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CONTRIBUTIONS TO SYMPOSIUM ON BREAKDOWN OF RUBBER.

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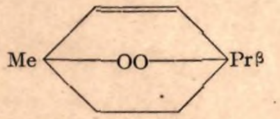
Oxidative Breakdown of Rubber

BY E. H. FARMER

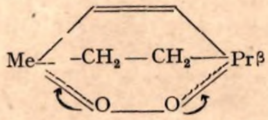
Scope of survey.—Autoxidation in the case of vegetable and animal drying oil causes solidification, hardening, and toughening of the original olefinic material, whereas absorption of oxygen in the case of natural rubber normally causes softening, with loss of strength and elasticity. Various synthetic rubbers appear to take up an intermediate position between the drying oils and natural rubber, but with none of the rubbers does autoxidation represent a quite simple phenomenon, leading uniformly to softening as opposed to toughening. The peroxidation process which forms the basis of autoxidation leads in general to two quite opposite effects, *viz.* to oxidative chain-scission (degradation) and to molecule-linking (polymerisation or oxygen-vulcanisation), and it seems logical to associate the former with the softening of olefinic materials and the latter with their toughening or oxygen-vulcanisation. What, however, is far from clear is the cause of onset under given conditions of softening on the one hand or oxygen-vulcanisation on the other, and the precise nature of the molecular changes which underlie the two phenomena. At present even qualitative information concerning the intricate course of autoxidative reactions amongst olefinic materials is far from abundant, and the necessary kinetic evidence which must both set the final seal of credibility on those chemical explanations which careful experimentation indicates to be sound, and in difficult cases discriminate between alternative possible explanations, is only beginning to become available. The most useful contribution therefore, which can be made at the moment is to clarify in terms of organic structure and reactions the basic issues involved, and to show how far existing chemical information provides certain or possible explanations of the broad lines of autoxidative molecular breakdown (and its converse) as it is encountered among rubbers.

Peroxidation the Pre-requisite of Autoxidative Molecular Change.—There is ever-growing evidence to show that the molecules of oxygen which are absorbed by olefinic substances are incorporated as a whole to form organic peroxides or peroxido-radicals. These peroxidic products may be so unstable as to have only a brief existence under the reaction conditions employed, in which case they will be represented in the reaction mixture by their secondary (decomposition or transformation) products, or alternatively they may be composed of molecules possessing considerable inherent stability, in which case they will survive in large measure to the end of the oxidation process and well beyond. Where the stability of the peroxido-groups is high the introduction of the latter must of course have a direct and specific effect, more or less permanent, and generally speaking tending towards hardening, on the physical properties of the autoxidised material; but where it is low, as happens generally with the various rubbers, the really important feature in relation to the quality, or physical properties of the autoxidised material, is not so much the introduction of the groups (although the number of these is connected with the degree of autoxidative change), as the manner of their decomposition. The decomposition of peroxides may in general be envisaged as arising from thermal, photo-chemical or from chemical causes, and although short-wave light is possibly an important degradative influence in certain circumstances, the most usual mode of peroxide-breakdown encountered in the normal (non-chemical) manipulation of rubbers is likely to be the thermally-promoted type. Therefore in order to be able to account for the changes in the properties of autoxidised rubber it is necessary to understand the courses of thermal breakdown of peroxides of appropriate types. Unfortunately knowledge of the fate of peroxides and of the use that is made of the chemical energy of which they are rich repositories must be based on studies of isolable (and therefore relatively stable) compounds, and deductions derived from these favourable cases applied to the more ephemeral examples. Consideration of the autoxidation process will be made easier if the more important characteristics of peroxides known to be formed by the action of oxygen on olefinic materials are reviewed.

Peroxide Types.—The most stable peroxide type is that represented by ascaridol, a cyclic peroxide (I) which occurs naturally in *Chenopodium* oil. This compound is sufficiently stable both to permit of its rectification at 10–15 mm. pressure, and to resist anything like complete reaction by the reducing agents which are ordinarily used in peroxide determination. The high stability probably depends on the possession of a semi-aromatic constitution to be represented by (II).

