297. *The Autoxidation of* trans-11-*Oxoheptadec*-9-*ene*-1-*carboxylic Acid and* trans-11-*Oxoheptadec*-8-*ene*-1-*carboxylic* (12-*Oxoelaidic*) *Acid, with Some Observations on the Autoxidation of Elaidic Acid.*

By GEORGE KING.

When heated at about 80° in the absence of oxygen, *trans*-11-oxoheptadec-9- and -8-ene-1-carboxylic acid undergo mutual isomerisation, an equilibrium being established in favour of the former, with little or no polymerisation. The rate of autoxidation of these acids with gaseous oxygen at this temperature is of the same order as that of elaidic or oleic acid. No epoxide is formed, nor much active peroxide, but considerable amounts of oxygenated oily products of high molecular weight were obtained on prolonged oxidation. These appear to consist of esters and, possibly, stable peroxides of the perdioxan type.

Preliminary evidence suggests that αβ-unsaturated keto-acids may be formed under certain conditions by decomposition of hydroperoxides in autoxidised elaidic acid.

THE formation of conjugated olefin-ketonic acids during the autoxidation of oleic and elaidic acids and their alkyl esters is now well established,[1,2,3] although none appears to have been isolated in a pure state. Considerable interest attaches to the origin and rôle of these αβ-olefin-ketones in the autoxidation process. It has been suggested[4] that they result from hydroperoxides by dehydration, a process which commonly requires a metal catalyst (see, *e.g.*, Farmer and Sundralingam[5]). In the uncatalysed autoxidation of oleic and elaidic acid at moderate temperatures maximum formation of peroxides always precedes that of αβ-unsaturated ketonic acids, but in the presence of cobalt the peroxide concentration remains uniformly low.[2] However, carbonyl formation is independent of a catalyst and its maximum concentration little affected by the presence of cobalt. Ellis[1] considered that 8- and 11-oxo-oleic and -elaidic acid are primary oxidation products, which give rise to dimeric and polymeric oils and resins and readily take up oxygen to form reactive peroxides which play an essential part in the autoxidation process. He found[6] that 12-oxo-oleic acid also is particularly susceptible to atmospheric oxidation, affording high yields of peroxide together with a crystalline product which was later shown to be 11 : 12-dioxo-oleic acid.[7]

Studies in this field are further complicated by the possibilities of double-bond migration,[8,9] *cis-trans*-isomerisation,[9,10] the formation of peroxides other than hydroperoxides,[11,12] and polymerisation. This paper is concerned primarily with the autoxidation of the readily accessible 12-oxoelaidic acid (I) and the isomer *trans*-11-oxoheptadec-9-ene-1-carboxylic acid[6] (II), which are closely related to the ketonic acids (III) and (IV) occurring in autoxidised elaidic acid. When the acid (I) was heated for several days at

(I) $CH_3\cdot[CH_2]_5\cdot CO\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ $CH_3\cdot[CH_2]_5\cdot CO\cdot CH{:}CH\cdot[CH_2]_8\cdot CO_2H$ (II)

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[1] Ellis, *Biochem. J.*, 1950, **46**, 129.

[2] King, *J.*, (*a*) 1954, 2114; (*b*) 1956, 587.

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

[4] Swern and Coleman, *J. Amer. Oil Chemists' Soc.*, 1955, **32**, 700.

[5] Farmer and Sundralingam, *J.*, 1942, 121.

[6] Ellis, *J.*, 1950, 9.

[7] King, *J.*, 1950, 2897.

[8] Swern, Scanlan, and Ault, *J. Amer. Chem. Soc.*, 1945, **67**, 1132; Ross, Gebhart, and Gerecht, *ibid.*, 1949, **71**, 282; Khan, *Canad. J. Chem.*, 1954, **32**, 1149; *J. Chem. Phys.*, 1954, **22**, 2090; Skellon and Thruston, *J.*, 1953, 138; Blekkingh, Janssen, and Keppler, *Rec. Trav. chim.*, 1957, **76**, 35.

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

[10] Khan, *Biochim. Biophys. Acta*, 1955, **16**, 159.

[11] Treibs, *Ber.*, 1942, **75**, 1373; 1943, **76**, 670; Farmer, *Trans. Faraday Soc.*, 1946, **42**, 228; O'Neill, *Chem. and Ind.*, 1954, 384.

