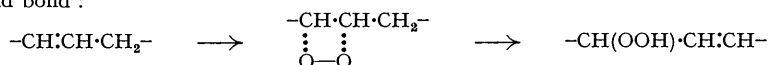**222.** *The Autoxidation of Methyl Oleate in Presence of Small Proportions of Methyl Linoleate.*

By F. D. GUNSTONE and T. P. HILDITCH.

The autoxidation of methyl oleate is strongly accelerated, and the induction period much reduced. in presence of 1% of methyl linoleate at 20°, or of 0·2% of the ester at 50°; the oxidation of the methyl oleate is catalysed by hydroperoxides resulting from the union of oxygen with methyl linoleate.
The mechanism of addition of oxygen to systems such as $-CH_2 \cdot CH\colon CH \cdot CH_2-$ and
$$-CH_2 \cdot CH\colon CH \cdot CH_2 \cdot CH\colon CH \cdot CH_2-$$
has been further considered. It is now suggested that oxygen molecules are primarily attached to an ethenoid bond, and not to an adjacent methylene group, hydroperoxide formation finally taking place with formation of a new ethenoid bond :

$$-CH\colon CH \cdot CH_2- \quad \longrightarrow \quad \begin{array}{c} -CH \cdot CH \cdot CH_2- \\ \vdots \quad \vdots \\ O-O \end{array} \quad \longrightarrow \quad -CH(OOH) \cdot CH\colon CH-$$

It was shown (*J.*, 1945, 836) that the rates of autoxidation of methyl oleate, linoleate, and linolenate at 20° were in the approximate ratio 1 : 12 : *ca.* 25, and that, at 20° and 50°, methyl oleate exhibited prolonged " periods of induction " before steady addition of oxygen set in, whereas methyl linoleate and linolenate showed no measurable induction periods. The union of gaseous oxygen, at 20° and 50°, with methyl oleate to which very small proportions of methyl linoleate had been added has now been similarly studied by observation of the development of peroxide value (Figs. 1 and 2). At 20°, presence of 1% of methyl linoleate caused considerable reduction of the induction period, whilst with 2% and 5% of methyl linoleate the induction periods were still more reduced ; after the induction periods, rapid absorption of oxygen proceeded in each instance at a steady rate over the ranges (usually to peroxide values of 400 or above) followed experimentally. At 50°, 1% of methyl linoleate caused great, and 0·5% or 0·2% of linoleate somewhat less, reduction of the induction period, the rate of subsequent increase in peroxide value again being rapid and almost linear in character :

	Oxidations at 20°.				Oxidations at 50°.			
Concn. of linoleate (%)	5	2	1	0	1	0·5	0·2	0
Induction period (hours)	85	185	320	800	75	100	120	210
Subsequent rate of increase of peroxide value (units per hour)	1·7	1·3	0·6	0·4	5·1	2·9	3·3	2·4

From these figures it is clear that the relatively slow autoxidation of the mono-ethenoid ester is powerfully catalysed by the presence of very small proportions of methyl linoleate, 0·2% of which is sufficient to cause marked acceleration of the union of oxygen with methyl oleate at 50°. The data definitely confirm the view, probably already widely held, that oxidative rancidity in edible fats is largely conditioned by linoleo-glycerides present rather than by oleo-glycerides, although the latter (as indeed is made plain by the above evidence) are also involved in its final development. Unfortunately, none of the natural materials employed in edible fats is free from linoleo-glycerides, whilst our present experiments prove that the presence of but small proportions of the latter provide the necessary catalyst for oxidative attack on the mono-ethenoid glycerides also present. (Mild hydrogenation of certain fats, *e.g.*, lard, increases their stability to oxygen owing to selective conversion of linoleo- into oleo- or *iso*oleo-glycerides; but for technical reasons this procedure is practicable only in a few restricted instances.)

FIG. 1.

