

112. The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part IX. The Primary Thermal Oxidation Product of Ethyl Linoleate.

By J. L. BOLLAND and H. P. KOCH.

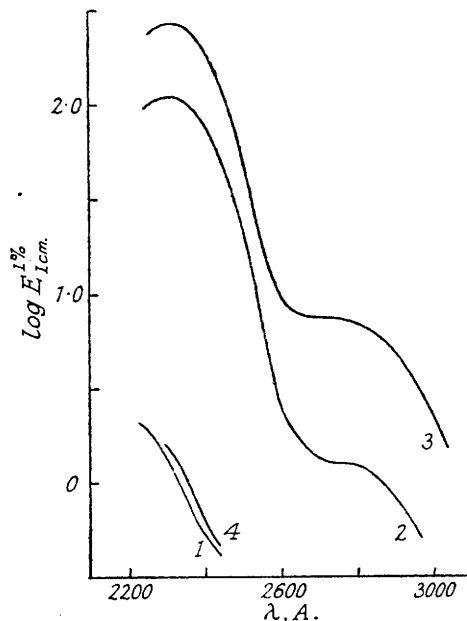
The primary product of the thermal reaction between ethyl linoleate and molecular oxygen is a mono-hydroperoxide which is shown by spectrographic analysis to contain at least 70% of conjugated diene isomers resulting from rearrangement of the unsaturated system $\cdot\text{C}:\text{C}\cdot\text{C}:\text{C}:\text{C}\cdot$. One of the first decomposition products appears to be ketonic according to similar evidence. The observed displacement of double bonds can be accounted for by a free-radical mechanism of oxidation.

IN Part IV (Farmer and Sutton, J., 1943, 119) it was reported that the photo-oxidation of methyl oleate gives rise to an unsaturated hydroperoxide which can be isolated from unchanged ester by selective adsorption on alumina; and it was subsequently demonstrated by spectrographic measurements (Part VII, Farmer, Koch, and Sutton, *ibid.*, p. 541) that conjugated diene and triene units are formed during the thermal peroxidation of more highly unsaturated esters of the drying-oil type, $\text{CHR}_1\text{:CH}\cdot\text{CH}_2\text{:CH}\text{:CH}\cdot\text{CH}_2\text{:CH}\text{:CHR}_2$. Quantitative chromatographic and absorption-spectra analysis has since been employed in the investigation of the course of thermal oxygenation of ethyl linoleate (I), and the nature of the primary reaction product is now described.

Chemical Examination.—Pure ethyl linoleate and oxygen gas react readily on shaking in the dark at 45°, and the extent of peroxidation as determined iodometrically (Dastur and Lea, *Analyst*, 1941, 66, 90) is in satisfactory agreement with accurate volumetric measurements of oxygen absorption at intakes lower than 4%. Peroxidised samples withdrawn during these early stages of oxidation evolve one molar volume of methane per mole of incorporated oxygen in high-vacuum Zerewitinoff determinations, indicating that all the primary oxygen groups formed are hydroperoxidic. Furthermore, by chromatographic adsorption of the peroxide from a known weight of oxidised material in light petroleum solution, followed by weighing of the unoxidised ester in the eluate, it can be shown that only one such hydroperoxide group is present in each of the adsorbed oxygenated molecules. It must therefore be assumed on the basis of the chemical evidence alone that the primary oxidation product of ethyl linoleate (I) is a monohydroperoxide.

Ultra-violet Spectra.—The absorption curves of pure ethyl linoleate, two oxidised samples, and the chromatographically recovered unchanged ester (all in alcoholic solution) are plotted in the accompanying figure. The most characteristic feature of the spectra given by the oxidised samples, apart from weak selective absorption near 2750 Å., is the intense band at 2315 Å., which is removed by adsorption on alumina and must therefore be associated with the peroxido-ester present in the samples. By allowing for the feeble absorption of unchanged ester at 2315 Å. ($E_{2315}^{1\%} = 1.25$), the maximum molecular extinction coefficient of ethyl linoleate peroxide can be calculated from the expression $\epsilon = 32(100 + m)[(\log I_0/I)_{\text{max.}} - 1.25lc/10]/mlc$, where m is the oxygen intake per 100 g. of starting material, and c the total solute concentration (in g./l.) of the spectroscopic solution contained in a cell of l cm. length. This ϵ value was obtained from the spectra of a number of independently autoxidised samples, and the results are in Table I.