[12] Swern, Coleman, Knight, Ricciuti, Willits, and Eddy, *J. Amer. Chem. Soc.*, 1953, **75**, 3135.

about 80° in the absence of oxygen, the isomer (II) was formed by migration of the double-bond, an equilibrium mixture containing 60—70% of (II) being obtained (Table 1).

TABLE 1. *The effect of heat on the unsaturated oxo-acids.*

	Original acids		After heating under N_2 at 78° for 7 days	
	(I)	(II)	(I)	(II)
M. p.	73°	50·5°	44—49°	44—47·5°
Equiv. wt.	296	296	314	315
M (in dioxan)	296	296	300	314
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	6	540	339	367
$E^{1\%}_{1\,\text{cm.}}$ at 272·5 mμ	2	0·5	2	6
Octanone on saponification (%)	37·5	38	36·8	36·2
Iodine value	120	86	115	98
Carbonyl (%)	9·46	9·46	9·44	9·25

The change was conveniently followed spectroscopically, the strong absorption at 224 mμ being due almost exclusively to the conjugated chromophore $CO\cdot CH{:}CH$.[2] Virtually the same mixture resulted on heating the acid (II) and the process was unaffected by the addition of cobalt. Nichols[13] converted acid (I) into (II) by refluxing it for a few minutes with acetic acid containing a trace of sulphuric acid. Therefore, although some migration of the double bond may occur in the acids (III) and (IV) during the autoxidation

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

of oleic or elaidic acid, this is not likely to be extensive, as the equilibrium favours the conjugated system; in any case the further oxidation of these acids readily accounts for the formation of small quantities of octanoic and suberic acid, as well as nonanoic and azelaic acid, which constitute important cleavage products of the autoxidation.[14] It is significant that little or no polymerisation occurred under the influence of heat alone.

The autoxidation of 12-oxoelaidic acid (I), m. p. 73°, by gaseous oxygen at 78—80° was accompanied by a rapid increase in the absorption of ultraviolet light at 224 mμ, as a result of its isomerisation to (II), reaching a maximum ($E^{1\%}_{1\,\text{cm.}}$ 185) in about 24 hours. The final products (Table 2) were very similar to those obtained by the autoxidation of the isomer (II), although this appeared to be oxidised rather more rapidly and to suffer greater cleavage than (I). The catalytic influence of the cobalt was not marked. At no time

TABLE 2. *The products of the autoxidation of the oxo-acids at* 78—80° (a) *for* 5 *days without a catalyst,* (b) *for* 3 *days with* 0·5% *of cobalt.*

	(I)		(II)	
	a	*b*	*a*	*b*
Physical condition	Viscous yellow oil	Very viscous red oil	Pale yellow semi-solid	Very viscous red-brown oil
Equiv. wt.	251	289	209	237
Iodine value	36	53	21	28
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	110	109	100	86
$E^{1\%}_{1\,\text{cm.}}$ at 272·5 mμ	38	36	13	23
Octanone on saponification with 0·5N-NaOH (%)	4·1	4·0	6·8	4·0
Saponification value	130	141	—	93
Carbonyl (%)	4·0	3·1	6·0	5·0
Oxiran-O (%)	0·0	0·0	0·0	0·0
Active O (%)	0·1	0·06	0·18	0·03
Steam-volatile acids mequiv. (%)	73	57	109	68
Steam-volatile acids as heptanoic (%)	9·5	7·4	14·2	8·85
Non-volatile, water-soluble acids, mequiv. (%)	90	57	123	82
as azelaic [from (I)] or sebacic [from (II)] (%)	8·5	5·4	12·4	8·3
CO_2 evolved (%)	3·4	4·3	4·8	4·5
Formic acid evolved as vapour (%)	1·0	0·8	1·7	0·9

[13] Nichols, *Chem. Abs.*, 1953, **47**, 9999; U.S.P. 2,623,888/1952.
[14] Ellis, *Biochem. J.*, 1936, **30**, 753.