Autoxidation of methyl oleate–methyl linoleate mixtures at room temperature (20°).
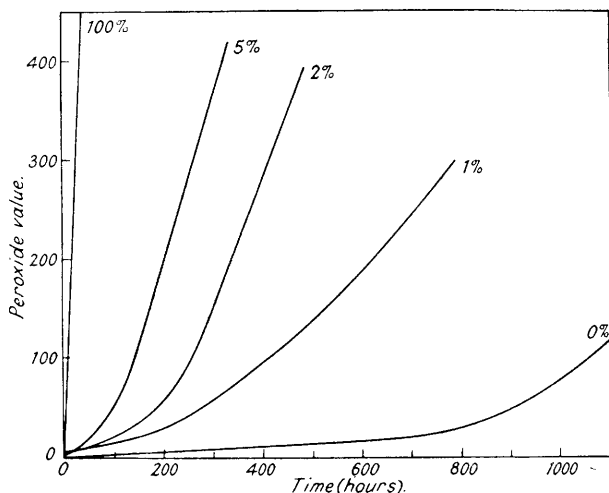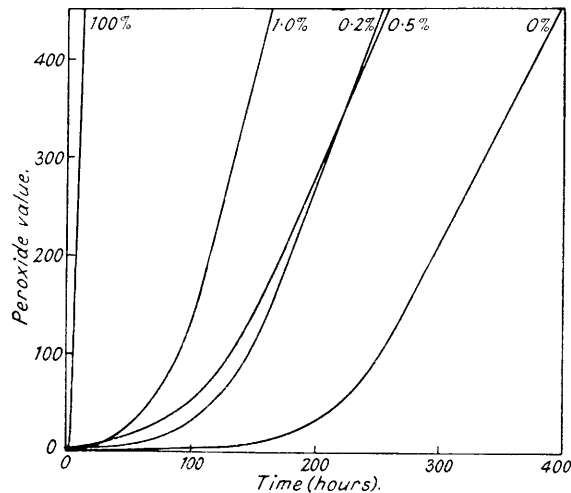
FIG. 2.

Autoxidation of methyl oleate–methyl linoleate mixtures at 50°.

The catalytic nature of the methyl oleate oxidation in the present study, and the probable nature of the oxidising catalyst, are briefly considered. It may first be pointed out that the peroxide values reached in these experiments do not represent maximum values, since oxidation was still proceeding in all cases at an approximately steady linear rate when they were terminated; nevertheless, the values reached are in each instance much in excess of that due exclusively to monohydroperoxide from the linoleate present (*e.g.*, the peroxide value due to complete transformation of 5% of linoleate into monohydroperoxide is 153, and correspondingly less for smaller proportions of the diethenoid ester). Next, it appears that the amount of diethenoid conjugation rises to a point at which it remains approximately constant, and at which it is proportionately higher than the maximum value reached with pure methyl linoleate (*J.*, 1945, 836). The spectrographic measurements on which this statement is based could only be made with sufficient accuracy on the mixture at 20° in which 5% of methyl linoleate was present, but here it appeared that a constant value of $E_{1cm.}^{1\%}$ at 234 mμ of about 20 was attained [corresponding to about 1·7% of diethenoid conjugation in the mixture, or about 34% on the linoleate present as compared with 23% maximum diethenoid conjugation observed (*loc. cit.*) with 100% methyl linoleate] :

Methyl oleate with 5% methyl linoleate at 20°.

Peroxide values	101	201	250	334	395	469	525
$E_{1cm.}^{1\%}$ at 234 mμ	9·7	15·0	17·5	22·1	19·8	20·5	19·8

The relatively high proportion of methyl linoleate present as diconjugated compound indicates that in dilute methyl oleate solution the conjugated form less readily undergoes further transformation than when methyl linoleate itself is autoxidised.

We now mention some considerations which have led us recently to modify, or to extend, current opinion on the probable mechanism of the addition of oxygen to the systems $-CH_2\cdot CH:CH\cdot CH_2-$ and $-CH_2\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot CH_2-$. Farmer and Sutton (*J.*, 1943, 119, 122) showed that the product of addition of oxygen to methyl oleate is the monohydroperoxide of an octadecenoic acid ester in which the peroxido-

