THE INFRARED ABSORPTION OF METHYL LINOLEATE
DURING AUTOXIDATION

by

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INTRODUCTION

Atmospheric oxygen is the most prevalent as well as the most economically important of the oxidizing agents for the fats and fatty acids. In some cases the action of oxygen is highly desirable, as in the production of the blown paint oils, while in other cases its action is to be avoided if it is at all possible. For example, the process of film formation is one involving oxidation, but the failure of these same films is due to prolonged exposure to atmospheric oxygen.

Both the favorable and the unfavorable results of the oxidative process follow the same type of reaction between oxygen and the unsaturated centers of the fatty acids. Because of this, an enormous amount of work has been done in an attempt to determine the mechanism involved in autoxidation so that these reactions may be better controlled. Theories regarding the course of the reaction are many and varied, and considerable experimental evidence has been offered in support of the hypotheses.

Modern theories concerning the oxidation process are generally considered to date from the works of Bach (2) and Engler (13). Prior to their publications it was believed generally that molecular oxygen was partially dissociated into atomic oxygen and that this was the agent responsible for the slow oxidation observed in organic compounds. Bach and Engler believed that the oxygen involved was molecular and that the oxygen added

at the site of the double bond to give a compound of the general formula ROOR. This compound could then in turn oxidize some other oxidizable compound.

Another investigator, Fahrion (14), assumed that the oxidation occurred in the fatty acid to form a cyclic peroxide which then rearranged to a dihydroxy ethylenic or hydroxyketo configuration in the following manner:

$$\underset{\text{RCH-O}}{\text{RCH-O}} \longrightarrow \underset{\text{RC-OH}}{\text{RC-OH}} \longrightarrow \underset{\text{RC=O}}{\text{RCHOH}}$$
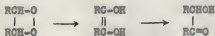
Fahrion also assumed that the cyclic peroxides could give rise to products having a more stable configuration, such as

$$\underset{\text{CH}_2\text{R}}{\text{RC=O}} \quad \text{or} \quad \text{RCH-CHR} \atop \text{O}$$
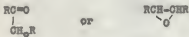
A theory of tautomeric ketohydroxy-dihydroxy rearrangement was proposed by Ellis (12) and was based on the detection of characteristic groups in linseed oil films. According to Ellis, autoxidation occurs as a result of the addition of a molecule of oxygen at the double bond to form a dihydroxy compound which then rearranges to a ketohydroxy compound.

Still another scheme was that proposed by Fokin (20) in which the first step of the reaction was the addition of oxygen at the double bond to form an ethylene oxide ring.

$$\text{RCH = CHR'} + \tfrac{1}{2}O_2 \longrightarrow \text{RCH-CHR'} \atop \text{O}$$
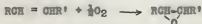
This configuration is known to be formed in the oxidation of monoethenoid acids with perbenzoic and peracetic acids. Evidence in support of Fokin's proposal is less extensive than that for some of the other hypotheses. Aside from the work of Fokin, some support for the theory is found in the work of Szent-Gyorgyi (40) who investigated the autoxidation of linolenic acid in the presence of sulfhydryl groups as catalyst and found that the molecular weight of the product, 293, indicated one atom of oxygen per mole of linolenic acid oxidized.

Staudinger (37) has proposed a theory in which the peroxide reaction of Bach and Engler is the second rather than the first step in the autoxidation of a double bond. This was based on a study of asym-diphenylethylene which yielded a stable peroxide. The primary product of oxidation was termed a moloxide and could not be isolated. It was assumed that the oxygen added at the double bond to form the moloxide which then rearranged to form the peroxide compound.

$$\begin{array}{ccc} \text{RCH=CHR'} & & \text{RCH-CHR'} \\ \underset{\text{O}}{\overset{\text{O}}{|}} & \longrightarrow & \underset{\text{O-O}}{|\quad|} \end{array}$$

Until recently this theory was widely accepted by the majority of the workers in this field. The evidence for the existence of such a structure has all been obtained indirectly on the basis of certain analytical data. Unfortunately, all the analytical methods involved are not definitely quantitative and it is a well known fact that the oxidation of a fatty acid leads to a

wide variety of products, making the proper interpretation of such analytical data quite complicated. It also should be noted that a product having such a structure has not been isolated and characterized as such from the oxidation products obtained. Those which have been characterized have all possessed structures quite different from the assumed heterocyclic peroxidic structure.

In 1936, Criegee (10) suggested that cyclohexene autoxidised to form a hydroperoxide having the structure


Following this, Ricche (35) suggested that unsaturated fats and oils probably behaved in a similar manner. According to Ricche the autoxidation of mono- or polyunsaturated compounds could occur through the formation of oxygen-activated methylene groups.

$$-CH = CHCH_2CH = CH- + O_2 \longrightarrow -CH = CHCHCH = CH-$$
$$\underset{OOH}{}$$
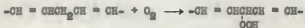
The hydroperoxide nature of certain types of olefinic compounds has been substantiated by the works of Criegee (10) and Stephens (38) on cyclohexene and also by the work of Criegee, Pils and Flygare (11) and of Hock and Susemihl (25) on tetralin.

The development of the hydroperoxide theory of autoxidation has been credited generally to the works of Farmer (15,16) and Farmer et al. (17,18,19). Farmer (15) originally postulated that the autoxidation of practically all unconjugated olefinic

compounds proceeded by the addition of a molecule of oxygen to the carbon atom in the α-position with respect to the double bond forming a hydroperoxide and leaving the double bond intact.

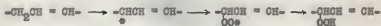$$-CH_2CH = CH- + O_2 \longrightarrow \overset{\displaystyle OOH}{-CH-CH} = CH-$$
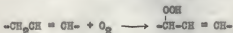
Farmer and Sutton (19), in studying the oxidation of methyl oleate, found that a mixture of mono- and di-hydroperoxides was produced, the hydroperoxide group being attached at C_8, C_{11}, or at both. Each of these hydroperoxides contained either one atom of active oxygen and one atom of active hydrogen or two atoms of active oxygen and an intact double bond. The peroxidised methyl oleate was estimated to not exceed 70 percent purity but re-fractionation gave a product which was estimated to be nearly 100 percent pure methyl peroxido oleate.

This work of Farmer and Sutton was repeated by Swift, et al. (39) who reported that the product obtained possessed the properties and responded to the reactions described by Farmer and Sutton. The identity of the product was further substantiated by the findings of Atherton and Hilditch (1) who subjected the peroxidised methyl oleate to further oxidation with powdered potassium permanganate. Among the products they identified were four acids, suberic, azelaic, octanoic and nonanoic, which were predicted by Farmer as some of the scission products of hydro-peroxido oleic acid.

