160. *The Oxidation of Monoethenoid Fatty Acids and Esters. Catalytic Oxidation of Ketol Derivatives of Oleic Acid.*

By T. L. PARKINSON and J. H. SKELLON.

The catalytic oxidation of the isomeric 9(10)-hydroxy-10(9)-oxostearic acids has been studied. Ultraviolet absorption spectra show that conjugated dienone groupings are formed as the carbonyl and hydroxyl contents decrease.

The primary oxidation product is 9 : 10-dioxostearic acid. After 20 hours' oxidation at 120° the product contained mainly highly oxygenated polymeric acids and small fractions of neutral ketonic oils. There was little evidence of scission.

AUTOXIDATION of monoethenoid acids and esters gives hydroperoxides, which decompose to products containing carbonyl groups. Skellon [1] showed that the oily product resulting from catalytic autoxidation of methyl oleate at 120° contained 21% of the isomeric 9(10)-hydroxy-10(9)-oxostearates. The corresponding isomeric acids were identified by King [2] among the products of autoxidation of elaidic and oleic acids at 47° and 78°. Similar ketol derivatives are formed on catalytic autoxidation of *n*-propyl oleate,[3] erucic acid, *n*-propyl

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[1] Skellon, *J.*, 1948, 343.

[2] King, *J.*, 1954, 2114; 1956, 587.

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

erucate, and esters of petroselinic acid. It is therefore important to study the behaviour of these ketols when oxidised by gaseous oxygen.

On oxidation at 100° or 120° by gaseous oxygen (catalyst, 0·05% of uranium as oleate) the ketols changed into a brown viscous oil and after 20 hr. at 100° or 8 hr. at 120° the product gave an increased acid value and molecular weight, and a small iodine value, and contained little peroxidic oxygen. Absorption in the ultraviolet region increased; the shape of the spectra and the positions of maxima were characteristic of the conjugated dienone chromophore,[4] R·CH:CH·CH:CH·COR′, which was subsequently further oxidised.

Autoxidation at 100° followed a parallel course.

9 : 10-Dioxostearic and nonanoic acid were primary oxidation products.

The product formed in 20 hr. at 120° contained a dark brown, petrol-insoluble, highly oxygenated polymeric acid, smaller fractions of petrol-soluble oil (mainly dimeric acids), and neutral ketonic oils.

Table 2 records the yields from autoxidation of 9(10)-hydroxy-10(9)-oxostearic acids. The polymeric acids produced had lower carbonyl contents than the ketonic compounds from which they were derived; the presence of carbon–oxygen and carbon-bonded linkages in the products was demonstrated experimentally by depolymerisation with hydriodic acid.

The oily complexes obtained in high-temperature catalytic autoxidation of monoethenoid acids may result from the following sequence : unsaturated acid ⟶ hydroperoxide ⟶ dihydroxy-acid ⟶ ketol acid ⟶ diketo-acid ⟶ dimeric oils ⟶ trimeric resins.

EXPERIMENTAL

Preparation of 9(10)-*Hydroxy*-10(9)-*oxostearic Acids*.—Pure oleic acid was prepared from high-grade olive oil by a lead and lithium salting method [5] and converted into mixed hydroxyoxostearic acids, m. p. 64·5—65°, by oxidation with neutral potassium permanganate [6] (Found : equiv., 312; CO, 9·0; OH, 5·3%. Calc. for $C_{18}H_{34}O_4$: equiv., 314; CO, 8·9; OH, 5·4%). The semicarbazones of the isomers were separated by fractional crystallisation from ethylene dichloride and decomposed to the individual acids by boiling formaldehyde and hydrochloric acid. Recrystallisation from aqueous alcohol yielded pure 9-hydroxy-10-oxostearic acid, m. p. 74° (Found : equiv., 31; CO, 8·8; OH, 5·4. Calc. for $C_{18}H_{34}O_4$: equiv., 314; CO, 8·9; OH, 5·4%), and 10-hydroxy-9-oxostearic acid, m. p. 75·5° (Found : equiv., 314; CO, 9·1; OH, 5·2%).