Ethyl linoleate spectra.



1. Pure starting material.
2. After 1.6% oxygen absorption.
3. „ 5.4% oxygen absorption.
4. „ chromatographic removal of oxygenated fraction.

TABLE I.

Oxygen intake (%)	0.431	0.629	1.20	1.95 *	2.6	3.3	1.6 †	2.65 †	5.4 †
$\epsilon_{\text{max.}}$ of oxidation product	22,900	23,000	22,300	22,500	21,100	18,000	22,100	20,000	15,900

* Reaction vessel packed with glass fragments.
 † Results of preliminary runs (cf. Experimental).

Up to an oxygen intake of about 2%, the extinction coefficient is reproducible within the limits of error of the spectrographic assay, so that its average value of 22,700 can be regarded as a characteristic constant of ethyl linoleate peroxide formed during thermal oxygenation. The subsequent decline from this figure may be due to the onset of secondary intermolecular or peroxide decay reactions.

Analysis of 2315 Å. Absorption Intensity.—It was reported in Part VII that a typical mono-olefinic hydroperoxide such as that of cyclohexene does not display high-intensity absorption in the ultra-violet which is exclusively characteristic of conjugated unsaturated centres. The peroxido-ester band at 2315 Å. must therefore be due to a rearrangement of double bonds into conjugation, and it may be compared in Table II with the

bands of analogous terminally disubstituted butadienes in alcoholic solution. Clearly, the extinction maximum of the ester hydroperoxide is located in the wave-length region typical of six similar conjugated linoleic compounds, while the smaller hexadiene molecules exhibit maxima at slightly higher frequencies. The presence of the hydroperoxide group on a carbon atom adjoining the conjugated system would not be expected to affect the position of this typical diene band, an assumption that is borne out by the spectrum of *cyclohexene* hydroperoxide in which the olefinic and peroxidic absorptions are roughly additive (Koch, unpublished observation), and further supported by the negligible effect of 1 : 6-oxy-substitution on the absorption wave-length of 2 : 4-hexadiene given in the table. The close similarity of the band position of the peroxido-ester to that of analogous conjugated linoleates is therefore not surprising.

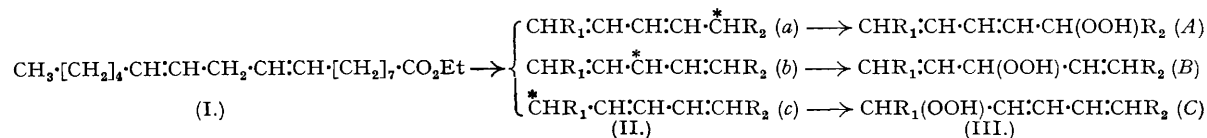
TABLE II.

Constitution of diene.	$\lambda_{\text{max.}}$ (A.).	$\epsilon_{\text{max.}}$	Ref.
Ethyl linoleate hydroperoxide	2315	22,700	This paper
$\Delta^{10:12}$ -Linoleyl alcohol	2325	32,000	4
$\Delta^{10:12}$ -Methyl linoleate	2325	29,700	4
$\Delta^{10:12}$ -Linoleic acid	2325	32,500	4
$\Delta^{9:11}$ -Linoleic acid	2325	26,600	4
"	2300	~33,000 ¹	5
Alkali-isomerised potassium linoleate	2340	24,400 ²	6
2 : 4-Hexadiene	2270	22,500 ³	7
1 : 6-Diethoxy-2 : 4-hexadiene	2280	26,800	7
1 : 6-Diacetoxy-2 : 4-hexadiene	2280	27,300	7

