

461. *The Autoxidation of Methyl Oleate and Linoleate, and the Decomposition of the Oxidation Products: A Theoretical Discussion.*

By G. PHILIP GIBSON.

By the logical development of a free-radical hypothesis an attempt is made to explain the results obtained when methyl esters of the C_{18} acids from palm oil are partly oxidised and then distilled. The activation of the molecules is considered to proceed by bond fission, each broken bond resulting in *two* centres of activity which may rearrange to form free radicals or new bonds. Components that may be activated are an oxygen molecule, and methylene, tertiary carbon, or unsaturated groups. The autoxidation is divided into two stages: (i) the induction period, during which the initial formation of a hydroperoxide from methyl linoleate takes place,

and (ii) the autoxidation proper, which is catalysed by the hydroperoxide. Stage (ii) is a chain-reaction cycle operating through the $\text{H}\cdot$ and $\text{HOO}\cdot$ free radicals. The structure of the hydroperoxides from methyl oleate and linoleate is forecast.

The hydroperoxides decompose more or less quickly and reaction occurs through either (A) an oxygen atom diradical, $\text{=O}\cdot$, or (B) a hydroxyl radical, $\text{=OH}\cdot$. A hydroperoxyl group attacks methylene, tertiary carbon, or unsaturated groups within its own or other molecules, which may, thereby, be split into two parts or give mono-, di-, or tri-meric products. The chief decomposition products are considered to be derivatives of α -unsaturated hydroxy-esters, $\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot$, $\alpha\beta$ -dihydroxy-esters, $\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot$, and carbonyl compounds, $\cdot\text{CO}\cdot$. Figures and tables are given illustrating the activation, autoxidation, and decomposition reactions which are likely to occur with methyl oleate and linoleate.

THE unsaturated system, comprising a mixture of oleate and linoleate, is of very frequent occurrence in oils and fats and it may be exposed to autoxidation and subsequent heat treatment in many natural or technical processes. Interest in this subject was stimulated by anomalous results obtained when working with methyl esters of unsaturated fatty acids which normally can be distilled without decomposition. The phenomenon was, therefore, investigated by deliberately autoxidising (p. 2290) and then distilling C_{18} methyl esters from palm oil which consist of methyl stearate, oleate, and linoleate. In the distillation of these autoxidised esters a high vacuum was not easily maintained, particularly during the initial and final stages of the operation. During the preliminary heating, the hydroperoxides present rapidly decomposed, the peroxide value quickly fell to zero, and unpleasant non-condensable vapours were evolved. The distillation products, briefly, were as follows: (1) A yellow aldehydic fraction, which amounted to 30—40% by weight of the initial hydroperoxide and was more volatile than the C_{18} methyl esters. (2) Colourless unoxidised esters. (3) A yellow oil less volatile than the C_{18} methyl esters. (4) A brown residue which was the main oxidation product and weighed twice as much as the hydroperoxide consumed; its iodine value, 63—65, showed to what extent the unsaturation had been reduced by oxidation, and it had a higher saponification value than that of the original ester in spite of the addition of oxygen to the molecule.

During autoxidation, hydroperoxidation was accompanied by loss of iodine value. This is in agreement with the work of Hilditch and Atherton (*J.*, 1944, 105) and Paquot (*Oleagineux*, 1947, 15). Farmer and Sutton (*J.*, 1943, 119) and Bolland (*Proc. Roy. Soc.*, 1946, *A*, 186, 218), however, maintain that hydroperoxidation proceeds without loss of unsaturation.

When saponified, autoxidised esters darkened appreciably; those that had been heated above 100° darkened more than those that had not.

In this paper an explanation is presented for the mechanism of autoxidation in the case of methyl oleate and linoleate, and for the simultaneous or subsequent thermal decomposition of the autoxidised products. The explanation follows from a consideration of experimental data both of the author and of many other workers. The basis of the hypothesis is the activation of covalent bonds before their breaking, and the sharing, between the affected atoms, of the liberated free energy which accompanies the activation. Thus when a bond is activated and is about to break, *two* centres or regions of activity are formed, one at each of the atoms to which the bond was attached. It appears probable that an active centre is in fact due to a particular state of excitation of one of the electrons which formed the original bond. Throughout this paper centres of activity are shown diagrammatically in short heavy lines.

Three cases have to be considered, as shown under activation of covalent bonds in Fig. 1. First, by breaking of a single bond, two free radicals are formed with a centre of activity in each of two separate molecules or atoms. Secondly, by rupture of one of the bonds in a double bond only a diradical can be formed with two centres of activity in one molecule. Finally, by breaking of the two bonds of a double bond simultaneously, two free diradicals are formed with centres of activity in each of two separate molecules or atoms. Centres of activity may be formed only momentarily and may react further according to the experimental conditions to form free radicals or new bonds as follows:

(I) The atoms or groups of atoms to which the centres of activity are attached may assume a separate existence as free radicals (Reaction I, Fig. 1).

(II) A free radical formed by Reaction I may attack an activated or breaking bond and give a new bond and a new free radical (Reaction II, Fig. 1). This mechanism is typical of a chain reaction and is the means whereby activity is transferred from atom to atom. Such reactions involving free radicals usually occur at a high speed.

(III) Two activated bonds may react together to form new bonds (Reaction III, Fig. 1). Reactions of this type take place at a low speed.

The extent of the activation is extremely small, possibly of the order 10^{-12} mole; it is to be

near each other. Such a situation arises frequently where there is free rotation of the methylene group about the C-C axis as in oleic acid, but not at all when the groups are locked in a ring as