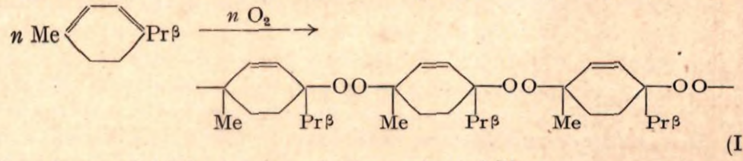


(I)



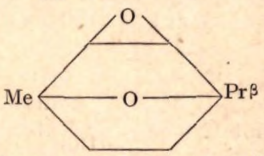
(II)

If the artificial preparation of this peroxide be attempted by reacting on the corresponding conjugated hydrocarbon diene (α-terpinene) with oxygen there results a low molecular polymeric peroxide which is doubtless a polymer-mixture containing but little monomer. This polymeric peroxide is almost certainly constituted in the main as in (III), the free ends of the dimer, trimer, etc. chains being joined to form ringed structures (Bodendorf, *Annalen*, 1933, **271**, 1), or more probably stabilised either by formation of terminal hydroperoxide groups or by disproportionation.



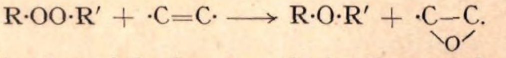
(III)

The observed high degree of thermal stability at temperatures below 100° probably arises from the presence of a semi-conjugated chain $-\mathrm{C}=\mathrm{C}-\mathrm{C}\cdots\overset{\frown}{\mathrm{O}}\cdot\overset{\frown}{\mathrm{O}}\cdots\mathrm{C}-\mathrm{C}=\mathrm{C}$. When the monomeric peroxide (I) is heated in inert solvents to 150° it decomposes fairly smoothly without explosion to give the dioxide (IV) (Thoms and Dobke, *Arch. Pharm. u. Ber. Deutsch. Pharm. Ges.*, 1930, **268**, 128).



(IV)

Exactly how the transformation from peroxide to oxide occurs, and especially whether it occurs by intramolecular means is still unknown. The most usual path of thermal decomposition of peroxide groups appears to involve scission between the peroxidic oxygen atoms (as also is the case with catalytic hydrogenation and chemical reduction processes), but whether the diradical which would be formed by such inter-oxygen scission occurring in (I) could yield (IV) by arrangement is somewhat uncertain; on the other hand bi-molecular reaction of the type:



$$\mathrm{R{\cdot}OO{\cdot}R'} + \cdot\mathrm{C}{=}\mathrm{C}\cdot \longrightarrow \mathrm{R{\cdot}O{\cdot}R'} + \cdot\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C}{-}\mathrm{C}}.$$

seems doubtful in view of the fact that the heating together of ascaridol and cyclohexene at 150° has not been found to yield recognisable amounts of cyclohexene oxide (Farmer, unpublished work).

There is little evidence available as to the detailed way in which the polymeric peroxides decompose thermally. Like most organic peroxides the polymers explode when heated above 130°, but under suitable conditions of dilution they can be decomposed quietly by thermal or reductive treatment. Much information regarding constitution can be derived by their reduction—especially reduction by catalytic hydrogenation, but even under the mild conditions of catalytic hydrogenation the peroxide does not usually escape some considerable measure of catalysed non-reductive breakdown or of a re-distribution of peroxidic oxygen which has been termed by Bodendorf isomerisation. Probably these side reactions are greatly accelerated by metallic surfaces or by reagent ions,* but it is unlikely that the so-called isomerisation involves smooth oxygen-redistribution without the occurrence of some degree of

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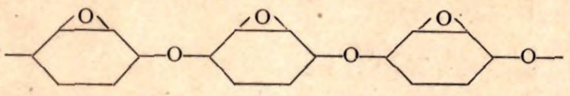
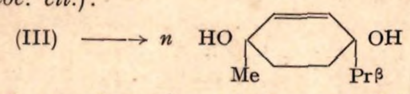
* Sodium sulphite often gives disappointing results as a reducing agent owing to the promotion of the side reactions.

oxidative scission. It may be noted that the strict polymeric analogue of the change I ——→ IV would yield polyether—polyoxide chains



(V)

Experiment shows that the three cyclic conjugated dienes α-terpinene, α-phellandrene and cyclohexadiene all behave alike in giving low-molecular polymeric peroxides on oxidation, and these latter in accordance with a constitution of the type shown in (III) give on catalytic hydrogenation considerable yields of the expected dihydroxylated monomers (Bodendorf, *loc. cit.*):



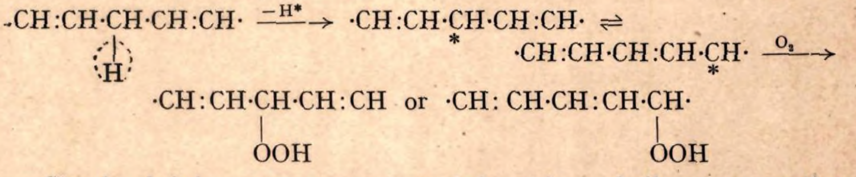
but no smooth transformation of the type III→V has ever yet been recognised.