Farmer et al., (17,18) believed that the reaction proceeded

by way of a free radical mechanism in which an active methylene group is somehow dehydrogenated to form a free radical. This free radical then absorbs oxygen, forming a new free radical which then adds a hydrogen atom to form the hydroperoxide.

$$-CH_2CH = CH- \longrightarrow -CHCH = CH- \longrightarrow -CHCH = CH- \longrightarrow -CHCH = CH-$$
$$\overset{\bullet}{} \qquad\qquad \underset{OO\bullet}{} \qquad\qquad \underset{OOH}{}$$

According to Farmer, Koch and Sutton (18), the first step in the autoxidation of an olefinic system of the methylene-interrupted type, such as is characteristic of the drying oil acids, was the severance of a thermally or photochemically activated C-H bond in the α-position with respect to the double bond leaving an olefinic free radical. This free radical could exhibit resonance between the two forms.
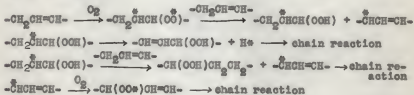
$$-CH = CHCH- \longleftrightarrow -CHCH = CH-$$
$$\overset{\bullet}{} \qquad\qquad\qquad \overset{\bullet}{}$$
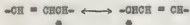
so that the addition of oxygen would most likely occur at C_1 or at C_3 and the double bond would then either remain at its original position or appear at the adjacent carbon atom. The most active methylene group was postulated to be the one flanked on either side by a double bond, such as the CH_2 group at C_{11} in linoleic acid.

In 1946 Farmer (16) modified his original hypothesis. In view of the fact that approximately 80 kcal of energy are required for the severance of a C-H bond and because of the apparent ease with which the oxidation occurs, the original hypothesis did not seem to be the most plausible. Experiments had shown
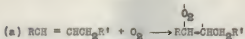
that in the case of conjugated compounds, even though the centers of unsaturation were flanked on either side by active methylene groups, autoxidation occurred additively leaving the methylene group intact. Because of this and remembering that the monomeric peroxides of simple olefins and unconjugated polyolefine are mainly α-methylenic hydroperoxides, there seemed to be justification for postulating universal initiation by addition at the double bond and a continuation of the attack substitutively by means of a chain reaction. The high expenditure of energy required for severance of the C-H bond would thus be reduced. By this scheme the actual extent of addition would be insignificant but would be sufficient to start the necessary chain reactions.

$$-CH_2CH=CH- \xrightarrow{O_2} -CH_2\overset{*}{C}HCH(O\overset{*}{O})- \xrightarrow{-CH_2CH=CH-} -CH_2\overset{*}{C}HCH(OOH) + \overset{*}{C}HCH=CH-$$

$$-CH_2\overset{*}{C}HCH(OOH)- \longrightarrow -CH=CHCH(OOH)- + H\bullet \longrightarrow \text{chain reaction}$$

$$-CH_2\overset{*}{C}HCH(OOH)- \xrightarrow{-CH_2CH=CH-} -CH(OOH)CH_2CH_2- + \overset{*}{C}HCH=CH- \rightarrow \text{chain reaction}$$

$$-\overset{*}{C}HCH=CH- \xrightarrow{O_2} -CH(OO\bullet)CH=CH- \longrightarrow \text{chain reaction}$$

It should be noted that intramolecular reaction of a type permitting the first formed di-radical, $-CH_2\overset{*}{C}HCH(O\overset{*}{O})-$, to become stabilised by the detachment of a hydrogen atom from the adjacent α-methylene group to form $-CH = CHCH(OOH)-$ is highly unlikely since it would not propagate reaction chains. There was also an indication of spontaneously occurring chain scission reactions which could be interpreted as indicating two kinds of oxidative attack occurring simultaneously.

Since, under proper conditions it is possible to obtain hydroperoxides in nearly quantitative yields, Bolland and Gee (6,7) have made a study of the autoxidation mechanism kinetically and thermochemically. The studies were carried out on ethyl linoleate, ethyl linolenate, methyl oleate and squalene. Absorption spectra in the quartz ultra-violet region indicated that the oxidation was accompanied by a displacement of the double bonds. This displacement was confined to oxidized molecules and, in the case of the linoleate ester, the primary product of oxidation was a conjugated hydroperoxide. In each case the process was identified as a chain reaction in which hydrocarbon radicals were formed, absorbed oxygen, and then reacted with a second molecule of olefin to form a hydroperoxide and a new free radical.

From their experiments, Bolland and Gee determined the energy of activation from the temperature dependence of the velocity constants obtained from kinetic data. They also have estimated the heats of reaction for various reaction paths, using the formal strengths of bonds broken and formed and making corrections for the estimated resonance energies of the reactants and products. These were then used, along with the activation energies, in an attempt to determine the most likely path of the reaction. Two possible points of attack were considered, attack at the double bond and at an active methylene group. For a mono-olefin these reactions may be formulated as follows:

(a) $RCH = CHCH_2R' + O_2 \longrightarrow R\overset{\overset{O_2}{|}}{CH}-CHCH_2R'$

(b) $RCH = CHCH_2R' + O_2 \longrightarrow RCH = CHCHR' + HOO-$

In the case of a 1:3 di-olefin, attack at one end of the double
bond would be assisted by the development of allyl resonance
while the other path, (b), would be assisted by a somewhat
greater gain of resonance energy. For a 1:4 di-olefin, attack
at the double bond would be equivalent to that in a mono-olefin,
but attack at an active methylene group would be easier because
of 11 kilocalories resonance energy in the radical. The values
of resonance energies employed in the calculations were

$C = C-C = C$	$C = C-C$	$C = C-C-C = C$
6.9 kcal	13.7 kcal	30.4 kcal

and the bond strengths used, though not identical with those of
Pauling (34), were

C–C	81 kcal	$C = C$	145 kcal
C–H	99 kcal	$C = O$	174 kcal
C–O	87 kcal	$O = O$ (O_2 molecule)	118 kcal
O–H	110 kcal	O–O (peroxide)	66 kcal

Using these values, the estimated heats of reaction were tabu-
lated as follows for the various olefins considered.