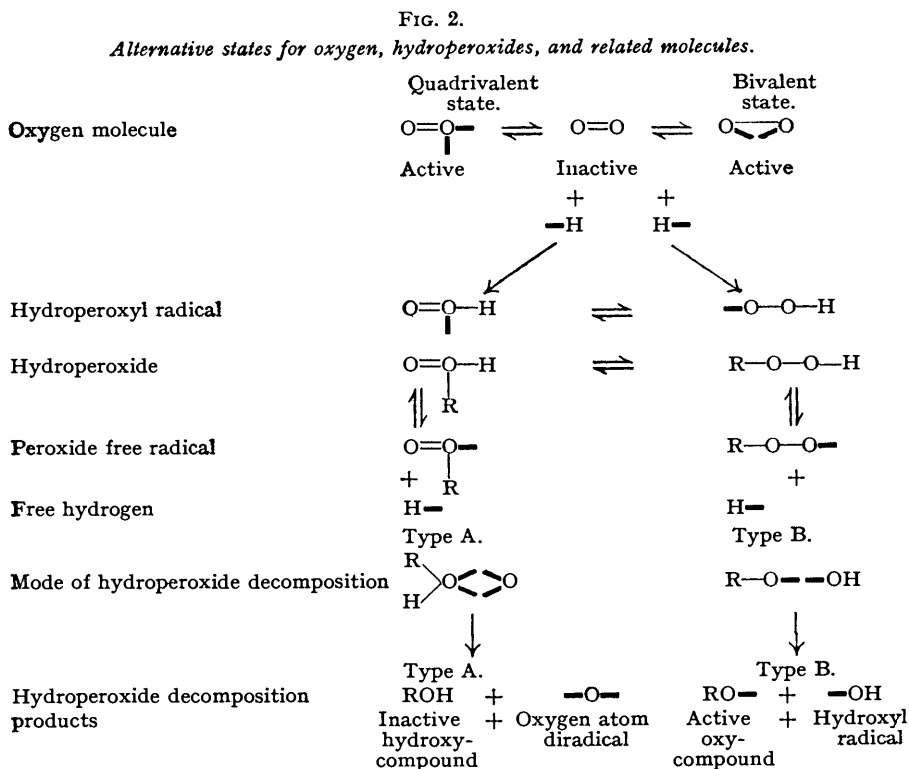
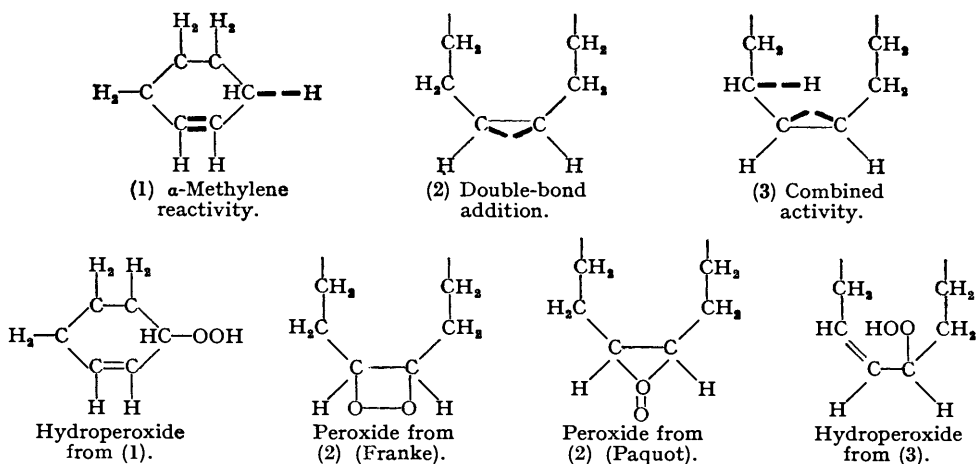


FIG. 3.
Modes of attack on double bonds.



in *cyclohexene*. The mechanism of autoxidising fatty unsaturated molecules is best explained by this combined activity [Fig. 3 (3)].

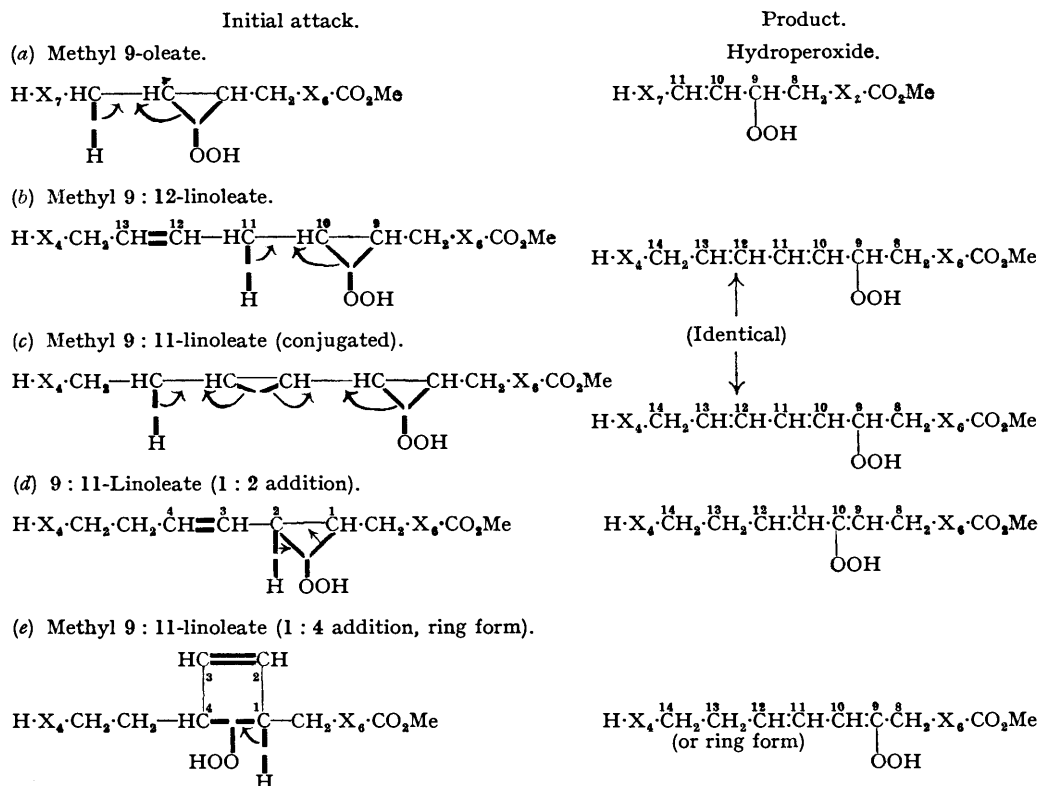
The activity associated with the linoleate system is of a much higher order than that of an isolated double bond. Unsaturated groups on either side of the 11-methylene group are

responsible for this enhanced effect. The activation of the linoleate molecule before autoxidation is shown in Fig. 4 (b).

For the activation of the conjugated linoleic system, free energy may be transferred along the chain of unsaturation so that a relatively distant α -methylene group becomes activated for hydrogen abstraction, as shown in Fig. 4 (c). The examples, Fig. 4 (a), (b), and (c), of activity in the system methyl oleate-methyl linoleate are cases of the combined activity previously discussed [Fig. 3 (3)]. In the conjugated linoleate, there is a further possibility. The resonating bonds present therein so reinforce or react with each other that α -methylene activity comes into play [Fig. 3 (1)] as in *cyclohexene* or *tetralin*. Thus, any of the four tertiary carbon atoms in the conjugated system may become activated because of their α -relationships

FIG. 4.

Types of hydroperoxides formed from methyl oleate and linoleate below 60°.



[Type of activity (cf. Fig. 3) is: (a)–(c), type (3); (d)–(e), type (1)].

to double bonds. The tertiary-carbon activation of the ordinary form of conjugated linoleate is shown in Fig. 4 (d), and that of the extreme 4-ring form in Fig. 4 (e). As autoxidation progresses, the types of activity shown in Fig. 4 (c), (d), and (e) develop and play an increasing part in the reaction, although they are not present originally.

The activation of molecules shown in Figs. 1–4 is concerned primarily with autoxidation, but it is evident that the principle is of very general application. The decomposition of hydroperoxides has been interpreted on this basis. The hypothesis could readily be applied to other processes requiring hydrogen abstraction such as condensation, or to those catalysed by light or heat such as polymerisation. Spatial proximity of reacting groups is an important factor in this connection; *e.g.*, reaction between the 1- and the 4-position may occur in suitable circumstances.

