14. *The Oxidation of Monoethenoid Fatty Acids and Esters. Union of Gaseous Oxygen with Ethyl,* n-*Propyl, and* n-*Butyl Oleate.*

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The catalytic oxidation at 120°, 85°, and 55° of ethyl, *n*-propyl, and *n*-butyl oleate has been studied. The results show that peroxide formation and subsequent decomposition are a characteristic feature of autoxidations at the higher temperatures. Changes in iodine and saponification values are also characteristic for each temperature. Prolonged oxidation at 120° produces some dimerisation together with formation of reducing substances. The nature of the terminal alkyl group influences the course of the reaction, maximum peroxide formation decreasing progressively from ethyl to *n*-butyl. Comparison with previous work indicates that the configuration of the monoethenoid acid molecule is an important factor, the (*cis*-)oleic esters reacting more rapidly than the corresponding (*trans*-)elaidic esters.

Considerable attention has been given in recent years to the oxidation of oleic acid and its methyl ester (see, *e.g.*, Skellon and Gordon, *Chem. and Ind.*, 1951, 629, for a review), but the autoxidation of the higher esters has been little studied. The oxidation of ethyl oleate was examined chemically by Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43T) and spectrochemically by Lundberg, Holman, and Burr (*Oil and Soap*, 1946, **23**, 10), and the oxidation of butyl oleate by Deatherage and Matill (*Ind. Eng. Chem.*, 1939, **31**, 1425).

The object of the present work was to compare the oxidation of the higher esters of oleic acid in the presence of a metallic catalyst with similar catalytic autoxidations of the methyl ester (see, *e.g.*, Skellon, *J.*, 1948, 343), especially in regard to the influence of the terminal alkyl group on the ease of entry of oxygen into the monoethenoid acid molecule.

Pure oleic acid was prepared by a combination of lead and lithium salting as previously described (Skellon, *J. Soc. Chem. Ind.*, 1931, **50**, 131T) and converted into its esters by a method based on that of Armstrong and Hilditch (*loc. cit.*). Uranium oleate (Skellon and Spence, *ibid.*, 1948, **67**, 365) was employed as the catalyst, it having been shown (Skellon, *ibid.*, 1950, **69**, 116) that uranium soaps are among the most effective autoxidation catalysts. The conditions of oxidation were such as to give high interim peroxide formation with minimum of fission or polymerisation.

For all esters, the highest peroxide values were obtained at 85° after 20—26 hours (Fig. 1), *viz.*, ethyl ester 1·50, *n*-propyl 1·23, *n*-butyl 1·16% (peroxide values expressed as % of active oxygen). In comparison, Gunstone and Hilditch (*J.*, 1945, 836) obtained for methyl oleate at 80° a maximum peroxide content of 1·95% after 68 hours. In all cases, the observed peroxidic oxygen content was below the theoretical maximum (calc. for esters: ethyl 4·67, *n*-propyl 4·49, *n*-butyl 4·32%); and it is evident from the curves that the peroxides are unstable, decomposing more or less rapidly to give secondary products.

At 120°, the rapid increase of peroxidation followed by a somewhat comparable rate of decrease was similar to that observed for methyl oleate by Gunstone and Hilditch (*loc. cit.*) and by Skellon (*J.*, 1948, 343), and for methyl and *n*-propyl elaidate by Skellon and Thruston (*J.*, 1949, 1626). The peroxide maxima were lower at this temperature, *viz.*, ethyl ester, 0·94, *n*-propyl 0·87, *n*-butyl 0·38%, but were attained much more rapidly (3—4 hours). Comparable data for methyl oleate are given by Gunstone and Hilditch (*loc. cit.*) who reported a peroxide maximum of 1·17% after 4 hours, and by Skellon (*loc. cit.*) who reported a maximum of 0·76% after 6 hours using a cobalt oleate catalyst.