	Mono-	1:3	1:4
ΔH_a	14 kcal	2 kcal	14 kcal
ΔH_b	7 kcal	3 kcal	-4 kcal

These reactions have heats lying below the experimentally determined energies of activation, 26 kcal, so that none of them can be ruled out on this basis. The order of reactivity of double bond attack was then determined as $1:3 >$ mono- or $1:4$; while for α-methylenic reactivity the order was $1:4 > 1:3 >$ mono-. The two reaction paths were thus postulated not to be mutually exclusive and would be expected to proceed simultaneously.

The double bond displacement which occurred during oxidation was explained by Bolland and Gee on the basis that one of the chain carriers was the radical $RCH = CHCH = CHR'$, since this radical will possess two other resonance hybrid configurations giving rise to a large resonance stabilization and permitting the formation of isomeric peroxide radicals on the attack of oxygen. The chain cycle was believed to be

(c) $RCH = CHCHR' + O_2 \longrightarrow RCH = CHCHR'$
$\overset{|}{O}O-$

(d) $RCH = CHCHR' + RCH = CHCH_2R' \longrightarrow RCH = CHCHR' + RCH=CHCHR'$
$\overset{|}{O}O-\overset{|}{O}OH$
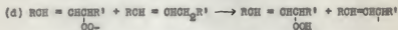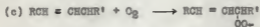
The estimated heats of reaction for reactions (c) and (d) for the olefins considered were

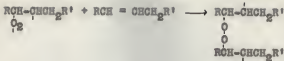|	Mono-	1:3	1:4
ΔH_c	-31 kcal	-27 kcal	-27 kcal
ΔH_d	-15 kcal	-19 kcal	-26 kcal

Because of the exothermic character of these reactions, they would be highly probable steps in a chain reaction and were consistent with the kinetically deduced energies of activation.

It has not been possible in all cases to isolate the hydroperoxide materials of the autoxidation, for, as pointed out by Farmer (15), chain scission reactions apparently set in unpreventably at the outset of the reaction, possibly by a direct mechanism of scission or occurring simultaneously with a less direct mechanism. Little study has been given to the course of the decomposition or chain scission reactions but experience has shown that the course is greatly affected by experimental conditions; i.e., the presence of catalysts, the acidity or alkalinity of the medium, the temperature at which the reaction is carried out, and incident radiation. For example, olefin hydroperoxides decomposed in acid media have been found to give rise to triols, probably derived from the corresponding epoxides, while an alkaline media leads to the formation of hydroxylated scission products, yielding aldehydes, ketones, and acids.

A polymeric tendency is also of rather general occurrence as a secondary reaction of the autoxidized material, for even in the most favorable examples of hydroperoxide formation, there usually has been an appreciable polymer fraction which may partially consist of dialkyl peroxides.

$$ROO- + RH \longrightarrow ROOR + H-$$

Bolland and Gee (7), have pointed out that polymers could be formed by the radicals formed in the direct attack of oxygen at the double bond and an unoxidized molecule of olefin.

$$\underset{\underset{O_2}{|}}{RCH}\text{—}CHCH_2R' + RCH = CHCH_2R' \longrightarrow \underset{\underset{\underset{RCH\text{—}CHCH_2R'}{|}}{\underset{O}{|}}}{RCH}\text{—}CHCH_2R'$$

The free radical ends thus produced could then react further with oxygen to again produce peroxide radicals which could then add olefin and thus build up a polymeric chain.

There is very little direct experimental evidence in support of any of the proposed polymeric reactions. Whatever the mechanism of the reaction, certain factors must be taken into consideration: (a) the autoxidation mechanism must be considered, (b) unoxidized carbon to carbon double bonds must not be involved, and (c) the general requirements of the general polymerization theory must be met.

In recent years, infrared spectroscopy has found wide application as an aid in the solution of various problems of both theoretical and practical importance and has been recently reviewed by Barnes et al., (4). The applications of infrared spectroscopy can be divided into two general categories, qualitative and quantitative. Qualitatively it has been used in the identification of compounds, in the recognition of specific chemical bonds, linkages or groups, and also in the fields of deutero-chemistry, polymerization, and isomerism. The qualitative analysis of mixtures is also facilitated by the study of the absorption spectrum, for the absorption spectrum of a mixture, except in the case of strong molecular interaction, is equivalent to a superposition of the spectra of the various com-

ponents of the mixture. Quantitatively, infrared spectroscopy is quite useful in the analysis of mixtures, for, if the nature of the components is known, it is usually possible to determine a frequency at which only one of these will absorb strongly, facilitating the determination of its concentration by comparison with standards. This same principle also has been applied in the study of reaction rates as a function of temperature, pressure, or catalyst. Certain thermodynamic constants also may be calculated from a knowledge of the infrared absorption frequencies.

When light of various wave-lengths is passed into a group of molecules, some of this light may be absorbed and some will pass through. Absorption can occur only if the molecule is capable of a rearrangement of its possible motions in such a way as to take up the energy associated with the incident radiation. A molecule is capable of three types of internal motion: motion of the electrons surrounding the nucleus, motions of the nuclei with respect to one another, and a rotation of the molecule as a whole. The energies associated with the three types of motion are of entirely different magnitudes, making it possible to correlate one of these types of motion with a particular region of the electromagnetic spectrum. The ultraviolet spectra are said to be due to electronic motions, the near infrared are due to nuclear vibrations, and the far infrared are due to molecular rotations. These regions are not sharply defined and there is considerable overlapping. The effect of electronic motions on

vibrations of the nuclei may be neglected for these are associated with relatively high energies.

Not all molecules have far infrared spectra and some few have no spectra even in the near infrared. Radiation may be absorbed or emitted only by a system whose electrical configuration is changing relative to a point in space, meaning that a vibration can result in absorption only if the electric moment of the molecule changes in the course of that vibration, and similarly for rotational absorption. According to the quantum theory, the frequency of vibration and rotation are limited to certain discrete values determined by the nature of the molecule so that there are only certain frequencies at which absorption can occur. Thus by irradiating a sample with a series of monochromatic bands of infrared radiation and plotting the percent of the radiation absorbed or transmitted as a function of either wave-length or frequency, the resulting graph may be interpreted in terms of the intramolecular motion of the molecule and is known as the infrared spectrum of the substance under investigation.

A molecule containing s atoms will have 3s degrees of freedom. Of these, three are associated with translation of the molecule as a whole and three are associated with rotation, so that the molecule will then possess 3s-6 internal degrees of freedom which will express themselves as 3s-6 normal modes of vibration provided that the molecule is non-linear. For a linear molecule there will be 3s-5 normal modes of vibration

since there are only two degrees of freedom associated with the
rotation of a linear molecule. A normal vibration is defined as
a vibration in which the center of gravity of the molecule does
not move, and in which all the atoms move with the same frequency
and in phase. Normal modes of vibration need not be independent,
for frequently several degenerate modes are found, depending on
the symmetry of the system.

