuell and Skellon, *J.*, 1954, 3414.

oleate, in which it is clearly due to the formation of simple hydroxy-derivatives. In autoxidised elaidic acid this increase arises in part from the formation of ketols and, in certain instances, dihydroxy-derivatives (Tables 2 and 4; columns A and C), but peroxide-rich fractions (columns B) may show a loss of dihydroxy-derivatives on heating, perhaps as a result of their further oxidation to ketols and the virtual absence of epoxides from which they may be formed. The uncatalysed autoxidation of methyl oleate gave little or no ketol esters (cf. Skellon [8]).

Surprisingly little increase of acidity occurs when peroxide-enriched fractions of autoxidised elaidic acid are heated under nitrogen, but similar fractions from methyl oleate show a significant increase in acid value and a corresponding fall in saponification value (Tables 5 and 7; columns B), consistent with ester hydrolysis, without chain scission at the double bond. Autoxidised ethyl oleate was found to resemble autoxidised methyl oleate closely in this and other respects, and detailed analyses have therefore been omitted. Incidental work on the precipitation of urea complexes under prescribed conditions is summarised in the Experimental section.

The available evidence suggests, therefore, that the principal secondary products arising from hydroperoxide decomposition during the early stages of autoxidation are hydroxy-compounds and αβ-unsaturated ketones. The peroxides in autoxidised elaidic acid lead in addition to ketols and to unsaturated compounds which are probably oxygen-bonded, but contain no other functional group. Peroxide-rich fractions from oleic esters, however, yield carbonyl compounds in which the carbonyl group is more remote from the double bond and which may be partly dimeric, but these do not appear in significant amounts in the whole autoxidation products during the early stages of autoxidation.[7] Peroxide decomposition does not result in extensive double-bond scission or epoxide formation under the conditions described.

EXPERIMENTAL

Materials.—Elaidic acid, recrystallised successively from acetic acid and ethanol, had m. p. 44·5°. Methyl oleate, after two fractionations, had b. p. 200—204°/13·5 mm. (Found: Iodine value, 84·4; Sap. value, 190. Calc. for $C_{19}H_{36}O_2$: Iodine value, 85·6; Sap. value, 189). Ethyl oleate similarly had b. p. 220—222°/19° (Found: Iodine value, 80·5; Sap. value, 180°. Calc. for $C_{20}H_{38}O_2$: Iodine value, 81·8; Sap. value, 181).

Methods.—Except as mentioned below, these were as previously described.[7, 16]

Neutral, Steam-volatile Oil from Autoxidised Oleic Esters.—The autoxidised ester (2 g.), or fraction obtained from it by the urea method, was shaken with water (100 ml.) and sufficient 0·1N-sodium hydroxide, as calculated from the acid value, to bring the pH to 8·0. Distillation into a special trap [27] gave a volatile oil, which afforded a 2,4-dinitrophenylhydrazone, m. p. 80—92° (Found: N, 17·45. Calc. for $C_{15}H_{22}N_4O_4$: N, 17·4%), shown by paper chromatography to be a mixture of nonan-2-one and nonanal derivatives. The volatile oil sometimes contained a small amount of unchanged methyl or ethyl oleate, due to the slight steam-volatility of the esters.

8- *and* 11-*Oxo-oleic Esters.*—The spectrophotometric determination was based on an $\varepsilon_{\text{max.}}$ value of 16,000 at 224 mμ for these esters in ethanol, *i.e.*, $E^{1\%}_{1\,\text{cm.}}$ 516 for methyl oleate, 493 for ethyl oleate. All measurements were made with a Unicam S.P. 500 spectrophotometer.

Periodate Oxidation of the Autoxidised Esters.—Oxidation with periodate at pH 8·0 afforded a steam-volatile oil whose 2,4-dinitrophenylhydrazone crystallised in orange-yellow plates, m. p. 95—100° (Found: N, 17·7%), shown by paper chromatography to be mainly the nonanal derivative, with traces of octanal derivative.

Carbonyl.—A pH meter was used, titrations being taken to pH 3·7.

Hydroxyl Value (cf. ref. 19*a*).—The substance (about 1 g.) was heated under reflux with a 20% solution of acetic anhydride (" AnalaR ") in ordinary pyridine (5 ml.) on a water-bath for 2 hr. Water (5 ml.) was then added, and heating continued for a further 5 min. The solution

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[26] Cf. Swern, Witnauer, and Knight, *J. Amer. Chem. Soc.*, 1952, **74**, 1655.
[27] King, *Nature*, 1953, **171**, 566.

was rapidly cooled, ethanol (25 ml.) and phenolphthalein (10 drops of 1% solution) were added, and the solution was titrated with methanolic potassium hydroxide. A blank was carried out simultaneously, omitting only the test substance.