In passing from cyclic to open-chain diolefinic materials of conjugated structure a variant of the above-described behaviour is encountered. The peroxides formed by autoxidation are again mainly of stable polymeric 1: 4-type, doubtless containing the basic chain $(\cdot C\cdot C:C\cdot C\cdot OO\cdot)_n$ with joined or otherwise stabilised ends, but a proportion of them (up to 20 per cent.) undergoes oxidative scission—scission which may occur wholly spontaneously and unavoidably during the absorption of oxygen, or otherwise may (apparently) first occur in the presence of metallic catalysts during attempted hydrogenation of the peroxides. Sorbic ester, $CH_2\cdot CH:CH\cdot CH:CH\cdot CO_2Me$, and αδ-diphenylbutadiene CHPh: CH·CH: CHPh, are examples of the spontaneous unavoidable type (Farmer and Sundralingam, in press) and βγ-dimethylbutadiene and isoprene of the catalysed type. According to Bodendorf (*loc. cit.*) the two last dienes give (maximally) 0·47 and 0·32 mol. respectively of formaldehyde or formic acid by the reductive treatment. The oxidative scission accompanies, the terminal peroxidation of the conjugated diene units, so that the question arises as to whether there are in fact two modes of peroxidation to be accounted for—a 1: 2- (or 3: 4)- and a 1: 4- type—or whether such chain-scission as occurs is merely due to spontaneous (i.e. thermal) or catalysed degradation of the 1: 4- peoxides in somewhat the same way that thermal decomposition of cyclohexene-3-hydroperoxide can yield open-chain derivatives by scission at the double bond. Against the latter conclusion, however, stands the consideration that if some of the relatively stable 1: 4-peroxide molecules are deemed to undergo spontaneous scission at 1: 2-positions (e.g. at *a* in $\cdot C\underset{a}{-\vdots-}C:C-C\cdot OO\cdot$) it is then necessary to accept the implication that the bonds so severed are saturated ones. In the carefully worked-out example of the triolefinic elaeostearic ester, $C_4H_9\cdot CH:CH)_3\cdot(CH_2)_7\cdot CO_2Me$ (Sundralingam, in the press), in which but little redistribution of peroxidic oxygen occurs during catalytic hydrogenation of the peroxide, the amount of 1: 4-peroxidation as deduced from the nature of the reduction products is high; nevertheless it has not been found possible to effect peroxidation without the appearance of some scission, and this scission apparently occurs not within a cyclic peroxido-system, but at one or other of the outer double bonds of the original triene system—i.e. at *a* in

$$\cdot\mathrm{C}\underset{a}{=\!\vdots\!=}\mathrm{C\cdot C(OO-)\cdot C:C\cdot C(OO-)\cdot}\quad\text{or}\quad\mathrm{\cdot C(OO-)\cdot C:C\cdot C(OO-)\cdot C}\underset{a}{=\!\vdots\!=}\mathrm{C}\cdot$$

A return to the question of one-mode or two-mode peroxidation will be made later.

Passing next to substances (e.g. animal and vegetable drying oils) containing the unconjugated olefinic systems $\cdot\mathrm{C:C\cdot C\cdot C:C}.$, $\cdot\mathrm{C:C\cdot C\cdot C:C\cdot C\cdot C:C}\cdot$, etc., the most striking observation is that the onset of peroxidation is accompanied by extensive re-arrangement of the double bond system to produce conjugated forms. Doubtless some degree of chain-scission accompanies the peroxidation, which at the beginning is of hydroperoxide type; although later, as perhaps might be expected in view of the production of conjugated forms, polymeric oxidation ensues. The chemical character of the peroxidation products suggests that the effective peroxidising actions (but not necessarily the initiatory steps) occurs at the reactive methylene groups between the double bonds by loss of hydrogen atoms and this enables the resonating radical residues to assume more stable conjugated forms (Farmer, Koch and Sutton, *J. Chem. Soc.*, 1943, 541)