The atoms of any molecule not at absolute zero are constant-
ly oscillating about their equilibrium positions. These oscil-
lations are of extremely small amplitude and high frequency.
The frequencies are of the same order of magnitude as are those
of infrared radiation so that some relationship might be expected
to exist between the motions of the atoms and their effects upon
incident infrared radiation. It also might be expected that a
mathematical calculation of the normal modes of vibration is pos-
sible, which should permit a unique determination of the struc-
ture of the molecule. The correct structure of the molecule
would then be that for which the calculated frequencies cor-
respond exactly to those observed experimentally. These calcu-
lations can be carried out if all the interatomic forces are
known, the complexity of the calculations depending on the number
of atoms and their symmetry. This has been done for a few mol-
ecules in which the number of atoms is small or which possess a
high degree of symmetry. However, since most molecules of in-
terest to the organic chemist are relatively complex, some other
method must be utilized. Considerable success in this direction

has been made by the purely empirical approach of Barnes etal., (4).

As has been pointed out by Hersberg (24), it is the bond force constant and not the frequency which is characteristic of a specific bond. If the restoring force between two atoms is the same in one molecule as in another, the conclusion would be that the electronic structures are the same in the two cases. And conversely, if the structures are the same then the force constants should also be the same. This actually has been found to be the case. For example, the bond-stretching force constant in HCN, ClCN, BrCN and $(CN)_2$ is approximately 17×10^5 dynes per cm throughout the series. Similar results have been obtained for other bonds. However, this principle holds strictly only if the bonds are in similar surroundings, since the force constants will be affected by such factors as the proximity of unsaturation and the degree of such unsaturation. This same principle holds for the bond-bending force constants and in this case the condition of similar surroundings is even more critical. It is not sufficient that the same bond type be adjacent to the bond under consideration, the atoms at the other end of the adjacent bond also must be the same.

Crawford and Brinkely (9) have shown for a number of molecules, that, by taking over not only the bond-stretching and bond-bending force constants but also the interaction constants from other molecules with the same groups, some or all of the normal frequencies may be predicted to within 1 or 2 percent of

the observed values. Such a procedure is of great importance
since in this way it is possible to determine the correct assign-
ment of the observed frequencies in the more complex molecules
or even to obtain the approximate values without actual observa-
tion. With increasing accuracy of observation and calculation,
slight differences in the bond force constants are to be expect-
ed since the surroundings of a given group are not the same in
different molecules.

The application of these principles to a correct assignment
of the observed vibrational frequencies is greatly simplified by
a corollary of the principle of invariance of bond force con-
stants, namely the constancy of bond or group frequencies in
different molecules. This was first established by observation
and later explained theoretically on the basis of the constancy
of bond force constants.

The observation of characteristic frequencies had led Mecke
(31,32,33) to the introduction of the concept of valence and de-
formation vibrations; that is, the idea that to every bond in a
molecule there corresponds a vibration in which this bond is
stretched and another vibration of smaller frequency in which it
is bent. An explanation of this can be given on the basis of the
mechanical molecular models of Kettering, Shutts and Andrews
(27) or simply by a consideration of the atoms taking part in
the vibration. If the C-H, O-H, and N-H vibrations are consider-
ed, it is seen that the masses of the other atoms are so much
greater than the mass of the hydrogen nucleus that the amplitude

of vibration of the hydrogen nucleus will be much larger than
those of the nuclei of greater mass. Therefore, to a first ap-
proximation, the hydrogen nucleus may be considered as oscil-
lating against an infinitely large mass so that the vibration
frequency depends practically only on the force by which the
hydrogen atom is bound to the remainder of the molecule and will
be nearly the same for different molecules with the same C-H,
O-H or N-H force constants. Since the hydrogen atom is always
an end atom, it can move only in the line of the bond or perpen-
dicular to it; that is, it can undergo only stretching or bend-
ing vibrations of frequencies corresponding to the respective
force constants. If two such groups are present, or more than
two, these will vibrate simultaneously and there will then be
several normal frequencies which will be of nearly the same mag-
nitude as for a single group, differing only by a small amount
which is an indication of the strength of interaction of the
equivalent groups. Apart from the end atoms thus far discussed,
experiments have shown that in many cases, bonds involving
heavier atoms have characteristic frequencies even if none of
these are end atoms.

The degree of definition of the characteristic frequencies
also depends on the angle between successive bonds in the chain
of atoms. It has been shown by Bartholome and Teller (5) that
if the angle is 90 degrees there will be no transfer of vi-
brational energy from one bond to the next so that the char-
acteristic frequencies will then be best defined. In the case

of the bond bending frequencies, the chance that in a molecule there is another frequency, not necessarily a bending frequency, of similar magnitude is much larger than for the bond-stretching frequencies. Thus, the bending frequencies are often not very characteristic.

In case a chain-like molecule has two or more equivalent bonds, there will be a resonance which leads to a splitting of the characteristic frequency and the stronger the coupling, the greater will be the degree of splitting. Also the greater the number of equivalent bonds, the greater will be the splitting into a correspondingly larger number of frequencies which will deviate increasingly from the characteristic frequency of a single bond of the same type.

Using these principles it is possible to obtain approximate values for some of the frequencies of a molecule, particularly an organic molecule, without actual observation, if the char-acteristic stretching and bending frequencies of the bonds in the molecule are known. Such predictions, even though only ap-proximate, are often quite helpful in the analysis of observed vibrational spectra.

As shown by Herzberg (23) the vibrations may be considered to obey Hooke's law. Therefore, any equation set up to describe these motions must be dimensionally similar to that which holds for simple harmonic vibrations, $\tilde{\nu} = (1/2\pi c)\sqrt{\frac{k}{\mu}}$, where $\tilde{\nu}$ is the frequency in cm^{-1}, c is the velocity of light, μ is the reduced mass of the vibrating atoms and k is the force constant existing

between the two atoms. The reduced mass is given by the equation $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ where m_1 and m_2 are the masses of the vibrating atoms. The constant k is related to the vibration by the equation $V = \frac{1}{2}kx^2$, where V is the potential energy and x is the displacement of the atoms from their equilibrium positions. Substitution of the proper constants reduces the dimensional equation to $\bar{\nu} = 1307 \sqrt{k/\mu}$ cm^{-1}, where k is expressed in units of 10^5 dynes/cm and μ is expressed in atomic mass units.