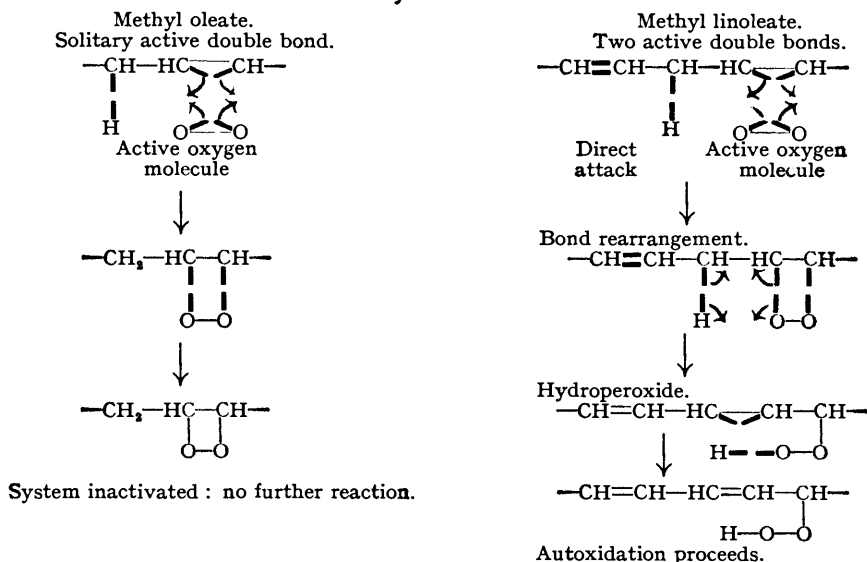
During recent years, many investigations have been carried out on the autoxidation of unsaturated esters, and with reference to Fig. 3, (1), (2), and (3), emphasis has been laid on: (1) attack at the methylene groups adjacent to the double bond assisted by the presence of

active or free atoms and radicals (Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Faraday Soc.*, 1942, **38**, 348) [Fig. 3 (1)]; (2) direct attack at the double bond (Hilditch and Gunstone, *J.*, 1945, 836; 1946, 1022).

It appears that in (1) hydrogen is removed from an α -methylene group and is replaced by a hydroperoxyl group. The double bond remains in position to yield in the case of oleate the 9-unsaturated 8- or 11-hydroperoxide. On the addition of oxygen to the double bond as suggested by Franke and Paquot [see Fig. 3 (2)], however, there is no hydrogen abstraction and the double bond is completely saturated. As there is no direct experimental evidence to support these hypotheses, Farmer has introduced the idea of mesomerism in an endeavour to harmonise the facts with his α -methylene theory [Fig. 3 (1)]. Such reactions, however, do not occur till 180° is reached and would involve the conjugative isomerisation of a large part of the linoleate which has not been observed. According to Hilditch [see (2) above], the primary addition of oxygen to the double bond is followed by an indefinite rearrangement of the bonds, including those of the methylene groups adjacent to the original double bond. On these grounds Hilditch explains the almost stoichiometric production of conjugated unsaturation in autoxidising

FIG. 5.

Comparison between methyl oleate and methyl linoleate : Initial formation of hydroperoxides from linoleate.



methyl linoleate. This led the author to consider the possibilities for bond movement in such a system and resulted in the idea of combined activity [Fig. 3 (3)], and this, in turn, led to the postulation of a satisfactory mechanism for the autoxidation of methyl oleate and linoleate.

The mixture of oleate and linoleate has already been considered by Hilditch and Gunstone (*loc. cit.*). They showed that methyl oleate free from linoleate is very resistant to autoxidation but that the reaction may be catalysed by methyl linoleate. A hydroperoxide also acts as a catalyst (Bolland, *loc. cit.*). Light or heat accelerates autoxidation and the induction period can then be reduced to vanishing point. During the autoxidation of methyl linoleate itself there is no appreciable induction period (Bolland, *loc. cit.*; Bergstrom, *Arkiv Kemi, Min., Geol.*, 1946, **21**, A, 1), and a hydroperoxide is obtained directly on treatment with oxygen. The reaction mechanism for methyl linoleate, therefore, differs from that for methyl oleate.

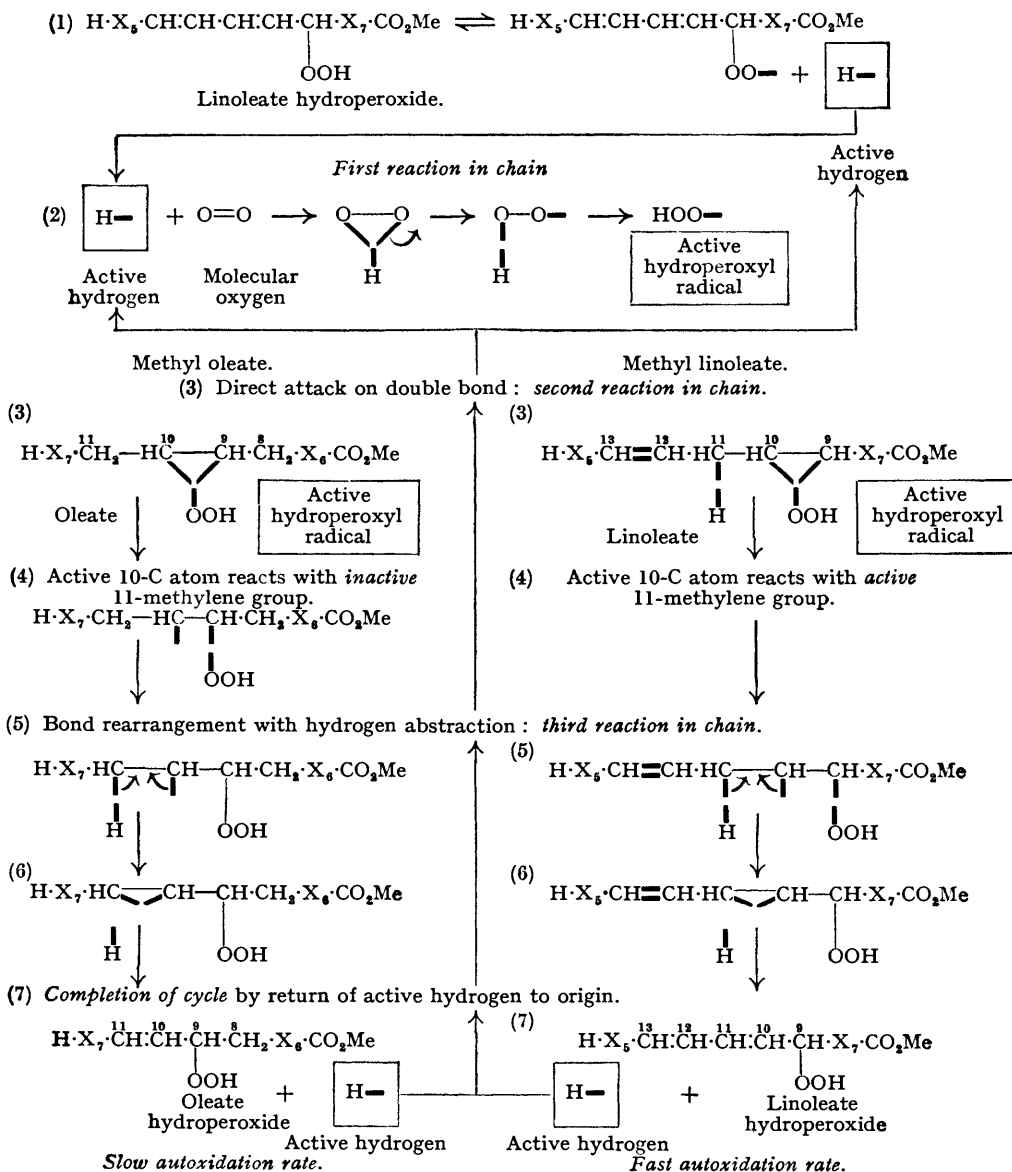
The autoxidation of a mixture of methyl oleate and linoleate, however, has a well-defined induction period and the reaction is typically auto-catalytic. It may be divided into two stages : (i) the induction period, when the initial formation of a hydroperoxide from methyl linoleate and oxygen is taking place, and (ii) the autoxidation proper, in which both methyl oleate and linoleate are undergoing oxidation catalysed by the hydroperoxide formed in (i).