¹ Measured in hexane. According to Booker *et al.* (*loc. cit.*), diene intensities are frequently somewhat higher in hexane than in alcohol. ² The linoleate is measured as a charged anion after heating with strong alkali which appears to have a gradual destructive effect superimposed on its isomerising agency. Our previous assumption (Part VII) that the maximum $E_{1\text{cm.}}^{0.1\%}$ value recorded by Mitchell *et al.* corresponds to the presence of 100% conjugated diene may therefore be inaccurate, and the calculated $\epsilon = 24,400$ value low. It is, moreover, subject to the uncertain "solvent effect" of the highly polar medium in which the measurements are made. ³ Probably low, owing to doubtful purity of the specimen (cf. Booker *et al.*, *loc. cit.*, p. 1461). ⁴ Kerns, Belkengren, Clark, and Miller, *J. Opt. Soc. Amer.*, 1941, **31**, 271. ⁵ Van der Hulst, *Rec. Trav. chim.*, 1935, **54**, 639. ⁶ Mitchell, Kraybill, and Zscheile, *Ind. Eng. Chem. Anal.*, 1943, **15**, 1. ⁷ Booker, Evans, and Gillam, *J.*, 1940, 1453.

As regards the ϵ values recorded in the table, the maximum intensity of the linoleate hydroperoxide absorption at 2315 A. appears to be unduly low if full conjugation is to be assumed, and the inconsistencies of the data from Kerns's laboratory—all obtained with extensively purified materials by an accurate photoelectric method—are rather unexpected. The extinction coefficient of a conjugated diene in this spectral region depends on the dipole moment of the excited state and may therefore be affected by changes in either the length or the charge of the dipole involved. Since the constitutional distinctions between the four linoleic compounds of Kerns *et al.* are all due to chemical modifications at carbon atoms far removed from the chromophoric centre, alterations of dipole charge could hardly occur, but spatial differences might be responsible for the observed intensity variations. Butadiene itself, in fact, is known at room temperature to consist of an equilibrium mixture of single-bond *cis*- and *trans*-isomers, in which the predominating and more elongated *s-trans*-displays considerably greater absorption near 2200 A. than the *s-cis*-form (Rasmussen, Tunnicliff, and Brattain, *J. Chem. Physics*, 1943, **9**, 432; Sugden and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 76). In the absence of other evidence, however, and in view of the relatively high intensities of the 1 : 6-oxy-substituted hexadienes, it is difficult to see why the extinction coefficient of a fully conjugated peroxido-linoleate should be lower than that of all the other compounds under discussion. The most probable conclusion would therefore be that the conjugative displacement of double bonds has been incomplete. If the range of ϵ values obtained by Kerns *et al.* is taken as a theoretical standard of extinction for a pure compound of this type, the linoleate oxidation product appears to contain between 70 and 85% of conjugated isomers. Although this estimate cannot be made more precise, a rearrangement of about 70% must be regarded as the minimum allowed by the available evidence, since diene intensities larger than 32,500 are unknown and not to be expected (Booker, Evans, and Gillam, *loc. cit.*; Koch, *Chem. and Ind.*, 1942, **61**, 273).

Course of Autoxidation Reaction.—On the basis of the free-radical mechanism of oxidation suggested in Part VII, oxidative attack at the active methylene group of ethyl linoleate (I) results in the formation of a free radical (II), which is a resonance hybrid composed of the three equivalent canonical structures (a)—(c). The hydroperoxidic product (III) derived from the radical would then be expected to contain the three isomeric forms (A)—(C). Quantitatively, 67% conjugation will result if these three are produced in equal amounts,



but if the conjugated forms (A) and (C) are favoured owing to their resonance energy, up to 100% conjugation might occur. It is not possible to distinguish between these possibilities on the above experimental evidence which characterises the primary oxidation product as a monohydroperoxide at least 70% conjugated. The postulated intermediate formation of a free radical of type (II) is also in accord with kinetic evidence (Bolland, *Proc. Roy. Soc., A*, in the press).