$$\cdot\mathrm{CH:CH\cdot}\underset{\mathrm{H}}{\mathrm{CH}}\mathrm{\cdot CH:CH}\cdot\xrightarrow{-\mathrm{H}^*}\cdot\mathrm{CH:CH\cdot}\underset{*}{\mathrm{CH}}\mathrm{\cdot CH:CH}\cdot\rightleftharpoons\cdot\mathrm{CH:CH\cdot CH:CH\cdot}\underset{*}{\mathrm{CH}}\cdot\xrightarrow{\mathrm{O_2}}$$

$$\cdot\mathrm{CH:CH\cdot}\underset{\mathrm{OOH}}{\mathrm{CH}}\mathrm{\cdot CH:CH}\quad\text{or}\quad\cdot\mathrm{CH:CH\cdot CH:CH\cdot}\underset{\mathrm{OOH}}{\mathrm{CH}}\cdot$$

Simple olefinic systems appear to behave in a similar manner, the peroxides again being of α-methylenic hydroperoxidic type, and the resonating 3-carbon systems, which are formed by detachment of hydrogen atoms probably cause isomerism but not conjugation:

$$\cdot\mathrm{CH_2\cdot CH:CH}\cdot\xrightarrow{-\mathrm{H}}\cdot\underset{*}{\mathrm{CH}}\mathrm{\cdot CH:CH}\cdot\rightleftharpoons\cdot\mathrm{CH:CH\cdot}\underset{*}{\mathrm{CH}}\cdot\xrightarrow[\mathrm{H}]{\mathrm{O_2}}$$

$$\cdot\mathrm{CH(OOH)\cdot CH:CH}\cdot\quad\text{and}\quad\cdot\mathrm{CH:CH\cdot CH(OOH)}.$$

These simple systems are interesting in view of their relation to, but differentiation from, those occurring in natural and in polybutadiene synthetic rubbers, for in these materials the double bonds are separated from one another by pairs of methylene groups. Absorption of oxygen leads to hydroperoxidation but any effective movement towards the production of conjugated peroxides would necessitate two successive double bond shifts, which could only be promoted by successive attacks by oxygen at the same methylenic pair:

$$\cdot\mathrm{Me:CH\cdot CH_2\cdot CH_2\cdot CMe:CH}\cdot\longrightarrow\cdot\mathrm{CMe:CH\cdot CH_2\cdot CH:CMe\cdot CH(OOH)}\longrightarrow$$

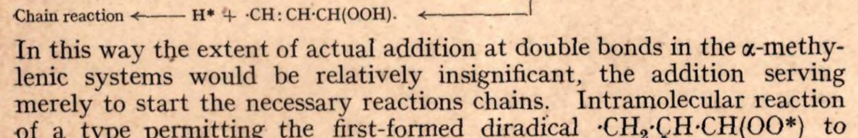
$$\cdot\mathrm{CMe:CH\cdot CH:CMe(OOH)\cdot CH(OOH)}\cdot\quad\text{or}$$

$$\cdot\mathrm{CMe(OOH)\cdot CH:CH\cdot CH:CMe\cdot CH(OOH)}.$$

In practice, conjugation is not realised to any appreciable extent, any more than is the corresponding isomerisation of natural rubber to conjugated forms by the action of boiling, strong alkali, although it can occur extensively with the systems

$$\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot,\quad \cdot CH:CH\cdot CH_2\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot \text{ etc.}$$

