414. *The Mechanism of Oxidation of Monoethenoid Fatty Acids. Factors influencing Hydroperoxide Formation and Transition in Catalytic Autoxidations.*

By J. H. SKELLON.

The formation and decomposition or transition of hydroperoxides during autoxidation of highly purified oleic acid under various conditions have been investigated. Ultra-violet light alone causes little or no direct hydroperoxide formation when the acid is exposed in a closed quartz cell or in benzene solution. In the presence of air and with limited humidity, small amounts of peroxide slowly develop. Aerial oxidation of oleic acid at room temperature in presence of strong ultra-violet light results in rapid formation of hydroperoxide, which then undergoes transition or decomposition. As with methyl esters, catalytic autoxidation of the free acid first results in an increased rate of peroxidation as the temperature increases, but hydroperoxide transition also increases, so that at the higher temperatures the maximum amount of peroxidation is much smaller.

The effects of metallic catalysts on *different stages* of oxidation have been examined. One group of metallic cations in the form of oil-soluble soaps exerts a maximum effect at the hydroperoxide transition stage, whilst another group is more efficient in the initial phases of oxidation.

Autoxidised oleic acid (in which hydroperoxide transition has occurred) containing metallic catalysts is again subject to slow peroxidation on storage with limited access to air and light.

CONSIDERABLE progress has been made in recent years on problems connected with the elucidation of oxidation mechanisms in monoethenoid fatty acids. Formation and transition or decomposition of peroxidic oxygen during aerial oxidation of oleic and elaidic acids and their esters have been established by various authors (see, *inter al.*, Gunstone and Hilditch, *J.*, 1945, 836; Skellon, *J.*, 1948, 343; Skellon and Thruston, *J.*, 1949, 1626), whilst the general influence of catalysts was described by Skellon and Spence (*J. Soc. Chem. Ind.*, 1948, 242). Aerial oxidation of methyl oleate and elaidate in the presence of ultra-violet light at 35° yields the corresponding hydroperoxidic ester (Farmer and Sutton, *J.*, 1943, 119; Sutton, *J.*, 1943, 242). It appears that catalytic autoxidations may proceed according to specific mechanisms and there is evidence that the hydroperoxide transitions invariably afford ketonic derivatives.

Whilst the general efficiency of catalysts in gaseous autoxidations is known, little information is available about their intrinsic influence at different stages of these complex processes.

In the work now described, the stability of the initial hydroperoxide under varying external influences has been studied in detail, particularly effects of ultra-violet light, temperature, time, and catalyst.

Whilst ultra-violet light accelerated hydroperoxidation to a limiting value in aerial oxidations at room temperature, exposure of oleic acid, in closed quartz vessels or in benzene solution, to ultra-violet rays alone caused no appreciable peroxidation although there was evidence of change in configuration. However, previous exposure of unsaturated fatty acids to ultra-violet light reduced the induction period in subsequent aerial oxidations.

Comparison of catalytic autoxidations of oleic acid at 65° and 120° for short periods showed that first there was an increase in the rate of peroxidation at the higher temperature, followed by an increase in the rate of transition, with consequent smaller maxima of hydroperoxidic oxidation, again indicating that, in high-temperature catalytic autoxidations, hydroperoxide formation and transition take place more rapidly than, and possibly in a different way from, that at lower temperature. The present results show that metallic cations of different periodic groups may exert specific catalytic influence at the primary or the secondary stage of autoxidation of 120°. One group of typical metals (such as lead, aluminium, or barium) appears to accelerate the primary stage of peroxidation but has only a moderate effect on the transition stage. Another group, represented by thallium and zinc, has generally little catalytic activity which, however, is particularly marked at the transition stage to ketonic derivatives.

On the other hand, metals such as cobalt, vanadium, etc., appear to exert a positive effect at both the primary peroxidation and the transition stage, although maximum contents of peroxidic oxygen are small owing to continuous decomposition at 120°.

These results have provided valuable data for controlled autoxidation of monoethenoid fatty acids and may explain the varying activity of metallic " driers," which appears to be closely related to the atomic structure of the metal present as cation; according to Vold and Hattiangdi (*Ind. Eng. Chem.*, 1949, **41**, 2311) " drier " action is a maximum during early stages of autoxidation of ethenoid chains rather than at the final polymerisation.

Finally, fatty acids and esters catalytically autoxidised at 120° for short periods appear to be susceptible to further slow changes on storage. Oleic acid, autoxidised for 7 hours at 120° (0·05% of metal catalyst) and subsequently left for long periods even in corked tubes with limited access to air and light, again slowly acquired an increased peroxidic-oxygen content, without gelation, whereas, in open dishes in films, the acid became viscous and even gelled. The increase in peroxidic-oxygen content on long storage may be caused by further slow saturation of residual ethenoid linkages, with little or no decomposition, consequent on the limited surface exposure to a minimum of air and light.