The value of k for practically all single bonds lies between 4 and 6 x 10^5 dynes per cm. The corresponding value for double bonds lies between 8 and 12 x 10^5 dynes per cm, while those for triple bonds generally lie between 12 and 18 x 10^5 dynes per cm. These values, along with the proper values of μ may be used to calculate the approximate vibration frequencies for a few typical atom pairs, as shown by Barnes et al. (4). For the C-H of methane the value of k has been found to be almost exactly 5 x 10^5 dynes per cm. The carbon atoms, because of its large mass relative to that of hydrogen, remains essentially at rest, and μ is close to 1. Substitution of these values gives $\bar{\nu} = 1307 \sqrt{5/1} = 2920$ cm^{-1}. Similarly, for the C-O of methyl alcohol, the value of k is still very close to 5 x 10^5 dynes per cm, but the value of μ is now 6.85 so that the frequency will be lower than in the case of the C-H bond. $\bar{\nu} = 1307 \sqrt{5/6.85} = 1110$ cm^{-1}. In the infrared spectra of these compounds there are strong absorption bands at 2915 and 1034 cm^{-1}. Also, a study of a series of compounds containing these linkages shows the characteristic bands

at approximately the calculated frequencies. Thus it is pos-
sible in many cases to use the exact frequency empirically as a
means of telling whether or not the particular atomic group is
present and also its relationship to the rest of the molecule.
And conversely, once the absorption frequency has been definite-
ly attributed to a particular atomic group, this frequency may
be used to calculate the value of k, the bond force constant.
This method of extracting a portion of the molecule and treating
it mathematically is, however, only an approximation and should
not be carried to extremes. The method is applicable to only a
few compounds. Barnes and his associates (4) have used an em-
pirical approach and examined the spectra of several hundred
organic compounds. Only rarely have they failed to find correla-
tions between bond frequencies and structural relationships.

It can thus be seen that infrared spectroscopy offers
promise of improved methods in biochemical and medical research
but very little work has as yet been reported. Mention has been
made by Jones (26) to investigations dealing with the appli-
cation to analysis of sterols and fatty acids. The infrared
spectra of linoleic and linolenic acids have been determined,
the only noticeable difference being at 9.38 microns (1168 cm^{-1}).
Bromination of these acids gave a much greater difference in the
spectra, as would be expected. Jones also states that prelimi-
nary measurements had been made on some of the epoxy and hy-
droxy acids obtained by a controlled oxidation of linoleic acid
and had indicated a possibility of following the successive

stages of oxidation of this acid.

McCutcheon et al. (30) have determined the infrared absorption spectra of the ethyl esters of oleic, elaidic, linoleic, linolelaidic and linolenic acids. They observed strong absorption in the region of 1667 cm^{-1} in the case of the esters of the oleic, linoleic and linolenic acids, while elaidic and linolelaidic acids exhibited relatively wider and weaker bands in this region. For ethyl linolenate there was a secondary absorption in the region of 1905 cm^{-1}. From theoretical considerations cis-acids should exhibit a strong absorption characteristic of the double bond in the 1667 cm^{-1} region. Since the ethyl elaidate and linolelaidate did not absorb strongly in this region, the results were interpreted as proof of the cis-cis and trans-trans configurations of these two esters respectively.

Gamble and Barnett (21) have examined the infrared absorption spectra of the methyl, glycol and glyceryl esters of oleic, linoleic, linolenic and elaeostearic acids. The glyceryl esters all showed absorption in the region of 1667 cm^{-1}, characteristic of the double bond. In addition to this, the elaeostearate showed an absorption at 1000 cm^{-1} which the authors attributed to conjugation. These same authors determined the spectra of the methyl esters of oleic and elaeostearic acids before and after exposure to ultraviolet light. A strong absorption band at 2940 cm^{-1} was found to have shifted to 3290 cm^{-1}. Absorption at 3450 cm^{-1} is generally attributed to the presence of an -OH group. The observed shift was thus attributed to the intro-

duction of -OH groups. More probably, however, the shift was
due to the introduction of hydroperoxide groups, -OOH, which are
readily formed in oleic acid when irradiated with ultraviolet
light in the presence of oxygen.

It was because of the diversity of opinion as to the autox-
idation mechanism and the increasing use of infrared spectroscopy
as an aid in such problems that the present investigation was
undertaken in an attempt to add spectroscopic evidence to the
chemical evidence supporting the hydroperoxide mechanism of
oxidation.

EXPERIMENTAL

Preparation of Materials

Unless otherwise stated, the methyl linoleate used in these
experiments was obtained by the debromination of tetrabromo-
stearic acid by the Rollett method (36).

Preparation of the Fatty Acid. Three hundred g of potassium
hydroxide were placed in a five liter round bottom flask, 1200 ml
of ethyl alcohol and 100 ml of water were added and the mixture
heated to near boiling on a steam bath. One thousand g of cot-
tonseed oil were then added, a reflux condenser attached, and
the mixture allowed to reflux for 30 minutes. The mixture was
then cooled to about 40° C. in a stream of tap water after which
1300 ml of cold distilled water were added. Five hundred fifty
ml of concentrated hydrochloric acid were then added in small
portions with cooling and agitation. The mixture was then placed

in a large separatory funnel and shaken to insure decomposition
of the soaps. The fatty acids were washed twice with about 1
liter of cold distilled water, being careful to avoid emulsifi-
cation. After drawing off the water, the fatty acids were dried
over anhydrous sodium sulfate. One liter of redistilled petro-
leum ether was then added and the solution allowed to stand
overnight at -5° C. The saturated acids and the sodium sulfate
were then filtered off and 1 liter of petroleum ether added to
the filtrate. The filtrate was then ready for bromination.

Preparation of Crystalline Tetrabromostearic Acid. A five
liter flask containing the solution of the fatty acids in petro-
leum ether was clamped firmly in an ice-salt bath, care being
taken that the flask was far enough from the bottom of the bath
to insure proper cooling. Bromine was added from a separatory
funnel at such a rate that the temperature of the reaction mix-
ture at no time exceeded 10° C. and stirred continuously with a
mechanical stirrer. Saturation of the fatty acids was indicated
by the persistence of the bromine color. The flask was then
tightly stoppered and allowed to stand overnight at -5° C. The
crude crystalline tetrabromostearic acid was then filtered off
using a Buchner funnel, washed with redistilled petroleum ether
and 1.5 liters of ether then added and the mixture heated on a
steam bath to effect solution. Twenty g of Norit were then added
and heating continued for a few minutes. The hot solution was
then filtered through a warm Buchner funnel and the filtrate al-
lowed to again stand overnight at -5° C. The crystalline prod-

uct was then filtered and washed with redistilled petroleum ether and the crystals dried at room temperature. The melting point was then determined (114-115°) and if low, the product was recrystallized as before from petroleum ether before proceeding.