In order to account for the slow initial reaction (i), it is suggested that molecular oxygen when activated by light or heat contains a small concentration of an active diradical in which

there are two points of activity as shown in Fig. 2. This active oxygen molecule attacks the linoleic molecule, which is activated as shown in Fig. 3 (3), by Reaction III, Fig. 1. After this initial attack, a second double bond is still present having its full capacity for activating the α -methylene group. One of the hydrogen atoms of this group is, therefore, transferred to one

FIG. 6.

Propagation of the chain reaction for forming hydroperoxides from methyl oleate and linoleate.



of the oxygen atoms again by Reaction III, Fig. 1, and a hydroperoxide is formed as illustrated in Fig. 5. The high activity in the linoleic system contrasts strongly with the very low activity in the oleic system (Fig. 5). When a double bond, as in methyl oleate, is attacked, the adjacent methylene groups lose their activity because the source of this activity—the double bond—has been saturated. The two molecules mutually deactivate each other and there is no further reaction.

Once a critical but small concentration of hydroperoxide is reached through reaction (i), corresponding in the present case to a Lea figure of 20, the system becomes autocatalytic (ii) and oxidation then proceeds at a high but steady rate. A mechanism depending on a chain-reaction cycle is required to account for this behaviour. It is evident that a hydroperoxide in the presence of oxygen can supply the active radicals necessary for the propagation of such a chain reaction. It is suggested, as shown in Fig. 6, that these active chain carriers are the free hydrogen and hydroperoxyl radicals (-H and -OOH , respectively). A hydroperoxide formed during the induction period (i) gives an active hydrogen atom by Reaction I, Fig. 1, which then reacts with molecular oxygen to give an active hydroperoxyl radical [Figs. 2 and 6 (2)]. The latter attacks any nearby double bond directly [Fig. 6 (3)] and, by bond rearrangement, forms a new double bond and liberates an active hydrogen atom [Fig. 6 (5)]. These three stages, Fig. 6 (2)—(6), proceed consecutively, each by Reaction II, Fig. 1, and form a typical chain reaction. This completes the cycle, and the system, which initially gives rise to the active hydrogen, is not disturbed and does not necessarily take part in the other stages of the autoxidation. During the induction period (i) the necessary concentrations of active radicals for propagating the chain-reaction cycle is being built up, and reaction becomes autocatalytic (ii) as soon as this is achieved.

The difference between the autoxidation of methyl oleate and that of methyl linoleate is again emphasised when considering it as a chain-reaction cycle (cf. the induction period above). This is very clearly demonstrated in Fig. 6, where the chain reactions are set out side by side. The first and the second reaction in the chain are identical for methyl oleate and linoleate, but a substantial difference arises in the third and the last reaction. In the case of methyl oleate, an active 10-carbon atom must attack an *inactive* 11-methylene group, whereas in that of methyl linoleate an 11-methylene group strongly activated by a 12-unsaturated group is available for attack by an active 10-carbon atom. The rate-determining factor in either case is the state of activity of the 11-methylene group for hydrogen abstraction. The rate of autoxidation under comparable conditions for methyl linoleate has been found to be 12 times that for methyl oleate (Gunstone and Hilditch, *J.*, 1945, 836).

A hypothesis based on the chain carriers $\text{H}\cdot$ and $\text{HOO}\cdot$ is considered by Bolland (*loc. cit.*) to be satisfactory from the kinetic standpoint but untenable from a structural point of view. A chemical theory based on these radicals and on an active oxygen molecule $\text{O}\cdot\text{O}\cdot$ is, however, given in the present paper. This, besides accounting for the autoxidation as catalysed by a hydroperoxide, also explains the formation of the catalyst during the induction period of the autoxidation.

The activity of hydrogen atoms, *i.e.*, the ease with which an active hydrogen atom is removed from a methylene or a tertiary carbon group, probably decides the positions taken up by the hydroperoxyl group and by the double bonds. These positions are shown in Fig. 4 and Table I for methyl oleate and linoleate. When autoxidation proceeds by combined activity as shown

TABLE I.
Changes in structural positions during autoxidation at below 60°.

Methyl ester.	No.	Double bond(s) :			Active hydrogen abstraction.	Type of activity (Fig. 3).	Type of initial attack (Fig. 4).	·OOH group.	Double bonds :		Remarks.
		Original.	Attacked.	Activating.					New.	Total.	
Oleate	1	9	9	—	8	3	(a)	10	8	8	} In equal amounts
	2	9	9	—	11	3	(a)	9	10	10	
Linoleate	1	9 : 12	9	12	11	3	(b)	9	10	10 : 12	} Conjugated in equal amounts
	2	9 : 12	12	9	11	3	(b)	13	11	9 : 11	
Linoleate after conjugation	1	9 : 11	9	11	13	3	(c)	9	10 : 12	10 : 12	} Conjugated in equal amounts
	2	9 : 11	11	9	8	3	(c)	12	8 : 10	8 : 10	
	3	10 : 12	10	12	14	3	(c)	10	11 : 13	11 : 13	
1 : 2-Addition	4	10 : 12	12	10	9	3	(c)	13	9 : 11	9 : 11	} Conjugated in equal amounts
	5	9 : 11	9	11	10	1	(d)	10	9 : 11	9 : 11	
	6	9 : 11	11	9	11	1	(d)	11	9 : 11	9 : 11	
1 : 4-Addition (ring form)	7	10 : 12	10	12	11	1	(d)	11	10 : 12	10 : 12	} Conjugated in equal amounts
	8	10 : 12	12	10	12	1	(d)	12	10 : 12	10 : 12	
	9	9 : 11	9 : 12	10	9	1	(e)	9	9 : 11	9 : 11	
	10	9 : 11	9 : 12	10	12	1	(e)	12	9 : 11	9 : 11	} Conjugated in equal amounts
	11	10 : 12	10 : 13	11	10	1	(e)	10	10 : 12	10 : 12	
	12	10 : 12	10 : 13	11	13	1	(e)	13	10 : 12	10 : 12	

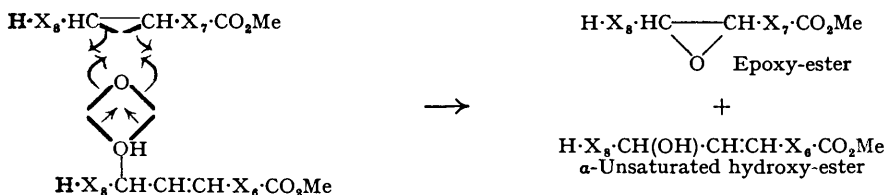
in Fig. 3 (3), the primary attack occurs at the double bond and the hydroperoxyl group becomes attached at one of the double-bond carbon atoms. The double bond itself is displaced one

FIG. 7.