Catalytic Oxidations.—Gaseous oxygen was bubbled through the molten material in an apparatus essentially similar to that used by Skellon and Thruston [7] in the presence of 0·05% of uranium (as oleate). Ultraviolet absorption spectra of ethanolic solutions showed the development of conjugated dienone structures, with maxima in the region 260—280 mμ (see Table 1).

TABLE 1. *Catalytic oxidation of* 10-*hydroxy*-9-*oxostearic acid at* 120°.

Time (hr.)	2	5	8	10	12	14	16	18	20
Acid val.	177	187	198	215	224	248	258	281	281
CO (%)	9·7	8·8	7·9	7·6	6·6	4·6	4·2	3·7	3·5
OH (%)	5·5	3·4	2·4	1·4	—	1·5	—	1·6	0·7
I val.	—	—	7·5	—	—	—	—	—	6·7
Active O (%)	—	—	0·004	—	—	—	—	—	0·011
M (Rast)	—	—	294	—	—	—	—	—	580
E (1%; 1 cm.) at 270 mμ	—	12·4	21·6	—	26·6	—	23·0	—	19·8

After oxidation of 9-hydroxy-10-oxostearic acid (cf. Table 1) for 20 hr., analytical values were: acid val., 289; CO, 3·3%; OH, 0·3%; active O, 0·012%; *E*(1%; 1 cm.) at 270 mμ, 30·0.

Catalytic oxidation of the mixed isomeric 9 : 10-ketols also followed a similar course at both 120° and 100°, being slower at the lower temperature.

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[4] Evans and Gillam, *J.*, 1943, 565; 1945, 432.

[5] Skellon, *J. Soc. Chem. Ind.*, 1931, **59**, 131T.

[6] King, *J.*, 1936, 1788.

[7] Skellon and Thruston, *J.*, 1949, 1626.

Examination of the Oxidation Product.—The results of typical fractionation of the oxidation products obtained from 30 g. of 9-hydroxy-10-oxostearic acid after at (*a*) 8 hr. and (*b*) 20 hr. are given in Table 2.

The products (3·8 g., *a*; 8·5 g., *b*) in ether were extracted with 20% sodium carbonate solution, and the alkaline extracts washed with ether, carefully acidified with 5N-sulphuric acid, and steam-distilled. Distillates were extracted with ether, yielding nonanoic acid [(*a*) 0·15 g.; equiv., 161; m. p. of Zn salt, 133°. (*b*) 0·47 g.; equiv., 158; m. p. of Zn salt, 133° (Found: Zn, 17·6%). Calc. for $C_9H_{18}O_2$: equiv., 158. Calc. for $C_{18}H_{34}O_4Zn$: Zn, 17·2%].

Residues from the steam-distillation were extracted with ether, evaporated, digested with chloroform, and cooled at 2° (16 hr.). 9 : 10-Dihydroxystearic acid was not precipitated; the chloroform was evaporated and the residues digested under reflux with boiling light petroleum. Some of the material was insoluble in the hot solvent and separated as a dark brown resin [(*a*) 0·4 g.; equiv., 329; *M* (Rast), 585; CO, 5·9; C, 67·9; H, 9·3%].

The petroleum-insoluble material was completely soluble in ethanol and acetone at all temperatures down to −60°, but was separated by *n*-hexane into a completely insoluble resin, a fraction soluble at room temperature but insoluble at −60°, and a fraction soluble at −60°, as follows:

	Insol. at room temp.	Sol. at room temp., insol. at −60°	Sol. at −60°
Weight (g.)	5·24	0·25	0·38
Equiv.	240	205	266
M (Rast)	518	349	394
CO (%)	3·0 *	3·2	2·9

* Also, OH, 0%; C, 64·4%; H, 9·1%.