Preparation of Methyl Linoleate. Two hundred g of tetrabromostearic acid and 200 g of granulated zinc were placed in a dry, ground-neck, round bottom flask. A reflux condenser was attached and 200 ml of methyl alcohol added. The acid was dissolved by carefully warming on a steam bath, cooling by a stream of tap water to control the initial reaction if necessary. The mixture was then allowed to reflux for two hours, after which the reaction mixture was cooled and poured into a separatory funnel containing 500 ml of distilled water. A small amount of hydrochloric acid was added to decompose any zinc soaps and then shaken vigorously. The mixture was then allowed to stand until the ester had separated completely. The aqueous phase was then drawn off and extracted twice with 200 ml of petroleum ether. The ester and the ether solution were added and washed twice with 500 ml of 2 percent sodium carbonate solution and twice with 100 ml of cold distilled water. The ether solution was then dried over anhydrous sodium sulfate, filtered, and the solvent removed by distillation under reduced pressure. The ester was distilled in an all-glass vacuum distillation apparatus and the fraction collected that boiled at 135-140°, 0.1 mm pressure.

Preparation of $\Delta^{10,12}$ Linoleic Acid. The conjugated linoleic acid was prepared by the method of von Mikusch (41).

Sixty g of solid potassium hydroxide were dissolved in 240 ml of 95 percent ethyl alcohol and 20 ml of distilled water. Two hundred g of dehydrated castor oil were then added to this solution and the mixture allowed to reflux for 1 hour on a steam bath. The reaction mixture was then cooled in a stream of tap water and 260 ml of distilled water added. The mixture was then acidified to litmus with concentrated hydrochloric acid, placed in a large separatory funnel and shaken to insure decomposition of the soaps. The aqueous phase was drawn off and extracted with Skellysolve B and the Skellysolve phase added to the acids. The solution was then dried over anhydrous sodium sulfate, filtered, and the solvent removed by distillation under reduced pressure.

The acids thus obtained were then isomerized by adding them slowly to a solution of 400 g of potassium hydroxide in 1100 ml of ethylene glycol at 180° C. in an oil bath and continuing the heating for 30 minutes. The heating was carried out in a large Erlenmeyer flask and stirred slowly to prevent local heating. Following the heating, the hot reaction mixture was poured into a beaker containing 1000 g of chipped ice, acidified to litmus with concentrated hydrochloric acid, transferred to a large separatory funnel and shaken vigorously. The acids were then extracted with Skellysolve F, washed with distilled water, dried over anhydrous sodium sulfate, filtered, and the solvent removed by distillation under reduced pressure. The ethylene glycol phase was extracted with Skellysolve F and the Skellysolve

fraction treated as before. The two fractions were then combined and refrigerated at 5° C. for 48 hours to allow crystallization of the solid acids. The solid acids thus formed were filtered on a Buchner funnel and recrystallized twice from each of the following solvents: Skellysolve F, 95 percent ethyl alcohol and diethyl ether at -17° C. This yielded $\Delta^{10,12}$ octadecadienoic acid of about 98 percent purity.

Preparation of Diazomethane. A mixture of 40 ml of ether and 12 ml of 40 percent aqueous potassium hydroxide were placed in a 250 ml Erlenmeyer flask and cooled to 3-5° C. in an ice-salt bath. This mixture was continuously stirred mechanically as 3.45 g of N-nitrosomethylurea were added in small portions as rapidly as the crystals dissolved. The yellow ethereal solution of diazomethane was separated from the aqueous fraction by means of a separatory funnel and the ethereal solution dried by allowing it to stand overnight over anhydrous potassium hydroxide pellets in the cold (4-6° C).

Preparation of the Methyl Ester of $\Delta^{10,12}$ Octadecadienoic Acid. Approximately one-half of the solution of diazomethane in ether was added from a burrette to a solution of 2.7 g of the conjugated linoleic acid in diethyl ether. Nitrogen gas was evolved and the methyl ester was obtained by removing the ether by distillation under reduced pressure.

Determination of Constants

Peroxide Value. The determination of the peroxide value
was carried out by the method of Wheeler (42). Approximately
100 mg of the sample was weighed into a 125 ml Erlenmeyer flask
and dissolved in 5 ml of a mixture of glacial acetic acid and
chloroform (2:1 by volume). One ml of a saturated solution of
potassium iodide was then added and the flask rotated slowly for
one minute. Five ml of water were then added and the liberated
iodine titrated with 0.01 N sodium thiosulfate solution, using
starch solution as the indicator. The peroxide value in milli-
moles of peroxide oxygen per kilogram of sample was then calcu-
lated by use of the formula $P = \dfrac{V \times N \times \frac{1}{2} \times 1000}{W}$ where V is
the volume of sodium thiosulfate expressed in ml, and of nor-
mality N, used in the titration of weight W, in grams, of the
sample.

Spectral Determinations

Spectrophotometric Analysis. The ultraviolet absorption of
the samples was determined by means of a Beckmann D. U. Quartz
Spectrophotometer. Samples of approximately 100 mg were weighed
into a 100 ml volumetric flask, dissolved in absolute ethyl al-
cohol and the flask filled to the mark. The absorption at 2320 A
was then determined, diluting if necessary to keep the absorption
in the region of maximum instrumental accuracy. The scale read-
ings were then calculated in terms of the specific absorption, α,

by the method of Kraybill (23), (log I_o/I)/Cl = α where C is the
concentration of the sample expressed in grams per liter and 1
is the length of the cell, in this case 1 cm.

Infrared Absorption Spectra. The infrared absorption spectra of the samples was determined by means of a Perkin-Elmer
Infrared Spectrometer, model 12B, using rock salt optics and
equipped with an automatic wave-length drive and a Leeds and
Northrup Speedomax recorder. The cell thicknesses used were
0.08 mm for the $\Delta^{10,12}$ methyl linoleate and 0.05 mm in the
case of the $\Delta^{9,12}$ methyl linoleate. These particular cell
thicknesses were chosen because they apparently gave the best
absorption on the unoxidized samples.