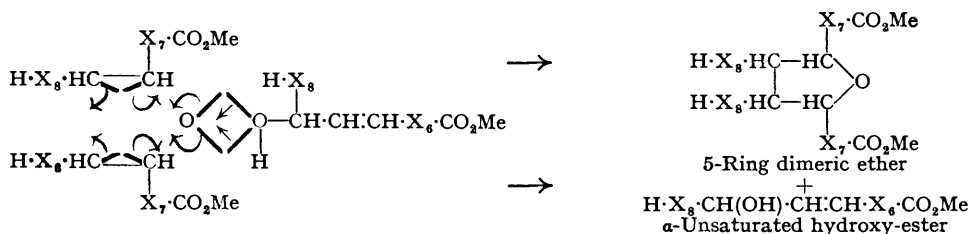
Initial ways of decomposing a hydroperoxide : Type A.

Type A : Reaction by addition of an —O— atom at 60° .

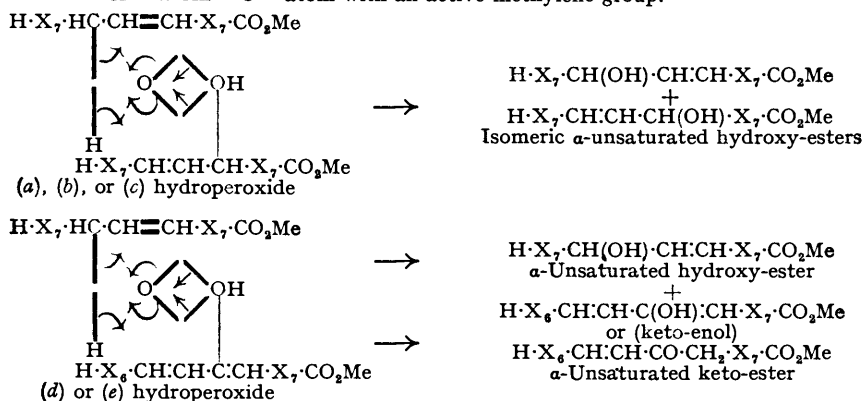
A I. An —O— atom with a double bond.



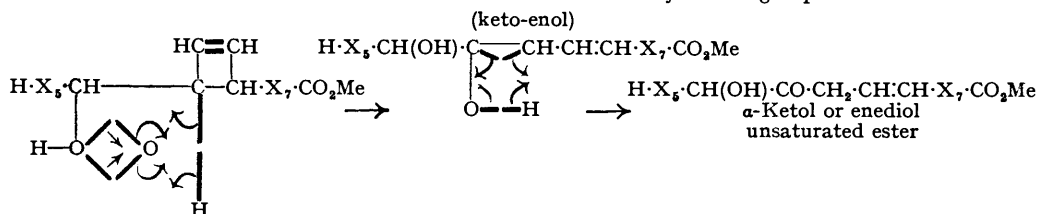
A II. An —O— atom with two double bonds.



A III. An —O— atom with an active methylene group.



A IV. An —O— atom with an active tertiary carbon group.



place away from its original position, and hydrogen abstraction takes place from one of the α -methylene groups. Combined activity, Fig. 3 (3), thus produces methylene hydroperoxides as shown in Fig. 4 (a), (b), and (c). A modified form of α -methylene activity [Fig. 3 (1)]—

tertiary-carbon activity—on the other hand, gives by Reaction II, Fig. 1, tertiary-carbon hydroperoxides as shown in Fig. 4 (d) and (e).

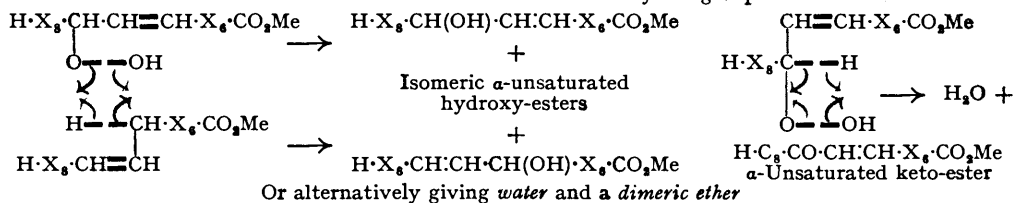
Methyl oleate gives isomeric α -unsaturated methylene hydroperoxides. Methyl linoleates all give conjugated diunsaturated hydroperoxides. The methylene hydroperoxides from 9 : 12- and from conjugated 9 : 11- or 10 : 12-linoleates are of identical type [Fig. 4 (b) and 4 (c)]. The tertiary-carbon hydroperoxides, however, are produced only from the conjugated linoleates and are of two types depending on whether the original linoleates react in the 1 : 2- or the 1 : 4-phase. The positions which may be occupied by double bonds and hydroperoxyl groups are somewhat restricted. In contrast, if the oleic and linoleic systems are first activated with

FIG. 8.

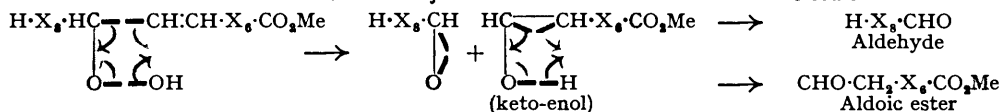
Initial ways of decomposing a hydroperoxide : Type B.

Type B : Reaction by fission of an O—O bond at 170°.

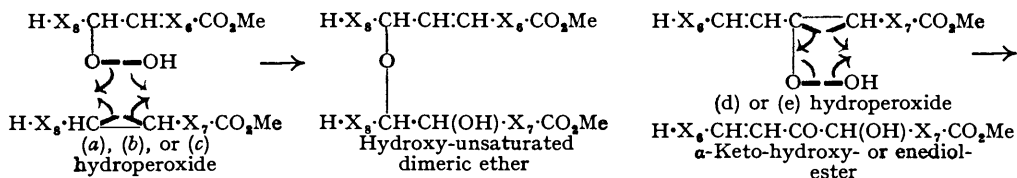
B I. An O—O bond with an active methylene group.



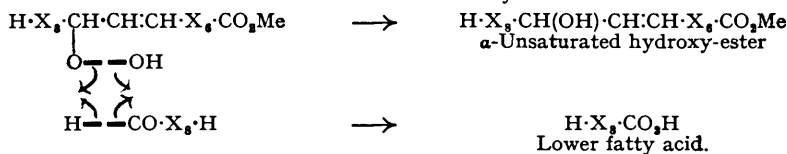
B II. An O—O bond with adjacent C—C bond. Fission of the molecule.



B III. An O—O bond with a double bond.



B IV. An O—O bond with an aldehyde from B II.



Or alternatively giving water and a dimeric ester.

the formation of free radicals as suggested by Farmer, mesomeric equilibrium conditions would immediately lead to the production of isomers (cf. the alkali isomerisation of linoleates and linolenates at 180° and 160, respectively).

The extent of activation by these mechanisms is probably a function of the temperature. At temperatures below 60° certain arrangements of double bonds in relation to the hydroperoxyl group as shown in Fig. 4 and Table I appear to be fairly stable. At 50° autoxidation proceeds at a steady rate in the presence of oxygen, with the production of hydroperoxides.