The Initiation of Oxidative Attack.—Three facts stand out in connection with the problem of how oxidative attack is initiated in mono-olefinic and rubber-like systems. The first of these is that any detachment of an α-methylenic hydrogen atom to leave an active 3-carbon radical, $\cdot\underset{*}{C}H\cdot CH:CH\cdot$, requires the expenditure of 80 k. cal. of energy, which must be supplied from some source; the second is that peroxidation (whether photochemically or thermally promoted) is substantially pressure-independent and autocatalytic; and the third is that experiment shows that in conjugated compounds, even those in which the diene or polymer systems are flanked by α-methylene groups (e.g. sorbic and elaeostearic esters), peroxidation affects only the double bonds, thus leaving the α-methylene groups intact. Since, therefore, it is clear (*a*) that molecular oxygen is intrinsically quite able to begin its attack at a double bond, presumably by adding at one end of it, (*b*) that the monomeric peroxides of simple olefins and of unconjugated polyolefins are undoubtedly α-methylenic hydroperoxides, (c) that the above-mentioned very high expenditure of energy at the outset of reaction, which is essential if the first step is deemed to be the radical dissociation of C–H, is greatly diminished if the oxygen begins its attack in some few of the olefin molecules by adding at double bonds and thereafter continues the attack by means of chain reactions, and (*d*) that the oxidation has none of the features of ionic reactivity, it then appears most sound and reasonable to postulate tentatively universal initiation of autoxidative attack in all kinds of olefinic systems by additive reaction occurring at double bond centres, and to formulate the α-methylenic reaction for unconjugated olefins by the intermolecular scheme:



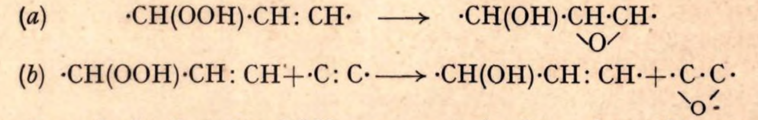
$$\cdot CH_2\cdot CH:CH\cdot \xrightarrow{O_2} CH\cdot{}_2\overset{*}{C}H\cdot CH(OO^*)\cdot \xrightarrow{\cdot CH_2\cdot CH:CH\cdot} \cdot CH_2\cdot\overset{*}{C}H\cdot CH(OOH) + \cdot\overset{*}{C}H\cdot CH\cdot CH\cdot \xrightarrow{O_2} \cdot CH(OO^*)\cdot CH:CH\cdot \downarrow \text{α-Methylenic chain reaction}$$

$$\text{α-Methylenic chain reaction} \longleftarrow \cdot\underset{*}{C}H\cdot CH:CH\cdot + \cdot CH(OOH)\cdot CH_2\cdot CH_2\cdot \xleftarrow{\cdot CH_2\cdot CH:CH\cdot}$$

$$\text{Chain reaction} \longleftarrow H^* + \cdot CH:CH\cdot CH(OOH). \longleftarrow$$

In this way the extent of actual addition at double bonds in the α-methylenic systems would be relatively insignificant, the addition serving merely to start the necessary reactions chains. Intramolecular reaction of a type permitting the first-formed diradical $\cdot CH_2\cdot\underset{*}{C}H\cdot CH(OO^*)$ to become stabilised by removal of hydrogen from the adjacent α-methylene group [$\longrightarrow \cdot CH:CH\cdot CH(OOH)\cdot$] is highly unlikely since it would not propagate chain reactions.

The Scission Problem.—Organic hydroperoxides, R·OOH, are, like hydrogen peroxide, effective oxidising agents for olefinic materials, especially when their decomposition is thermally or catalytically facilitated. The atom of active oxygen in each molecule is applied to the oxidation of susceptible materials within reach. When, however, the radical R is unsaturated, it seems possible that the oxidising capacity of the ·OO· groups may be applied to the oxygenation of unsaturated centres in the same or near-by molecules in some regulated or standard way which is economical in oxygen. Thus the author has earlier suggested that the secondary reactions of olefinic hydroperoxides may commonly involve one or other of the changes (respectively intra- and inter-molecular):

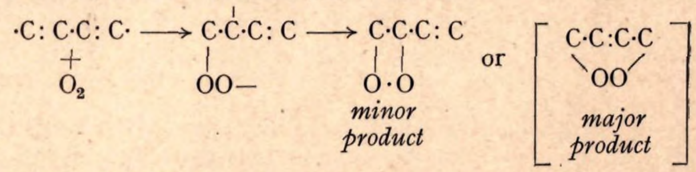


$$(a)\quad \cdot\mathrm{CH(OOH)\cdot CH:CH\cdot} \longrightarrow \cdot\mathrm{CH(OH)\cdot}\underbrace{\mathrm{CH\cdot CH}}_{\mathrm{O}}\cdot$$

$$(b)\quad \cdot\mathrm{CH(OOH)\cdot CH:CH}+\cdot\mathrm{C:C}\cdot \longrightarrow \cdot\mathrm{CH(OH)\cdot CH:CH}\cdot+\cdot\underbrace{\mathrm{C\cdot C}}_{\mathrm{O}}\cdot$$