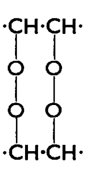
was a high concentration of reactive peroxide (measured by Lea's method) observed, the highest value found for active oxygen being only 0·28%, obtained by oxidising the acid (II) for 2 days at 78°, and much lower values were recorded in the presence of the catalyst (cf. King [2]). The amounts of carbon dioxide and formic acid evolved, as well as the total extent of cleavage, were of much the same order as with oleic and elaidic acids,[2] but in contrast no evidence of epoxide formation was obtained.

Prolonged oxidation of the oxo-acids yielded considerable amounts of viscous, coloured oils of high molecular weight, but more or less normal equivalent weight, sparingly soluble in light petroleum or carbon tetrachloride (Table 3). These resinous oils were highly oxygenated, corresponding to an absorption of about one molecule of oxygen per molecule of oxo-acid, but had very low epoxide values as measured by the usual methods. Their saponification values (excluding acid values) indicated a consumption of 1—2 equivalents of alkali per mole, and their iodine values the presence of 0·5—2 double bonds. Sebacic acid was formed on saponification of the fraction of high molecular weight isolated from autoxidised (II), and it seems probable that such fractions are composed partly of esters of dibasic acids, analogous to, but not identical with, the esters occurring in autoxidised oleic or elaidic acid.[1,2] The composition and high molecular weight of the resinous fractions suggest the presence also of polymeric peroxides of the perdioxan type, (*A*), which are relatively stable structures.[11] All these fractions reduced Fehling's solution, but had a much reduced carbonyl content and yielded little octanone on hydrolysis. A low content of the conjugated enone group, CO·CH:CH, was also indicated by the relatively small absorption of ultraviolet light at 224 mμ. On the other hand, the absorption curves all showed an inflexion or feeble maximum at *ca.* 270 mμ, which has previously been encountered in autoxidised unsaturated fatty acids and their derivatives and is usually attributed to small amounts of triply conjugated systems, such as ·CO·CH:CH·CO·[15] (or its enolic form) or ·CH:CH·CH:CH·CO·.[16] The author has observed a similar shoulder ($E^{1\%}_{1\,\text{cm.}}$ 7 at 270 mμ) in oleic acid containing 0·4% of cobalt through which oxygen had been bubbled for 28 days at room temperature.

TABLE 3. *Fractions of high molecular weight isolated after autoxidising the oxo-acids at* 80° (a) *for* 3 *days*; (b) *with* 0·5% *of* Co *for* 3 *days*; (c) *for* 5 *days*; (d) *with* 0·5% *of* Co *for* 5 *days.*

Origin	(I)		(II)	
	a	b	c	d
Physical nature	Viscous pale yellow oil	Resinous reddish oil	Viscous yellow oil	Resinous red-brown oil
Composition (%) * C	65·3	66·88	64·03	—
Composition (%) * H	8·95	9·05	8·98	—
Equiv. wt.	291	327	259	290
M (in dioxan)	605	940	530	850
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	84	95	52	69
$E^{1\%}_{1\,\text{cm.}}$ at 270 mμ	38	45	23	36
Octanone on saponification (%)	4·0	1·4	2·9	1·2
Iodine value	48	50	20	32
Saponification value	190	170	182	116
Carbonyl (%)	3·7	3·4	4·1	2·5
Active O (%)	0·2	0·1	0·2	0·1
Saponification products: Volatile acids, mequiv. (%)	134	79	98	49
Saponification products: Volatile acids, as heptanoic (%)	17·4	10·3	12·7	6·4
Saponification products: Non-volatile, water-soluble acids, mequiv. (%)	—	192	280	99
Saponification products: Non-volatile, water-soluble acids, as sebacic (%)	—	19·4	28·3	10·0

* Calc. for $C_{18}H_{30}O_5$: C, 66·2; H, 9·3%. Calc. for $C_{18}H_{28}O_5$: C, 66·7; H, 8·7%.



(*A*)

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[15] Holman, Lundberg, Lauer, and Burr, *J. Amer. Chem. Soc.*, 1954, **67**, 1285.

[16] Evans and Gillam, *J.*, 1945, 432; Bolland and Koch, *J.*, 1945, 445; Parkinson and Skellon, *J.* 1957, 851; cf. Jones and Lahey, *Univ. Queensland Papers, Dept. Chem.*, 1942, **1**, 22; *Chem. Abs.*, 1943, **37**, 3342.