Apart from the thermal decomposition of a hydroperoxide into free radicals, Fig. 6 (1) (cf. Bolland, *loc. cit.*), hydroperoxides may also decompose by being themselves reduced in the ways indicated below. The reaction proceeds only slowly at 50° but rapidly at higher temperatures and may occur at even lower temperatures, particularly with esters containing more than one double bond (cf. Bergstrom and Holman, *Nature*, 1948, 161, 55). Hilditch and

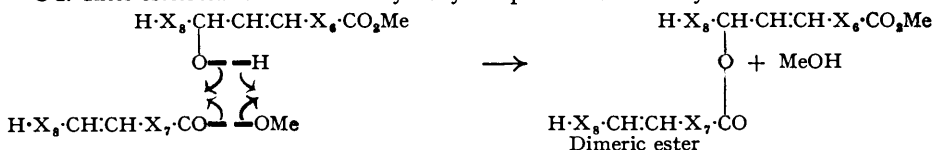
Gunstone (*loc. cit.*) have investigated autoxidations at temperatures up to 120°, and it is evident that formation and decomposition of hydroperoxide are proceeding simultaneously.

The initial decomposition of hydroperoxides (Fig. 2) can be accounted for in two ways, Type A and Type B. These reactions, as shown in Figs. 7 and 8 respectively, may take place additively at double bonds, with loss of iodine value [Fig. 3 (2)], or by hydrogen abstraction at active methylene or tertiary-carbon groups [Fig. 3 (1)], or by fission of an adjacent C-C bond. Decomposition reactions, Type A, occur at temperatures up to 60°. Hydroperoxides are assumed

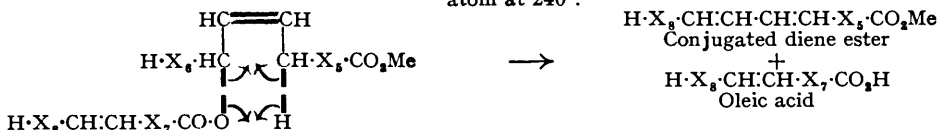
FIG. 9.

Secondary and miscellaneous reactions : Type C.

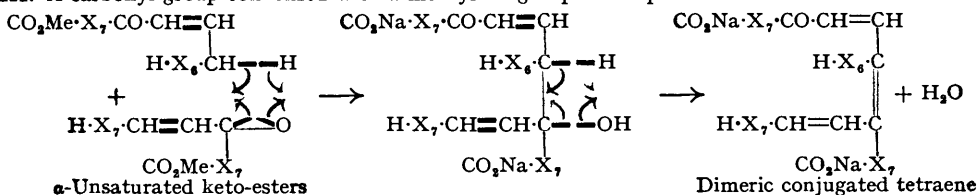
C I. Inter-esterification between a hydroxy-compound and a methyl ester at 240°.



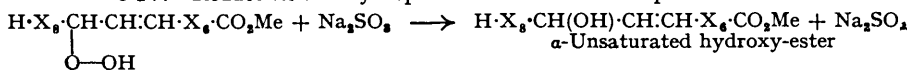
C II. Conjugated unsaturation by bond rearrangement in conjunction with an active hydrogen atom at 240°.



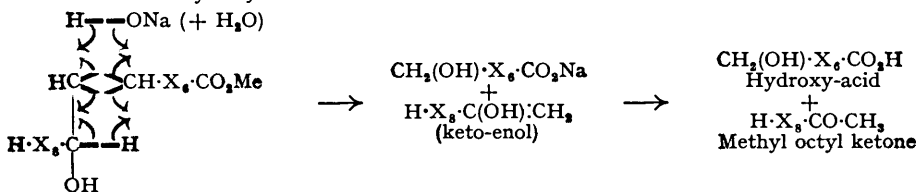
C III. A carbonyl group condensed with a methylene group in the presence of alkali at or below 80°.



C IV. Reduction of a hydroperoxide with sodium sulphite at 40°.



C V. Hydrolytic fission of an α -unsaturated alcohol with alkali at 190°.



to contain quadrivalent oxygen (Paquot, *loc. cit.*) and their decomposition proceeds through an $-\text{O}-$ atom by Reaction III, Fig. 1. Type A (Fig. 7) resembles the oxidation of conjugated double bonds by perphthalic acid or perbenzoic acid, which proceeds in dilute solution at low temperatures (40°) (Karrer and Jucker, *Helv. Chim. Acta*, 1945, 28, 427).

Type B occurs at temperatures above 100°, and decomposition proceeds normally through the rupture of an $-\text{O}-\text{O}-$ group by Reaction III, Fig. 1, and the intermediate formation of an active hydroxyl radical; $-\text{OH}$, Fig. 2. At 170°, and in the absence of oxygen, this type of reaction (Fig. 8) is very rapid and all the hydroperoxide soon disappears.

At higher temperatures up to 240° the slow secondary reactions (Type C) shown in Fig. 9 take place during distillation by Reaction III, Fig. 1. A number of miscellaneous reactions are also included in Type C.

An attempt has been made to apply the above decomposition reactions to the hydroperoxides of methyl oleate and linoleate in the presence of an excess of methyl oleate without considering possible structural isomerism. The results of this extensive inquiry are summarised in the following discussion.

Recent work on the autoxidation of methyl oleate and linoleate shows that the initial products are respectively mixtures of α -unsaturated hydroperoxides and of $\alpha\gamma$ -di-unsaturated hydroperoxides, but the actual numerical location of these groups is not so certain. The separation of the mixed hydroperoxides is no easy matter, but concentration as far as 90% hydroperoxide in the case of methyl oleate has been achieved by molecular distillation (Farmer and Sutton, *loc. cit.*), and also by crystallisation at -80° (Swift, Dollear, and O'Connor, *Oil and Soap*, 1946, 23, 255). Bergstrom (*loc. cit.*), in the case of methyl linoleate, has concentrated the autoxidation products by a process of fractional adsorption and desorption. Further structural delineation of the oxidised molecules has been attempted by these and other workers, but no clear evidence has been adduced regarding the structures of these hydroperoxides. Bergstrom has some evidence that, for methyl linoleate, the hydroperoxide groups are in the 9- or the 13-position and this evidence fits in with the present theory. On the other hand, Swift, Dollear, and O'Connor, in the case of methyl oleate, claim positions 8 and 11 for the hydroperoxide groups, contrary to the present theory.

TABLE II.

Aldehydic and acidic fission of hydroperoxides according to B II and B IV (Fig. 8) at 170°.

Fission products: (i) Dicarboxylic part.