The decreases in iodine value (Fig. 2) and increases in saponification value (Fig. 3) are characteristic for each of the three temperatures, and obviously suggest differences in the mode of catalytic oxidation under varying thermal conditions, in agreement with observations of the various investigators cited above.

The final products resulting from the 120° oxidations all gave positive and rapid reactions in qualitative tests for reducing agents, suggesting the presence of carbonyl compounds, whilst the increased molecular weights indicated the onset of some form of

FIG. 1.

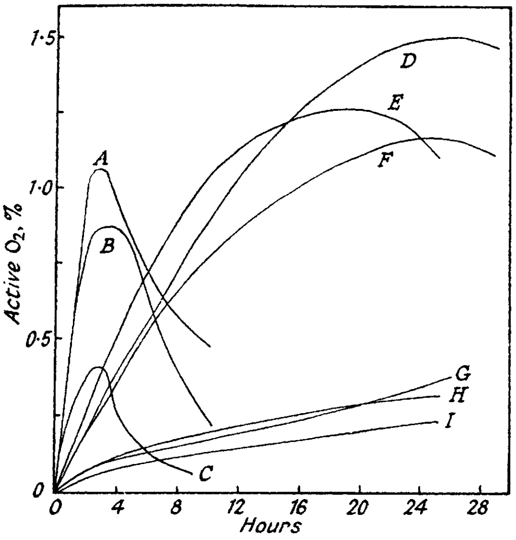


FIG. 2.

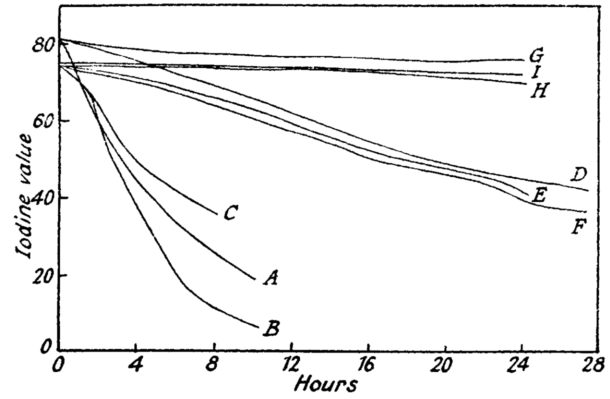
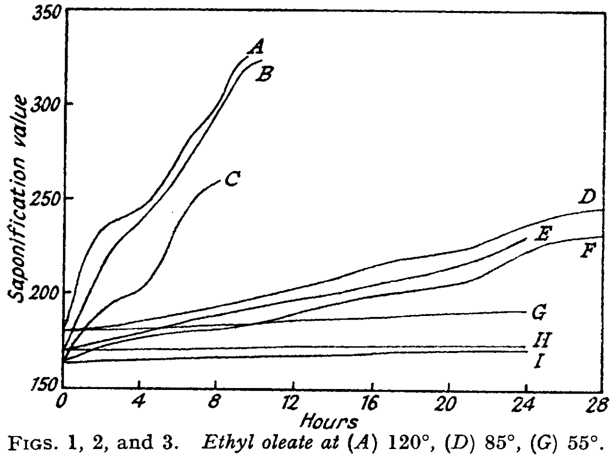


FIG. 3.



FIGS. 1, 2, and 3. *Ethyl oleate at* (*A*) 120°, (*D*) 85°, (*G*) 55°.
n-*Propyl oleate at* (*B*) 120°, (*E*) 85°, (*H*) 55°.
n-*Butyl oleate at* (*C*) 120°, (*F*) 85°, (*I*) 55°.

polymerisation. At 85°, the final products gave only slight reactions for reducing substances; but the decreased molecular weights pointed to some degree of fission. At 55°, little change was observed even after 24 hours' oxidation.

Ease of entry of oxygen into the monoethenoid acid molecule is clearly influenced by the size of the terminal alkyl group, a progressive decline in reactivity being apparent as the homologous series is ascended from ethyl to *n*-butyl. A similar effect was noted by Skellon and Thruston (*loc. cit.*) for methyl and *n*-propyl elaidate.