The mechanism of the formation of the conjugated unsaturated ketonic acids in autoxidised elaidic acid is still not clear. Preliminary experiments on the oxidised acid have shown that thermal decomposition of the peroxides is strongly catalysed by cobalt, but that this is accompanied by a definite increase in the content of carbonyl conjugated with the double bond only when the acid has been oxidised at low temperature (Table 4). Further work on this problem is being done.

TABLE 4. *The effect of heat on the products obtained by autoxidising elaidic acid* (a) *at* 50° *for* 15 *days*; (b) *at* 80° *for* 24 *hr.*

			After heating under N_2 at 80° for 90 min.			
	Before heating		Alone		With 0·5% of Co	
	(a)	(b)	(a)	(b)	(a)	(b)
Active O (%)	0·52	0·44	0·41	0·33	0·008	0·016
$E^{1\%}_{1\,\text{cm.}}$ at 224 mμ	21·8	56·2	24·8	54·0	37·7	56·4
8- and 11-Oxoelaidic acids (%)	3·90	10·2	4·44	9·8	6·85	10·3
Total carbonyl (%)	0·78	1·70	0·73	1·51	1·07	1·93
Iodine value	71	38	70	39	69	40
Oxiran-O (%)	0·47	1·06	0·51	1·20	0·25	0·92

EXPERIMENTAL

trans-11-Oxoheptadec-8-ene-1-carboxylic acid (12-oxoelaidic acid) (I), m. p. 73°, was prepared from ricinelaidic acid [6] and was converted into *trans*-11-oxoheptadec-9-ene-1-carboxylic acid (II), m. p. 50·5°, by way of the hydrogen bromide adduct.[17].

Methods.—The methods of autoxidation and analyses of the products were similar to those described in connexion with the autoxidation of oleic and elaidic acid.[2] In the determination of carbonyl, however, it was found necessary to use a pH-meter instead of an indicator in titrations to pH 3·7, owing to the colour of the products. For the same reason a pH-meter was used in the determination of saponification values.

Steam-volatile Acids.—The autoxidation product from acid (I) or (II) was distilled with water as previously described [2a] and the neutralised distillate was evaporated to small bulk. Addition of zinc sulphate solution precipitated zinc heptanoate, which crystallised from pure ethanol in plates, m. p. and mixed m. p. 137·5°.

Non-volatile, Water-soluble Acids.—After removal of the volatile acids, the residual solution was filtered hot and the insoluble oil washed with hot water. The filtrate and washings were evaporated to small bulk and cooled. From acid (I) a small amount of slightly impure azelaic acid was obtained. This crystallised from water in plates, m. p. 102—103°, not depressed by pure azelaic acid. From acid (II) the less soluble sebacic acid was obtained in better yield; it crystallised from hot water in plates, m. p. and mixed m. p. 130—131° (Found: equiv., 103. Calc. for $C_{10}H_{18}O_4$: equiv., 101).

Octan-2-*one*.—Distillation of acid (I) or (II) with 0·5N-sodium hydroxide afforded octan-2-one as a volatile oil in good yield.[6, 17] The volatile oil similarly obtained from the autoxidised acids gave a 2 : 4-dinitrophenylhydrazone, m. p. 68°, not depressed by octan-2-one 2 : 4-dinitrophenylhydrazone (Found: C, 54·2; H, 6·5; N, 17·6. Calc. for $C_{14}H_{20}O_4N_4$: C, 54·5; H, 6·5; N, 18·2%).

Fractions of High Molecular Weight.—The autoxidised acids were freed from steam-volatile and water-soluble acids, and the residual oils dissolved in ether. The ethereal solution, dried and filtered, was treated with 3 volumes of light petroleum (b. p. 40—60°) and left in a separating funnel for 24 hr. The supernatant solvent was removed by decantation and the precipitated oil was again dissolved in ether and precipitated with light petroleum. The oil was washed with light petroleum, and the residual solvent removed *in vacuo* at 40°. The viscous products were almost insoluble in light petroleum and, unlike the original oxo-acids, very sparingly soluble in carbon tetrachloride. The analytical results are summarised in Table 3.

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[17] King, *J.*, 1951, 1980.