The following corrections were applied: (*a*) For active oxygen. Hydroperoxides of the type found in autoxidised fats react under these conditions to the extent of about 50% of the theoretical; [28] hence an amount equal to 17·5 × % active oxygen was subtracted from the apparent hydroxyl value.

(*b*) For epoxides. *trans*-9,10-Epoxystearic acid was shown to react to the extent of 10% of the theoretical, hence 7·0 × % oxiran-oxygen was subtracted.

The concentration of hydroxyelaidic acid or hydroxyoleic ester was calculated from the corrected hydroxyl value, allowances having been made for the 9,10-ketols (1·784 × % ketol-stearic acid) and dihydroxy-compounds (1·772 × % dihydroxystearic acid), the latter being assumed to be in the monoacylated form.[7]

Fractionation by the Urea-complex Method.—The following procedure was typical. Methyl oleate (60 g.) was autoxidised at 83° for 24 hr. with a rapid stream of oxygen. Two samples, A(i) and A(ii) (each of about 10 g.), were withdrawn, and the remainder of the product was poured into a hot solution of urea (230 g.) in methanol (650 ml.) with stirring. The mixture was set aside for 30 min., cooled at room temperature for 2 hr., and filtered. The crystalline complex was decomposed by stirring with water (1 l.), and the resulting oil (26·5 g.) was isolated by ether extraction and divided into two parts, C(i) and C(ii). The filtrate from the urea complex was diluted with water (2 l.), and saturated sodium sulphate solution (400 ml.), and extracted with ether. Removal of the solvent at room temperature under reduced pressure left a pale yellow oil (15 g.), which was divided into two parts, B(i) and B(ii). Fractions A(ii), B(ii), and C(ii) were heated under nitrogen in stoppered tubes at 85° for 2 days, and all fractions were then analysed.

Isolation of trans-9,10-*Epoxystearic Acid from Autoxidised Methyl Oleate.*—The crystalline urea complex obtained from methyl oleate (50 g.) which had been autoxidised at 80° for 2 days was decomposed with water (1 l.), and the resulting oil (23 g.) was hydrolysed by boiling it gently with 0·5N-sodium hydroxide (400 ml.) in an open vessel for 2 hr. to remove volatile products. Acidification of the cooled solution gave a semi-solid, which was resolved by filtration into an oil and a fatty solid (5 g.), containing a little dihydroxystearic acid, m. p. 130°, and fatty acids. The former was shaken with light petroleum (100 ml.; b. p. 40—60°) and water (50 ml.) in a separator and left overnight. A small deposit of *threo*-dihydroxystearic acid, m. p. 92°, was removed by filtration, and the dried petroleum layer was concentrated to about 30 ml. and cooled at 0° overnight. The precipitate of crude elaidic acid oxide (0·75 g.) was recrystallised successively from light petroleum and ethanol, and gave the pure epoxide (0·5 g.), m. p. 55·5°, not depressed by an authentic specimen. Hydrolysis of the oxide was best effected by refluxing it for 1 hr. with acetic acid (2·5 ml.), followed by dilution with water (12·5 ml.), and further refluxing with 40% sodium hydroxide solution (9 ml.) for 1 hr. Dilution and acidification then gave *erythro*-dihydroxystearic acid, which crystallised from ethanol in plates (0·47 g.), m. p. 132°.

Urea Complexes.—The addition of saturated methanolic urea (10 ml.) to the pure substance (0·1—0·2 g.) in methanol (1 ml.) at room temperature gave a crystalline precipitate of inclusion compound within 2 hr, with oleic or elaidic acid and their methyl or ethyl esters, the 9,10-epoxystearic acids, *trans*-11-oxoheptadec-9-ene-1-carboxylic acid, 12-oxoelaidic acid (incomplete), undecan- or decan-2-one, and nonan-2-one (incomplete), but not with the 9,10-dihydroxy-,[26] acetoxyhydroxy-, or hydroxyoxo-stearic acids, ricinoleic, nonanoic, or azelaic acid, octan-2-one, octanal, or nonanal (some oil separated).

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[28] O'Neill, Ref. 19, pp. 23, 24.