Spectral Evidence of Decomposition.—The absorption curves of all the thermally autoxidised samples show a well-defined shoulder at 2750 Å. which is absent from pure mono-olefin peroxide spectra and cannot be attributed to triene conjugation since no fine structure is revealed even on careful inspection of the photographic records (cf. Fig. 2 in Part VII). The intensity of this band increases markedly on keeping the peroxidised ester for some time at 45° in a vacuum and is evidently associated with a small amount of secondary decomposition product. The absorption region in question is that typical of conjugated diene ketones; thus, the spectrum of crotonylideneacetone, $\text{CH}_3\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, displays a broad and intense maximum near 2730 Å. (Jones and Lahey, *Chem. Abs.*, 1943, **37**, 3342). There can be little doubt that the long-wave bands shown in the figure are due to small amounts of the analogous diene ketone resulting from decomposition of the conjugated hydroperoxide. According to this interpretation, about 1% of the peroxide present in the sample characterised by curve 2 has decomposed in such a manner. The ketone of crossed conjugation which might be produced in even smaller amounts by secondary decay of the hypothetical unconjugated hydroperoxide (III, B) would be expected to absorb at shorter wave-lengths, where its extinction could be neglected relatively to that of the conjugated hydroperoxide present.

EXPERIMENTAL.

Ethyl linoleate was prepared from cottonseed oil (*Org. Synth.*, 1942, **22**, 75). The intermediate tetrabromostearic acid had m. p. $115.7^\circ \pm 0.1^\circ$ and theoretical bromine content, 53.3%. The final product was free from conjugated isomers, as selective absorption near 2315 Å. was negligible (cf. figure).

Samples of ethyl linoleate, carefully shielded from light, were shaken vigorously at 45° under an oxygen pressure of about 100 mm. The volume of oxygen absorbed was determined accurately in a constant-pressure gas burette system attached to the reaction vessel. In a preliminary series of runs oxygen was absorbed by a stationary surface exposed to the atmosphere at 35° in the dark, in amounts determined by weighing.

The peroxide content of the oxidised samples was estimated by the method of Dastur and Lea (*loc. cit.*). Extended experience with this method has shown (Bolland, *loc. cit.*) that the peroxidic oxygen content corresponds quantitatively with the amount of oxygen absorbed (in the range, 1–4%, and presumably also at lower degrees of oxidation).

Duplicate active hydrogen analyses (Bolland, *Trans. Inst. Rubber Ind.*, 1941, **16**, 257) of three samples of oxidised ethyl linoleate, gave severally 0.286, 0.282, and 0.124 mol. of methane per mol. of ethyl linoleate, and the corresponding peroxide contents (based on iodometric estimations and on measured extents of oxidation) were 0.290, 0.272, and 0.120 mol. of absorbed oxygen per mol. of ethyl linoleate.

For chromatographic separation of the peroxide from the unoxidised ester, a short column of activated alumina (Savory and Moore) was found effective; light petroleum (b. p. 40–60°) was employed as solvent and eluent, and the operation carried out under a slight pressure of purified nitrogen. Ethyl linoleate (containing less than 0.01% of peroxidic oxygen) recovered in this manner from an oxidised sample containing 2% of peroxidic oxygen, and freed from solvent in a vacuum, gave the spectrum indicated in the figure; it is virtually identical with that of the starting material. The rapid diminution in the amount of residue in successive portions of the eluate (all of which gave negligible peroxide tests) showed that the separation was quantitative. In one instance 4.2500 g. of oxidised ethyl linoleate, containing 1.83% of peroxidic oxygen, yielded a total of 3.4206 g. of ethyl linoleate. It follows that the 0.8294 g. of oxidised material remaining in the column contained 1.01 mols. of oxygen per mol. of ester.

The ultra-violet spectra were obtained by means of a Hilger quartz spectrograph equipped with the Spekker photometer and a condensed tungsten-steel spark source of light. The maximum optical densities ($\log_{10} I_0/I$) at 2315 Å. were determined by visual examination and interpolation of the match-points on Kodak B-10 plates with an error not greater than 2%. The photometer was carefully calibrated before each measurement by the determination of blank match-points, and the recording of spectra was completed in each case within 20 mins. of admitting air to the specimen in order to prevent further significant oxidation.

The authors express their gratitude to Dr. G. Gee for his encouragement and criticism during the course of this work, which forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48, TEWIN ROAD, WELWYN GARDEN CITY, HERTS.

[Received, April 17th, 1945.]