From these various observations it seems likely that the oily complexes present in the products of short thermal catalytic oxidations contain another type of peroxide not identifiable with the original hydroperoxide. Subsequent decomposition of such complexes by hydrolysis leads to a variety of scission products which appear to justify this view.

According to a mechanism of catalytic gaseous oxidation applicable to monoethenoid fatty acids and esters previously advanced (Skellon, *loc. cit.*), initially formed hydroperoxides are transformed in part into ketols, and further entry of oxygen affords mainly a monomeric oily product, little polymerisation occurring up to 10 hours. The oily product from methyl oleate had an approximate composition $C_{19}H_{36}O_6$ but liberated little iodine from potassium iodide.

Ellis (*Biochem. J.*, 1950, 129), as a result of more prolonged autoxidation of oleic and elaidic acids (45—100°), indicated that the products contained monoacyl derivatives of dihydroxystearic acid, α- and β-unsaturated keto-acids, and products of dimerisation and polymerisation containing β-keto-acids. He also isolated *cis*- and *trans*-11-ketoheptadec-8-ene-1-carboxylic acid (λ-keto-oleic and -elaidic acids) by chromic acid oxidation of ricinoleic acid (*J.*, 1950, 9), and considered that the autoxidations yielded successively olefinic acid, olefinic keto-acid, olefinic keto-peroxide, and peroxidation products (including an epoxide). Separate experiments on the autoxidation of this keto-oleic acid at 42° apparently gave high peroxide yields (27%) after 24 hours.

The results serve to emphasise the complexity of these autoxidations, which depend on external conditions. In this laboratory, work is continuing on *short* catalytic high-temperature autoxidations of pure monoethenoid fatty acids and derivatives, under conditions which it is hoped will prevent undue dimerisation or polymerisation.

EXPERIMENTAL.

Preparation of Pure Oleic Acid.—Oleic acid was prepared from olive oil (500 g.) by methods previously described (*J. Soc. Chem. Ind.*, 1931, **50**, 131T) (Found: I.V., 89·9, 89·8; equiv., 281·8, 282·2. Calc. for $C_{18}H_{34}O_2$: I.V., 90·1; equiv., 282).

Influence of Ultra-violet Light on Peroxide Formation in Mono-ethenoid Fatty Acids. Pure Oleic Acid.—Pure oleic acid, in quartz cells, was exposed to the full rays of a mercury-vapour lamp (i) in presence of a slow stream of oxygen, (ii) in open quartz cells with subsequent oxidation, (iii) with limited access to air, (iv) in closed quartz cells, and (v) in benzene solution. The results are given in Table I.

TABLE I.

Influence of ultra-violet light on peroxidic oxygen content of pure oleic acid.

1. Oleic acid exposed in open quartz vessel in presence of a slow stream of oxygen at room temp. :

Time of exposure (hrs.)	2	4	6	8	10	12
Peroxidic oxygen, found, %	0·43	0·50	1·06	0·65	0·57	0·50

	Peroxidic oxygen, found, %.
2. Oleic acid exposed for 10 hrs. in an open quartz cell. Subsequently oxidised for 7 hours at 120°	0·61
3. Oleic acid exposed in a flat dish of large surface area to direct rays for 48 hrs.	0·47
4. Oleic acid exposed in open quartz cell, with limited access to air, for 16 hrs.	0·04
5. Oleic acid exposed in a closed quartz cell, for 16 hrs.	0
6. Oleic acid in benzene solution in an open quartz cell, exposed for 8 hrs.	0

When oxygen was passed into oleic acid exposed to ultra-violet light at room temperature, the peroxidic-oxygen content rose to 1·06% in 6 hours, the acid thereafter commencing to undergo transition. Farmer and Sutton (*J.*, 1943, 119) found 0·64% of active oxygen on photochemical oxidation (4 hours) of methyl oleate at $<35°$.

Ultra-violet light, even in presence of a limited amount of air, caused development of small peroxidic-oxygen content. Subsequent aerial oxidation of 120° of such activated acid caused rapid peroxidation (Found after 7 hours: acid val., 176·1; I.V., 48·4; sap. val., 252·8; peroxidic oxygen, 0·64%). The effect of previous exposure to ultra-violet light thus gave an autoxidation product similar to that obtained by using catalysts such as benzoyl peroxide (0·5%) (Found: acid val., 169·9; I.V., 56·1; sap. val., 230·0; peroxidic oxygen, 0·51%) or blown whale oil (Found: acid val., 171·6; I.V., 42·4; peroxidic oxygen, 0·517%). It may be noted, however, that the intrinsic effect of ultra-violet light in absence of air is minute.