Experimental Procedure. The oxidation was carried out by
bubbling dried air through the compound contained in a small
test tube suspended in a thermostatically controlled water bath
maintained at 30° C. At various recorded time intervals samples
were withdrawn for a determination of the infrared absorption
spectra and the corresponding peroxide values in the manner
described. Two determinations were made for each sample, the
first with the cell in place in the instrument and the second
with no cell to eliminate errors in the absorption due to atmospheric carbon dioxide and water vapor.

For comparative purposes the absorption spectra of cyclohexene and tetralin were determined both before and after oxidation in the described manner. In addition, mixtures of the
two methyl linoleates were made up for a determination of the

infrared absorption and the ultraviolet absorption at 2320 A. The region of 2320 A is known to be the region in which conjugated double bonds absorb strongly. The percent conjugation could thus be determined by multiplying the specific absorption by the factor 1.095. This factor was determined on the basis of a theoretical absorption of 115 for the pure acid and the relationship between the molecular weights of the acid and ester. These were then used to determine the degree of conjugation from the corresponding infrared absorption band for the various samples withdrawn during the oxidation.

RESULTS

The absorption spectra of the two methyl linoleates preceeding oxidation are shown in Fig. 1. These are seen to have the absorption bands which would be expected of compounds having their respective structures. The essential difference in the two spectra is in the absorption band at 10.15 μ where the Δ 10,12 methyl linoleate absorbs strongly due to the conjugation. This same band is also present in the unconjugated compound but to a much lesser extent, showing that a small amount of conjugated material is present. The other apparent differences in the absorption are due to the differences in the thickness of the cells used.

The preliminary experiments with cyclohexene and tetralin and also with the conjugated and unconjugated esters indicated a gradual change in the amount of absorption in the region of

2.9 μ, the region in which absorption is generally attributed to bonded OH groups, in all cases except that of the conjugated ester. The absorption spectra of the esters of the conjugated and unconjugated acids gave the same result, as shown in Fig. 2, the lower of the curves represents the unoxidized material.

As the oxidation time increased, there was also an increase in the amount of absorption at 10.15 μ in the case of the unconjugated methyl ester (Fig. 3). The band remained constant for the conjugated ester. As a result of this increase, mixtures of the two esters were made up and the percent of conjugated material present determined by the ultraviolet absorption at 2320 A. The infrared absorption spectra of these samples showed an increase in the degree of absorption at 10.15 μ with increasing conjugation as shown in Fig. 4.

Still another change was noted in the oxidation of the unconjugated ester which was not found in the conjugated material. This was a gradual decrease in the amount of absorption at 13.82 μ with increasing oxidation time as shown in Fig. 5. This change is not directly connected with the increase in the amount of conjugation as the mixtures previously described showed no such change, indicating therefore, that this is a result of the oxidation.

The results of the determinations of peroxide values made during the oxidation are shown in Fig. 7. The peroxide value of the unconjugated methyl linoleate is seen to rise rather rapidly with oxidation time while that for the unconjugated ester rises only very slowly.
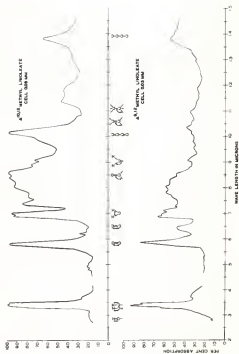
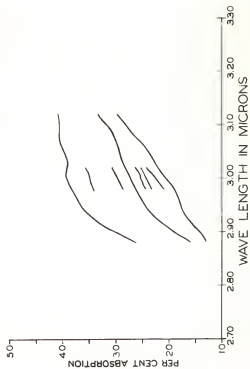Fig. 1. The absorption spectra of the unoxidized esters.

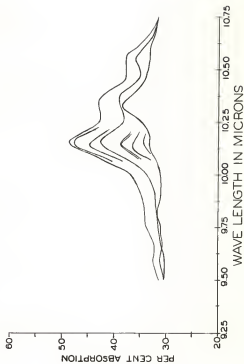Fig. 2.   The increase in absorption at 2.9 μ region during autoxidation of the unconjugated ester.

Fig. 3. The increase in absorption at 10.15μ during
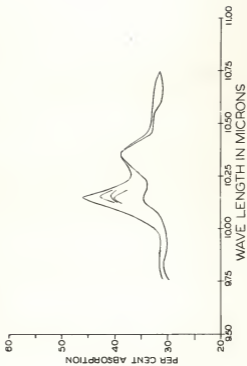autoxidation of the unconjugated ester.

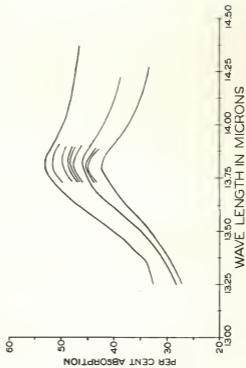Fig. 4. The increase in absorption at 10.15 μ with increasing conjugation of prepared mixtures.

Fig. 5. The decrease in absorption at 13.82 μ during
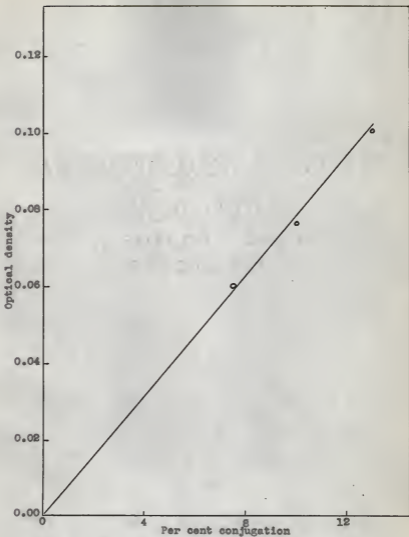autoxidation of the unconjugated ester.

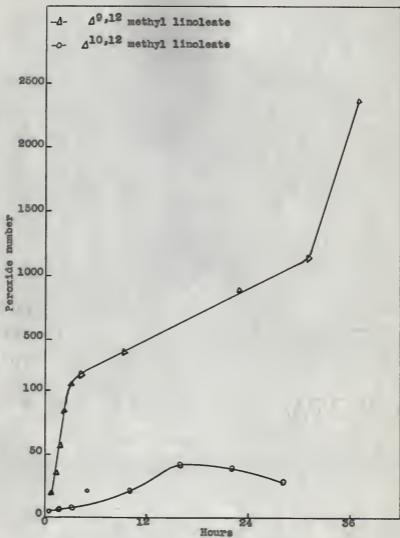Fig. 6. Changes in optical density at 10.15 μ with increasing conjugation of prepared mixtures.
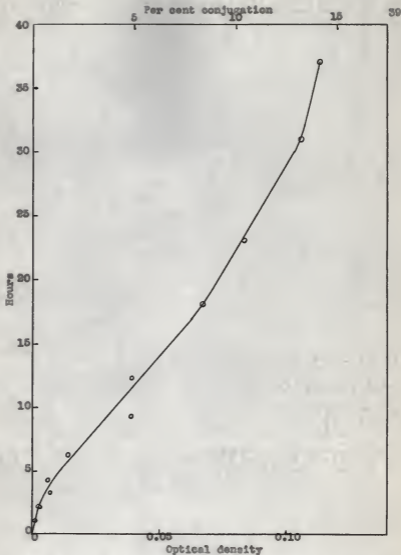
Fig. 7. Peroxide numbers during autoxidation.