After removal of the insoluble resin, the light petroleum solutions were cooled at 2° for several hours. Resulting pale yellow precipitates were filtered off and the filtrates evaporated, yielding yellow oils [(*a*) 1·04 g.; equiv., 290; *M* (Rast), 660; CO, 5·9; C, 67·5; H, 10·2%. (*b*) 1·02 g.; equiv., 251; *M* (Rast), 281; CO, 2·9; OH, 0·3; C, 67·5; H, 10·3%].

The precipitates obtained by cooling the light petroleum solutions to 2° were dried *in vacuo*, dissolved in hot absolute ethanol, and allowed to cool. 9 : 10-Dioxostearic acid separated at room temperature and was filtered off and dried *in vacuo* (0·47 g.; m. p. 84·5°) (Found: equiv., 308; CO, 18·1. Calc. for $C_{18}H_{32}O_4$: equiv., 312; CO, 17·9%). Identity was confirmed by preparing the 2 : 4-dinitrophenylhydrazone, m. p. 146—148°, which gave an intense violet colour with ethanolic potassium hydroxide.

The filtrates were treated with sufficient distilled water to lower the ethanol concentration to 60% and left for several hours at room temperature. A precipitate formed in experiment (*a*) and was filtered off and dried (0·19 g.), m. p. 84° (Found: equiv., 324; CO, 9·6%). The resulting filtrates were diluted with water and extracted with ether, yielding straw-coloured solid or semisolid materials [(*a*) 0·98 g.; equiv., 191; *M* (Rast), 304; CO, 4·6; OH, 1·3; C, 63·6; H, 9·2%. (*b*) 0·17 g.; equiv., 106; *M* (Rast), 281; OH, 1·3%].

Similar fractions were obtained from the other oxidation products. The yields for the various fractions are given in Table 2.

TABLE 2. *Catalytic oxidation of* 9(10)-*hydroxy*-10(9)-*oxostearic acid.*

Temp.	Time (hr.)	Acid taken (g.)	9 : 10-Dioxostearic acid (%)	Nonanoic acid (%)	Acidic yellow petrol-sol. oil (%)	Acidic brown petrol-insol. resin (%)
			10-*Hydroxy*-10-*oxostearic acid.*			
120°	8	30	10	4	21	10
120	20	30	Nil	8	13	63
			9-*Hydroxy*-10-*oxostearic acid.*			
120°	8	30	12	4	27	10
120	20	30	Nil	5	12	62

Depolymerisation of Typical Fractions with Hydriodic Acid.—Polymeric fractions were examined for the presence of oxygen linkages. 0·5—1·0 g. was refluxed with 5 g. of hydriodic acid for 3 hr. Ether was added and the solution washed with sodium thiosulphate and water. The ethereal solution was evaporated and the residue refluxed with aqueous-alcoholic 0·5N-potassium hydroxide, acidified, and tested for the presence of iodide by addition of silver nitrate solution. All the samples gave positive results, confirming the presence of oxygen-linkages of ether or peroxide type. The resulting resin was extracted with ether and analysed. Typical results were : for the petrol-insoluble brown acidic resin separated from the oxidation product of 10-hydroxy-9-oxostearic acid (20 hr., 120°), *M* (Rast), before depolymerisation 530, after polymerisation 313; equiv., before depolymerisation 196, after polymerisation 184.

A proportion of each fraction consisted of dimers not depolymerised by hydriodic acid, indicating presence of carbon–carbon bonds.

Ultraviolet Absorption Spectra of Complex Fractions.—Fractions isolated after 8 hours' oxidation at 120° showed maxima at 260—280 mμ. No maxima were observed in fractions after 20 hours' oxidation at 120°. In no case was a maximum observed beyond 320 mμ, showing that conjugated unsaturated structures longer than triene were absent.

CHEMISTRY DEPARTMENT, ACTON TECHNICAL COLLEGE.

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