Catalytic Oxidations. Catalyst Influence in Primary and Secondary Phases of Aerial Oxidation. Changes in Peroxidic-oxygen Content of Pure Oleic Acid during Autoxidation at 120°.—(a) *In presence of pure metallic soaps.* Catalysts used in the following experiments included oleates of Co, Pb, V, Al, Ba, Tl, and Zn, and cobalt linoleate and naphthenate. Preparations and analyses were by the following methods : preparation and analysis of cobalt and vanadium compounds (*J. Soc. Chem. Ind.*, 1948, **67**, 365); thallium oleate (Menzies, *J.*, 1924, 1148); barium oleate (*J. Soc. Chem. Ind.*, 1931, **50**, 131T). Oleates of lead, aluminium, and zinc were prepared by double decomposition from sodium oleate. Typical analysis of the oleates were: Co, 10·1 (calc. 9·5%) ; Pb, 25 (calc. 26·9%) ; V, 7·5 (calc. 8·1%) ; Al, 3 (calc. 3·1%) ; and Zn, 10·1% (calc. 10·3%).

TABLE II.

Catalyst influence on the rate of autoxidation of pure oleic acid (120° ; 7 *hours*).

	Catalyst, 0·05% of metal as oleate.						
	Co.	Pb.	V.	Ba.	Tl.	Zn.	Al.
Maximum peroxidic-oxygen content, found, %	0·78	1·70	0·57	0·92	0·83	0·76	1·30
Time to attain above maximum peroxide content (hrs.)........	6	2	5	5	5	5	2
Rate of increase of peroxidic-oxygen content (units per hr.)	0·15	0·85	0·11	0·18	0·17	0·15	0·65
Minimum peroxidic-oxygen content (7 hrs.), found, %	0·26	0·26	0·20	0·35	0·68	0·59	0·21
Rate of transition of peroxidic-oxygen content (units per hr.)	0·52	0·29	0·18	0·28	0·07	0·08	0·20
Iodine value (7 hrs.)	47·9	43·6	50·7	52·2	52·6	63·7	33·9
Rate of fall of iodine value (units per hr.)	6·0	6·6	5·6	5·4	5·4	3·8	8·0
Acid value (7 hrs.)	170·5	160·4	170·4	168·9	173·2	175·4	170·8
Rate of fall of acid value (units per hr.)........	3·9	5·4	3·9	4·1	3·9	3·2	3·8

TABLE III.

Peroxidic-oxygen content, %.

Time (hrs.).	1	2	3	4	5	6	7
65°	—	0·09	—	0·87	0·32	—	0·21
120°	0·21	0·33	0·38	0·40	0·37	0·34	0·20
120° (second specimen of vanadium oleate)							0·16

TABLE IV.

Changes in perioxidic-oxygen content (%) *of previously oxidised oleic acid.*

Catalyst (0·05% of metal).	After oxidation.	After storage in loosely corked tubes for 15 months.	18—30 months.
Cobalt oleate (commercial)	0·02	0·39	—
Cobalt oleate (pptd.)	0	0·10	0·33 (30 months)
Cobalt linoleate (commercial)	0·02	0·47	—
Cobalt " tungate " (commercial)	0·04	0·35	—
Vanadium oleate II	0·16	0·49	0·66 (18 months)
Molybdenum oleate	0·21	0·27	—
Titanium oleate	0·19	0·94	—
Lead oleate	0·26	0·37	—
Nickel oleate	0·12	—	0·33 (30 months)
Copper oleate	0·36	0·57	—

(b) *Autoxidations.* Oxidation experiments were carried out in a glass vessel fitted with a Bakelite cover, with arrangements for efficient mixing and for temperature control (±1°) as previously described (Skellon, *loc. cit.*). Samples were withdrawn at regular intervals during oxidation for determination of acid value, iodine value, and peroxidic-oxygen content (iodometrically). The changes in peroxidic-oxygen content with a series of catalysts are illustrated in Table II, expressed as percentage of active oxygen (Calc. for $C_{18}H_{34}O_4$, 5·09%). The rates of decrease of acid value and iodine value during autoxidation are also given.

Influence of Temperature.—The results of catalytic oxidations of pure oleic acid at 65° and 120° are recorded in Table III, the catalyst being vanadium oleate (0·05% of metal).

At the lower temperature, peroxide formation was slower during the first 2 hours; after 4 hours it rapidly accelerated to twice the value obtained at 120°, thereafter diminishing rapidly.

Slow " After-effect " of Catalyst in Presence of a Limited Amount of Air and Light.—Autoxidised oleic acid (7 hours; 120°; 0·05% of metal as soap) was left in loosely corked tubes with limited access to air and light. Peroxidic-oxygen content was redetermined at intervals of 15—30 months. The results are recorded in Table IV.

In these conditions peroxidic-oxygen content increased, the change depending on the nature of the catalyst; with cobalt and other transition-metal cations, the amount of "after-effect" change was high. The conditions, it should be noted, were entirely different from those prevailing when unsaturated fatty acids or parent oils are exposed in films to excess of air and light, decomposition of peroxide then being followed by polymerisation and gelation.

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