Finally, an interesting series of comparisons may be made with the results obtained, under very similar conditions of catalytic oxidation, for the methyl and *n*-propyl esters of the corresponding *trans*-isomer, elaidic acid (Skellon and Thruston, *loc. cit.*). The most notable feature is that although the *trans*-esters attained similar peroxide maxima, these were reached only after a considerably longer period : *e.g.*, at 85°, *n*-propyl elaidate required 42—48 hours compared with 20—22 hours for *n*-propyl oleate; at 120°, the two *trans*-esters required 6—10 hours compared with 3—4 hours for the three *cis*-esters. The configuration of the molecule thus appears to affect the rate of formation and decomposition of peroxides in thermal oxidations.

The results of detailed examination of the oxidation products of the esters at various stages will form the subject of further communications.

EXPERIMENTAL

Oleic Acid.—Pure oleic acid was prepared from high-grade olive oil (1·5 kg.), by a lead and lithium salting method (*J. Soc. Chem. Ind.*, 1931, **50**, 131T), in a yield of 300 g., as an almost colourless oil, n_D^{20} 1·4603 (Found : Sap. val., 197·2; I val., 90·0. Calc. for $C_{18}H_{34}O_2$: Sap. val., 198·6; I val., 89·9).

Esters.—Oleic acid (80 g.), the appropriate alcohol (160 g.), and concentrated sulphuric acid (4 ml.) were refluxed for 2 hours. Excess of alcohol was distilled off and the residue poured into water (400 ml.) and extracted with ether. The ethereal extracts were washed with dilute sodium carbonate solution and dried (Na_2SO_4). After filtration, the ether was removed under reduced pressure, giving 80—85 g. of almost colourless liquids with the following characteristics: Ethyl oleate, n_D^{20} 1·4502 (Found: Sap. val., 181·2; I val., 80·3. Calc. for $C_{20}H_{38}O_2$: Sap. val., 180·8; I val., 81·7); *n*-propyl oleate, n_D^{20} 1·4500 (Found : Sap. val., 170·2; I val., 74·3. Calc. for $C_{21}H_{40}O_2$: Sap. val., 172·9; I val., 78·2); *n*-butyl oleate, n_D^{20} 1·4550 (Found : Sap. val., 165·5; I val., 75·8. Calc. for $C_{22}H_{42}O_2$: Sap. val., 165·7; I val., 75·0).

Catalytic Oxidations.—The ester (25 g.) was mixed with uranium oleate (0·05 g.) previously dissolved in a few ml. of the ester by warming. The uranium oleate was prepared by the

Catalytic oxidation of ethyl oleate.

At 120°.

Time (hours)	2	4	6	8	10
Peroxide value	1·044	0·939	0·674	0·571	0·488
I value	57·9	46·7	34·4	29·5	19·5
Sap. value	235	244	276	294	323
M (Rast) *	—	—	—	—	328
n_D^{20}	1·4541	1·4554	1·4561	1·4573	1·4588

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Rapid

At 85°.

Time (hours)	4	8	12	16	20	24	28
Peroxide value	0·329	0·751	1·034	1·246	1·426	1·480	1·476
I value	76·4	68·7	62·1	54·1	50·1	46·3	40·7
Sap. value	186	193	202	217	221	238	244
M (Rast) *	—	—	—	—	—	—	257
n_D^{20}	1·4520	1·4530	1·4539	1·4547	1·4552	1·4560	1·4562

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Slight

At 55°.