group is formed from a methylene group and not at the ethenoid bond, and that hydrogenation of the peroxide yielded a mixture of methyl hydroxystearates. Further, since with polyethenoid esters containing the system —CH:CH·CH₂·CH:CH— isomeric rearrangement to conjugated forms was observed, these authors suggested that under the influence of oxygen a hydrogen atom was detached from the reactive methylene group between the double bonds, leaving a system —CH:CH·ĊH·CH:CH— which could reappear either in the original or in the conjugated form. In either case Farmer and his co-workers have suggested that autoxidation is dependent upon direct union of oxygen with a —CH₂— group, a hydroperoxide —CH(OOH)— being produced therefrom. Recently, however, Bergström (*Nature*, 1945, **156**, 717; *Arkiv Kemi, Min., Geol.*, 1945, **21**, A, Nos. 14, 15) has observed that hydrogenation of methyl linoleate hydroperoxide furnishes a mixture of 9- and 13-mono-hydroxystearic acid, no 11-hydroxystearic acid being obtained. Bergström concluded that an initially produced 11-hydroperoxido-octadeca-9 : 12-dienoate must undergo rapid rearrangement into a mixture of 9-hydroperoxido-octadeca-10 : 12-dienoate and 13-hydroperoxido-octadeca-9 : 11-dienoate.

Dr. J. P. W. Houtman, of the Laboratory for Chemical Engineering of the Delft Technical University (Holland), has had some discussion recently with us as to the possible mechanism by which molecular oxygen at room temperature should effect the detachment of a hydrogen atom or a proton from a reactive methylene group, in the course of which he suggested that initial interaction between oxygen and an ethenoid bond might nevertheless prove to be the determining factor. It appears to us that this conception in fact affords a more consistent explanation of autoxidation phenomena in these unsaturated systems than that of direct hydroperoxide formation at a methylene group, and one which is equally in accordance with the facts at present experimentally established, since initial loose attachment of oxygen at a double bond may well render still more detachable one of the hydrogen atoms on an adjacent carbon atom (methylene group).

This could result, in the case of methyl linoleate, in the direct production of 9- and 13-hydroperoxido-derivatives of a diconjugated ethenoid system, as indicated by Bergström's observations; it would also imply that autoxidation in either mono- or poly-ethenoid systems of the types present in natural fats involves the " displacement " of a double bond with consequent ultimate formation of a hydroperoxide at one of the carbon atoms of the ethenoid group originally attacked by oxygen. In the case of oleic (octadec-9-enoic) acid, the possible products would, on this hypothesis, be a mixture of 9-hydroperoxido-octadec-10-enoic and 10-hydro-peroxido-octadec-8-enoic acids. The hydroxystearic acids obtained by Farmer and Sutton (*loc. cit.*) from autoxidised methyl oleate would similarly be a mixture of 9- and 10-, and not of 8- and 11-monohydroxystearic acids. Further, the products obtained by oxidative scission of autoxidised methyl oleate (Atherton and Hilditch, *J.*, 1944, 105) or linoleate (Gunstone and Hilditch, *J.*, 1945, 836) would be the same mono- and di-carboxylic acids on either hypothesis.*

The modified mechanism which we have suggested brings into harmony the action of oxygen on simple unsaturated aliphatic systems of diverse kinds and in different circumstances, since direct union of oxygen and the unsaturated system is generally agreed to occur in conjugated unsaturated systems and, to a considerable extent, in those containing separate ethenoid groups when autoxidised at temperatures above about 80° (Atherton and Hilditch, *loc. cit.*). Its application to systems of the linoleic and linolenic type renders more apparent the mechanism by which the central methylene groups are involved. Finally, the corollary that autoxidation of linoleo- or linoleno-glycerides in the manner suggested necessarily involves the production of a conjugated di(or tri)-ethenoid system also adjacent to a hydroperoxide group appears to have an important bearing upon the mechanism of the conversion of linseed and similar " drying " oils (rich in linoleo- and linoleno-glycerides) into polymerised products when exposed as films to the action of atmospheric oxygen. Autoxidised fatty oils of the non-conjugated group (typified by linseed oil) are thus transformed under the influence of atmospheric oxygen into conjugated derivatives, which are entirely analogous to those present in oils (such as tung oil) which contain conjugated (elaeostearic) glycerides and which autoxidise and polymerise extremely readily to hard films (as in varnishes).

EXPERIMENTAL.