Hydroperoxide methyl ester.	No. (Table I).	Chain length.	Ester group.	Aldehyde or acid group.	Double bond.	Theoretical wt. (%) from hydroperoxides.				
						Aldehyde.	Acid.	Total fission products (i) + (ii). Aldehyde. Acid.		
Oleate	1 } 2 }	9	1	9	—	56.7	30.8	—	—	
Linoleate	1	9	1	9	—	28.5	15.5	—	—	
	2	12	1	12	9	34.7	18.6	—	—	
				Linoleate, total		63.2	34.1			
Linoleate after conjugation	1	9	1	9	—	14.3	7.8	—	—	
	2	11	1	11	8	16.3	8.7	(below)	—	
	3	10	1	10	—	15.3	8.3	—	—	
	4	12	1	12	9	17.4	9.2	—	—	
				Linoleate after conjugation, total		63.3	34.0			
Fission products: (ii) Monocarboxylic part.										
Oleate	1 } 2 }	9	—	1	—	43.3	24.1	100.0	54.9	
Linoleate	1	9	—	1	3	21.5	12.0	50.0	27.5	
	2	6	—	1	—	15.3	8.9	50.0	27.5	
				Linoleate, total		36.8	20.9	100.0	55.0	
Linoleate after conjugation	1	9	—	1	3	10.7	6.0	25.0	13.8	
	2	7	—	1	—	8.7	5.0	25.0	13.7	
	3	8	—	1	3	9.7	5.5	25.0	13.8	
	4	6	—	1	—	7.6	4.5	25.0	13.7	
				Linoleate after conjugation, total		36.7	21.0	100.0	55.0	

Since the decomposition products (Type B II *) more volatile than the original esters, and arising from fission of the molecule, indicate the positions initially occupied by the hydroperoxyl groups, a summary of the possibilities is given in Table II (cf. Swift, Dollear, Brown, and

* Type B II refers to Decomposition Reaction Type B II, Fig. 8.

O'Connor, *J. Amer. Oil Chem. Soc.*, 1948, 25, 39). The molecule breaks into two parts at the site of a double bond before it is hydroperoxidised. One part of the broken molecule is an aldehyde and the other an aldoic ester. Methyl oleate thus gives C₉-aldehyde and 9-aldoic methyl ester. Methyl linoleate may divide at either the 9- or the 12-double bond; the second double bond then appears as a β -unsaturated aldehyde or acid. The fission products for conjugated methyl linoleate are of the same general nature but show more variation in chain length. The mode of formation of volatile unsaturated acids at an advanced stage in the autoxidation of methyl linoleate (Hilditch and Gunstone, *loc. cit.*) is thereby explained (Type B IV).

Similarly, the hydrolytic fission (Hargreaves and Owen, *J.*, 1947, 750, 753, 756), of the α -unsaturated hydroxy-compounds produced by the reduction of the hydroperoxides (Types A, B I, B IV, C V) may have some structural significance, for the oxygen of the hydroxyl group then appears in an acetyl group. The above scission products of roughly half the original molecular weight should be easy to separate and identify.

Farmer contends that there is no loss of unsaturation on autoxidation, as the absorption of oxygen is proportional to the degree of peroxidation; both Hilditch and Paquot, on the other hand, record a fall in iodine value roughly proportional to the extent of peroxidation. A fall of iodine value (4.5 units) is shown in Table III for 6.1% wt. peroxidation at 60° and a further fall (1.8 units) on distillation. The iodine value is not necessarily a correct index of the extent of unsaturation, for a discrepancy between them is well known with conjugated compounds. As these are almost absent in the present case at the beginning of an autoxidation, it would appear that the fall in iodine value represents a genuine loss of unsaturation. These apparently conflicting results, probably due to different experimental conditions, can, however, be reconciled on the assumption that hydroperoxidation occurs initially without loss of unsaturation, and that hydroperoxides decompose more or less slowly with loss of iodine value and of unsaturation (cf. Bergstrom and Holman, *loc. cit.*). Hilditch's data support this view very strongly, for towards the end of the absorption of oxygen, the extent of the hydroperoxidation, as shown by Lea figures, rises to a maximum and then falls equally sharply. There is apparently a change in the nature of the oxidation at about 70°; as this temperature is reached, the rate of decomposition of the hydroperoxide accelerates with increase of temperature, the rate being doubled for a 10° rise. The loss of iodine value has been frequently attributed to the formation of a stable peroxide of the cyclic ether type, particularly at high temperatures. Two possibilities, one due to Franke and Monch (*Annalen*, 1944, 556, 1, 200) and the other due to Paquot (*loc. cit.*), involving quadrivalent oxygen, are illustrated in Fig. 3 (2). Both forms retain the peroxidic character and should still react with hydriodic acid, possibly at a slower rate, giving dihydroxystearic acid or a derivative thereof. The loss of unsaturation by the formation of dihydroxystearic compounds (Type A I, B III) may be balanced by the production of additional unsaturation, particularly at high temperatures, in the form of conjugated diene esters (Type C II; cf. pyrolysis of polyricinoleic acid to conjugated linoleic acid).

The most likely way in which the additive character of the double bond, with loss of unsaturation, is brought into play at low temperature is through Type A reactions (Fig. 7). Type B reactions (Fig. 8) are not, however, entirely ruled out. The mass-action effect of the presence of a large amount of methyl oleate should not be neglected.

Theoretically, the stable decomposition products may be placed in the following order of probability: (1) The most frequent product is an α -unsaturated hydroxy-compound (Types A, B I, B IV) or its ethers (Type B III) or esters (Types B IV, C I), which retains all the additive and α -methylene activities of a double bond. (2) Dihydroxystearate or its ethers (Type B III) including epoxy-groups (Types A I, B III), or esters (Types C I, C II) which, in contrast, are completely devoid of unsaturation but function entirely as $\alpha\beta$ -dihydroxy-compounds. (3) Finally, a carbonyl group may be formed in which there is residual unsaturation between the carbon and oxygen atoms.

For any complete explanation of autoxidation, the oxygen distribution at the different stages in the process (*e.g.*, autoxidation, thermal decomposition, and saponification) is important in determining the course of reaction. Oxygen may be combined in any of the following ways: carboxyl ($\cdot\text{CO}_2\text{Me}$, $\cdot\text{COO}\cdot$, and $\cdot\text{CO}_2\text{H}$), hydroxy ($\cdot\text{OH}$), epoxy and ether ($\cdot\text{O}\cdot$), carbonyl ($\cdot\text{CO}\cdot$), $\alpha\beta$ -dihydroxyl [$\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot$] and enediol [$\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot$].

No satisfactory explanation is available to account for the production of a dark brown colour on saponification of autoxidised products. It is unlikely that an α -unsaturated hydroxy-compound [see (1) above] or dihydroxystearate compounds (2) give coloured products on saponification; but carbonyl derivatives (3), particularly α -unsaturated keto-compounds,

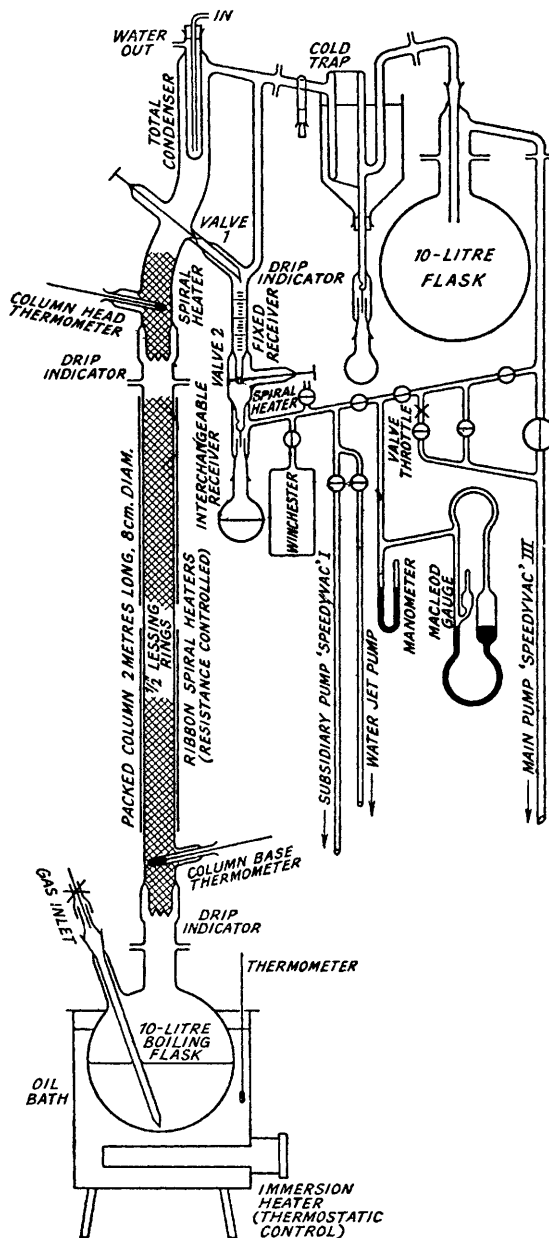
TABLE III.
Products from the distillation of autoxidised C₁₈ unsaturated methyl esters.