Time (hours)	4	8	12	16	20	24
Peroxide value	0·102	0·124	0·187	0·239	0·277	0·341
I value	78·5	77·5	76·5	76·0	75·8	76·0
Sap. value	183	184	185	186	189	191
M (Rast) *	—	—	—	—	—	343
n_D^{20}	1·4515	1·4519	1·4521	1·4522	1·4523	1·4524

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... None

* Calc. for $C_{20}H_{38}O_2$: M, 310·5.

method of Skellon and Spence (*J. Soc. Chem. Ind.*, 1948, **67**, 365) (Found: U, 27·6. Calc.: U, 28·6%). The oxidation was carried out in an apparatus essentially similar to that used by Skellon and Thruston (*J.*, 1949, 1626), except that temperature control (±1°) was by means of a thermostatic air-oven. As the oxidations at 120° and 85° were exothermic in the initial stages it was necessary to keep the ambient temperature 5—10° below the required reaction temperature. The oxygen rate was 50 ml. per minute (approx.), and the gas emerged as a fine stream of bubbles from the delivery tube. The stirring rate was 300 r.p.m. (approx.). Samples were withdrawn by a fine pipette at suitable intervals.

The oxidations were conducted at 55°, 85°, and 120°. Changes studied are recorded in the Tables, peroxide values being expressed as % of active oxygen (method of Skellon and Wills, *Analyst*, 1948, **73**, 78). The course of the various oxidations is shown by the curves of Figs. 1, 2, and 3.

Catalytic oxidation of n-*propyl oleate.*

At 120°.

Time (hours)	2	4	6	8	10
Peroxide value	0·821	0·864	0·671	0·387	0·231
I value	56·3	36·9	17·8	11·9	7·5
Sap. value	217	236	264	303	325
M (Rast) *	—	—	—	—	365
n_D^{20}	1·4543	1·4551	1·4560	1·4564	1·4577

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Rapid

At 85°.

Time (hours)	4	8	12	16	20	24
Peroxide value	0·524	0·904	1·150	1·230	1·232	1·104
I value	71·8	66·2	58·3	50·7	47·6	39·2
Sap. value	178	190	195	205	215	232
M (Rast) *	—	—	—	—	—	263
n_D^{20}	1·4521	1·4535	1·4541	1·4547	1·4550	1·4553

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Slight

At 55°.

Time (hours)	4	8	12	16	20	24
Peroxide value	0·106	0·147	0·201	0·253	0·288	0·312
I value	74·5	74·1	72·0	71·3	69·8	69·5
Sap. value	171	172	172	173	174	173
M (Rast) *	—	—	—	—	—	327
n_D^{20}	1·4508	1·4518	1·4522	1·4523	1·4527	1·4530

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... None

* Calc. for $C_{21}H_{40}O_2$: *M*, 324·5.

Catalytic oxidation of n-*butyl oleate.*

At 120°.

Time (hours)	2	4	6	8
Peroxide value	0·331	0·219	0·120	0·085
I value	62·1	49·1	43·4	36·1
Sap. value	192	201	243	257
M (Rast) *	—	—	—	414
n_D^{20}	1·4568	1·4583	1·4603	1·4620

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Rapid

At 85°.

Time (hours)	4	8	12	16	20	24	28
Peroxide value	0·375	0·633	0·851	0·967	1·059	1·160	1·103
I value	72·5	63·7	58·6	51·6	46·7	39·9	38·0
Sap. value	177	180	190	197	205	226	231
M (Rast) *	—	—	—	—	—	—	271
n_D^{20}	1·4562	1·4569	1·4576	1·4577	1·4584	1·4591	1·4596

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... Slight

At 55°.

Time (hours)	4	8	12	16	20	24
Peroxide value	0·078	0·092	0·127	0·160	0·185	0·235
I value	75·6	74·7	74·6	73·7	74·3	72·5
Sap. value	167	169	170	172	173	174
M (Rast) *	—	—	—	—	—	348
n_D^{20}	1·4560	1·4562	1·4564	1·4567	1·4568	1·4571

Reduction of Fehling's soln. and ammoniacal $AgNO_3$ .... None

* Calc. for $C_{22}H_{42}O_2$: *M*, 338·6.

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