Fig. 8. Changes in optical density and per cent conjugation at 10.15 μ with autoxidation time.
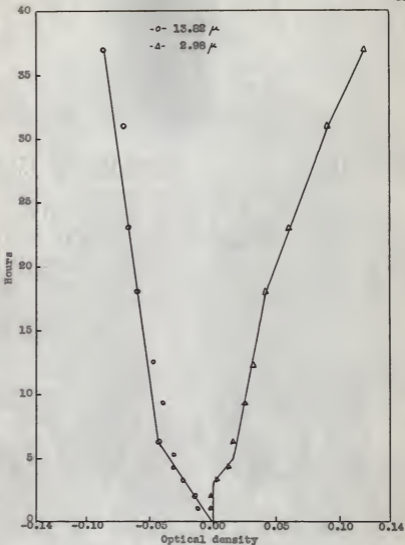
Fig. 9. Changes in optical density at 2.98 μ and 13.82 μ with autoxidation time.

DISCUSSION

There are four functionally distinct groups containing the
OH linkage which presumably could be formed as a result of the
autoxidation process and thus account for the increase in the
absorption at 2.9μ. These groups are the hydroperoxide group,
the OH of water, the simple alcoholic OH and the carboxylic OH.
However, since the reaction conditions were very mild, the
likelihood of formation of a carboxylic OH is very slight, at
least in the early stages of the reaction. The presence of
peroxide oxygen leads to the theory of the formation of a hydro-
peroxide group as one of the primary steps in the autoxidation
process rather than the alcoholic OH since this group would not
contain peroxidic oxygen. Alcohols are possible products of
secondary reactions as shown by Farmer (15) so that this possi-
bility cannot be entirely discredited. Later reaction stages
may result in the release of water by a condensation of the
hydroxy compounds to form polymers so that all of these groups
may be accounted for by the autoxidation mechanisms advanced.
On the basis of this, it therefore seems most likely that the
peroxides formed in the initial stages of the autoxidation re-
action are essentially all hydroperoxides which is in agreement
with the theory advanced by Farmer (16). There is no evidence
to indicate that the initial step is the addition of oxygen to
the double bond although, as Farmer pointed out (16), the actual
amount of addition necessary to start the reaction chains would

be insignificant and probably could not be detected.

On the other hand, there is no increase in the amount of absorption at 2.9 μ over the 48.5 hour oxidation period of the conjugated methyl linoleate. The peroxide value does increase slightly with increasing oxidation time, but comparison with the unconjugated ester indicates that the amount of peroxide oxygen present is probably so small that it could not be detected in the absorption spectra. The mechanisms involved in the autoxidation of these two esters is evidently of a different nature.

The increase in absorption at 10.15 μ in the spectra of the unconjugated ester indicates an increase in conjugation occurring as a result of the autoxidation reaction. This band also did not change in the autoxidation of the conjugated methyl linoleate. From the prepared mixtures it was calculated that the actual amount of conjugation occurring in the unconjugated ester during autoxidation increased to a value of about 17 percent after background corrections were applied by conversion of the absorption to optical densities. This increase in conjugation is in agreement with the hydroperoxide theory of autoxidation in which diolefins of the methylene-interrupted type form a free radical capable of resonance between two conjugated isomeric structures leading to the formation of isomeric hydroperoxides. This free radical is formed in both the theory which involves an initial addition of oxygen at the double bond and that of initial detachment of hydrogen in the α-position with respect to the double bond.

The third change in the absorption spectra was a decrease in the absorption at 13.82 μ and this again was found in the unconjugated ester but not in the conjugated compound. It was at first believed that this was in some way connected with the absorption at 10.15 μ since both of these involve carbon to carbon linkages. The prepared mixtures in which the amount of conjugated material was varied exhibited a constant absorption in this region indicating that the decrease in absorption is a result of the autoxidation process. This absorption band generally is attributed to straight chain carbon compounds in which the chain length is greater than four. Since the number of carbon to carbon linkages or the type of these linkages is not altered merely by a conversion of an unconjugated to a conjugated diene, this decrease is due apparently to chain scission reactions. It has been stated (15) that the formation of hydroperoxides may lead to scission between an ethylenic bond and an α-carbon atom, and also that such scission might occur during the original autoxidation by momentary formation and immediate decomposition of cyclic peroxides. Due to the evidence in support of the hydroperoxide theory and its incompatability with the theory of cyclic peroxide formation in the early reaction stages, it seems more likely that the decrease noted is due to scission reactions of the former type.

It seems, therefore, in view of the results obtained, that the reaction of the unconjugated methyl linoleate with oxygen results in the formation of a free radical which may then become

conjugated and lead to the formation of isomeric hydroperoxides.
A second free radical may be formed during this process, thus ac-
counting for the chain reaction. The hydroperoxide formed may
undergo secondary reactions leading to a wide variety of end
products. The mechanism by which the conjugated and unconju-
gated esters undergo autoxidation apparently is different as
evidenced by the changes in the absorption spectrum of the un-
conjugated ester and the constancy of the spectrum of the con-
jugated ester during the autoxidation periods of this investi-
gation. It seems possible that the oxidation of the conjugated
ester may result in a polymerization of this compound by a more
direct mechanism than is the case with the unconjugated ester.

SUMMARY

The autoxidation of the conjugated and unconjugated esters
of linoleic acid was studied by means of infrared absorption
spectra and a correlation with the theories of autoxidation at-
tempted.

The unconjugated material is shown to undergo autoxidation
in a different manner than that of the conjugated material as
evidenced by a constancy of absorption during the autoxidation
of the conjugated ester and changes at 2.9, 10.15, and 13.82 μ
in the case of the unconjugated ester. These changes may be
explained on the basis of the hydroperoxide theory of autoxi-
dation very satisfactorily.

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