Autoxidation no.	Distillate no.	Aeration for C ₁₈	Quality.	Colour.	Colour on saponification.	Light absorption.	Smell.	Remarks : all distillations.			
									Initial palm oil methyl esters : I.V. 51.1. C ₁₈ methyl esters : I.V. 93.9. (Stearate 6.8%, oleate 77.2, linoleate 16.0%).	Very strong : characteristic of the lower fatty aldehydes	
4	5	Vapours condensable in cold trap; two layers, water and oil	Yellow	Very dark brown	Very dark brown	Strong 270 m μ max.	Very strong : characteristic of the lower fatty aldehydes	Strong 270 m μ max.			
5	3	Recovered esters, b. p. 160°/1 mm.	Colourless	Very pale yellow	Very pale yellow	Very weak	None	None			
6	4	End distillate	Yellow	Brown	Brown	Strong 270 m μ max.	Slight	Slight			
5	5	Column extract	Brown	Brown	Brown	Strong	Slight	Slight			
6	6	Slightly viscous residue	Brown-yellow	Brown-yellow	Brown-yellow	Strong	Slight, like castor oil	Strong			
4.											
Autoxidation no.	Distillate no.	Wt., %.	I.V.	Sap. value.	Wt., %.	I.V.	SCN val.	Sap. value.	Setting point.	Wt. % according to I.V. and SCN val.	
1	1	0.52	69.3	224	(Water) { 0.71 } { 0.09 }	43.1	—	220	—	—	—
2	2	1.49	—	—	(a) 4.46 (b) 13.02 (c) 13.56 (d) 13.08 (e) 12.66 (f) 14.75	60.4 74.6 75.1 75.3 73.8 70.8	—	222.5 192.5 191 191 189.5 190	—	—	—
3	3	77.66 (middle fraction)	76.0 78.8	—	—	61.8	49.3	189	{ 22.6 } { 24.8 }	42.7	42.8
4	4	7.04	58.1	186.5	6.17	59.9	—	188.5	—	—	—
5	5	1.82	58.4	214	2.79	61.1	—	207.5	—	—	—
6	6	8.83	63.7	199.5	8.71 (Start of distillation)	65.3	—	202	—	—	—
						71.5 (After d)	—	—	—	—	—

could be responsible for discoloration by auto-condensation (Type C III). The present investigation on heated autoxidation products indicates that a considerable degree of the darkening is due to aldehydes produced by fission (Type B II); but the darkening of the distillation

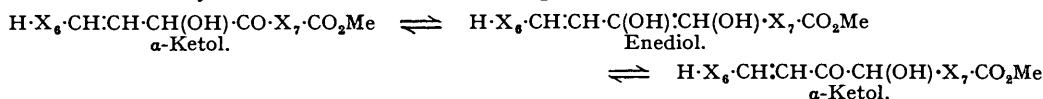
FIG. 10.

High-vacuum still with 10-litre boiling flask and efficient reflux column.



residue suggests the presence therein of other ketonic substances unstable to alkali. Bergstrom (*loc. cit.*) has identified a yellow product, probably an $\alpha\gamma$ -diunsaturated ketone, from methyl linoleate, and he attributes this to the dehydrative action of alumina on the initial hydroperoxide. A similar change may have taken place in the present experiments, as water was always obtained

in the early stages of distillation (Type B I internally; cf. Robertson and Waters, *Trans. Faraday Soc.*, 1946, **42**, 201; Waters, Faraday Society Discussion 1947, "The Labile Molecule"). The systematic theoretical treatment of these reactions given earlier indicates that a most probable source of keto-compounds lies in the activation of a tertiary carbon atom [Fig. 4 (*d*) and (*e*); Treibs, *Ber.*, 1944, **77**, 69] which is most likely to arise in a conjugated system. The product of such an activation, a tertiary-carbon hydroperoxide, immediately gives, on reduction, a keto-group by keto-enolic change (Types A, B I, B IV, C IV) and in some circumstances an α -keto-hydroxy-compound (Types A III internally, B III internally). The linoleic methylene hydroperoxide [Fig. 4 (*b*) and (*c*)], by reacting with an active tertiary carbon group, can give an α -ketol or enediol (A IV internally). Morrell *et al.* (*Trans. Faraday Soc.*, 1942, **38**, 862) prove the presence, in autoxidising conjugated compounds, of pseudo-acidic α -keto-hydroxy-compounds which form dark yellowish-brown solutions on saponification:



Dimeric products are no doubt contained in the distillation residues, but whether they are of the ether (Type B III), the ether ring (Type A II), or the ester (Types B IV, C I) types, requires further investigation.

EXPERIMENTAL.

The above hypothesis was developed in order to explain the results obtained in the course of numerous autoxidation experiments carried out as briefly described below. Practical observations are recorded in Table III for products from the autoxidation and distillation of C_{18} unsaturated methyl esters.

For the autoxidations, a current of air was bubbled daily (for 8 hours in diffused daylight) through a tall bottle, containing the unsaturated ester, immersed in a water-bath at 55–60°.

The fractional distillation of the original palm oil methyl esters and of the autoxidised C_{18} methyl esters was carried out in an efficient, high-vacuum, Pyrex still (Fig. 10) with a 10-litre boiling flask immersed in an electrically-heated (Sunvic-controlled) oil-bath. It had an electrically-heated (resistance-controlled) column, 8 cm. in diameter, packed with $\frac{1}{2}$ " porcelain Lessing rings surmounted by a variable-reflux still-head regulated to a reflux ratio of not less than 10:1 by a glass valve (Gibson, *J. Soc. Chem. Ind.*, 1939, **53**, 317; *Analyst*, 1945, **70**, 453).

The original palm oil methyl esters were made by treating a neutralised N'dian palm oil with a solution of sodium hydroxide in methanol according to Procter & Gamble Co. and E. W. Eckey (B.P. 567,682). This process has been found to be very efficient and economical and to be less drastic than the usual preparation of the fatty acids and acid-catalysed esterification.

The author wishes to thank his colleagues for helpful criticism and suggestions.

LEVER BROTHERS & UNILEVER LTD., RESEARCH DEPARTMENT,
PORT SUNLIGHT, CHESHIRE.

[Received, February 19th, 1948.]