Methyl Oleate.—The specimen used had been isolated from the mixed acids of *Allanblackia* fat as described in our previous paper (*J.*, 1945, 836), and was the material (286 g.) mentioned therein as having an iodine value of 83·4.

Methyl Linoleate.—The specimens used, prepared as described (*loc. cit.*), had iodine values of 173·4 and 173·8.

Procedure.—The oxidations were carried out in the apparatus described (*loc. cit.*). Typical data for the peroxide and iodine values observed during the course of the oxidations are given in the tables.

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* (*Note, added July 2nd, 1946.*) This paper was submitted before the contributions of Farmer and of Bolland and Gee to the Faraday Society's discussion on oxidation in September 1945 were available (*Trans. Faraday Soc.*, 1946, **42**, 228, 236, 244). Here Farmer has now accepted the view that " there is perhaps good justification for postulating universal *initiation* of autoxidative attack in all the various kinds of olefinic systems by *addition* occurring at double bond centres," and has shown how the α-methylenic reactions characteristic of unconjugated olefins may then be formulated on an intermolecular basis. Bolland and Gee, in kinetic studies of olefin oxidation, similarly state that, of the two possible points of oxidative attack—the double bond, and an active methylene group—the argument that the latter must be the site (because of high yields of α-methylene hydroperoxides) is certainly invalid unless the chain length of the oxidation is extremely short.

These statements concede the point we have chiefly been concerned to make in the present paper, namely, to stress in general terms the initial association of oxygen with a double bond (or one of its carbon atoms), and not with an adjacent methylene group. That such initial association is not inconsistent with possible mechanisms of the ensuing chain-reaction is clearly indicated in the papers referred to above.

Oxidations of Methyl Oleate at 20°.

Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).
No methyl linoleate present.			*1% Methyl linoleate present.*			*2% Methyl linoleate present.*			*5% Methyl linoleate present.*		
0·0	0	83·5	0·0	4·4	84·9	0·0	4·6	85·4	0·0	2·3	87·3
317·9	8·4	83·2	50·3	10·3	—	37·1	9·4	85·6	36·6	14·3	88·2
466·8	11·1	82·7	152·9	22·7	—	73·2	15·8	85·8	73·9	24·8	87·5
648·8	17·3	83·1	200·6	33·2	84·2	151·2	34·3	85·7	106·8	64·8	87·6
778·2	25·8	82·8	352·4	73·5	83·6	234·5	77·1	85·0	137·9	93·3	87·0
850·3	33·0	82·5	399·4	99·5	83·7	277·4	123	84·8	171·1	163	87·2
906·7	56·6	83·0	504·0	134	83·7	317·4	158	84·1	240·5	254	86·7
975·2	69·8	83·0	598·3	178	83·5	359·7	214	83·6	280·9	323	85·3
1033·6	85·1	82·5	710·2	247	83·1	402·3	286	83·7	328·1	419	83·9
1106·8	122	82·7	784·0	301	82·6	484·6	396	82·3	371·9	525	81·8

Oxidations of Methyl Oleate at 50°.

Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).	Time (hours).	Peroxide value.	I.V. (Wijs).
No methyl linoleate present.			*0·2% Methyl linoleate present.*			*0·5% Methyl linoleate present.*			*1·0% Methyl linoleate present.*		
0·0	0·0	83·6									
147·9	11·2	83·3	0·0	3·2	83·9	0·0	4·2	84·5	0·0	2·9	85·3
210·3	41·1	83·4	48·0	8·9	83·6	65·8	24·2	84·0	31·0	11·5'	—
256·5	105	82·9	89·5	28·5	83·4	105·0	56·5	—	66·1	43·1	—
303·6	219	81·0	127·9	70·8	83·0	132·3	106	84·3	86·2	92·6	84·1
350·2	336	80·3	163·3	143	83·1	164·6	177	82·6	106·0	158	83·1
399·5	465	79·3	201·3	237	81·8	197·8	269	81·7	126·9	253	82·8
444·1	618	78·5	241·5	406	80·4	234·7	384	80·7	146·9	364	81·3
535·0	963	75·1				265·2	504	79·7	169·8	488	80·2
609·1	1053	72·6									