There is no doubt that the ·OOH groups pass in the main on decomposition to ·OH groups and that some roughly comparable number of double bonds become simultaneously oxygenated (saturated) and some few completely severed. Three facts, however, militate against ready acceptance of a general scheme of double bond scissions which starts from the peroxido-olefin and passes by decomposition of the ·OOH group through the epoxy-compound to ultimate chain-severance. In the first place epoxy groups are saturated in character and when once they are formed normally display a high degree of resistance to further oxidation;* at the same time experiments with rubber show that from a dozen to a score or so of molecules of oxygen (ample for a haphazard scheme of attack) may be absorbed for each complete scission effected. Secondly the scission sets in quite unpreventably during the absorption of oxygen by natural rubber (or by shorter-chain polyisoprenes) right at the outset of reaction, and seems to occur with such extraordinary facility that a very direct mechanism might well be suspected. It is this scission which is responsible for the amazing fall in the molecular weight of natural rubber as oxygen attacks it (from 350,000 to 80,000 during absorption of < 1 per cent. of O_2), and indeed for the characteristic softening and perishing of the rubber. Thirdly, there is the undoubted and compelling fact that a considerable amount of facile and unpreventable scission ordinarily occurs at the $\beta\gamma$-double bond of sorbic ester and of $\alpha\delta$-diphenylbutadiene in addition to the more widespread attachment of molecular oxygen at the terminals of the conjugated diene system in each case.

As the 1:4-peroxidation of the conjugated dienes is found to involve the addition of oxygen at the double bond system the reaction presumably starts at one end of one double bond and may conceivably succeed in some degree and in some examples in linking up, at least momentarily, with the other end of the double bond attacked.



Such a 1:2-peroxide if it were sufficiently stable to have more than momentary existence could hardly fail to give the corresponding 1:2-diol on reduction, but in no single one of numerous examples studied has

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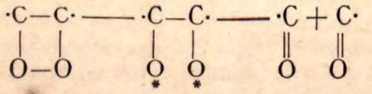
* Yields of epoxide up to 15 per cent. survive in the peroxide-catalysed autoxidation of oleic or elaidic and at 70°, but little or none appears to be formed in the photo-oxidation of methyl oleate at 35°.

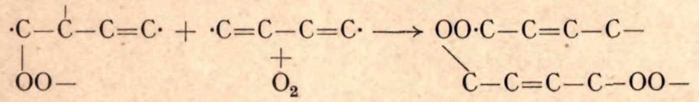
search for a 1:2- diol been successful, although αδ-diphenylbutadiene gives a small yield of the 1:2- epoxide.* Any successful 1:2- linking of oxygen which may occur would thus appear to be of the most transient character, and in so far as it occurs doubtless undergoes immediate ring-scission followed by scission of the active diradical to give the corresponding aldehyde or keto-fragments:



$$\begin{array}{c}\cdot\mathrm{C{-}C}\cdot\\ |\quad|\\ \mathrm{O{-}O}\end{array} \longrightarrow \begin{array}{c}\cdot\mathrm{C{-}C}\cdot\\ |\quad|\\ \underset{*}{\mathrm{O}}\ \underset{*}{\mathrm{O}}\end{array} \longrightarrow \begin{array}{c}\cdot\mathrm{C}+\mathrm{C}\cdot\\ \|\quad\ \|\\ \mathrm{O}\quad\ \mathrm{O}\end{array}$$

Such a direct mechanism would be the most economical possible in oxygen, and would explain the apparently utter unpreventability of scission in certain examples where relatively stable 1:4- peroxides form the main product. In the case of mono-olefins and unconjugated polyoleans such a scission mechanism might run side by side with normal peroxidation as formulated above, and the degree of its successful occurrence might well be affected by temperature conditions. On the other hand it may quite well be that 1:2-peroxidation has no existence in fact, and that to interpret the experimental observations it is necessary to distinguish clearly between two phenomena, viz. (*a*) the purely thermal decomposition of peroxidised diene or olefin systems at *a* and *b* in $\cdot\mathrm{O}\underset{a}{\vdots}\mathrm{O{\cdot}CH{\cdot}}\underset{b}{\vdots}\mathrm{CH{:}CH{\cdot}\dot{C}H}\cdot$ or $\cdot\mathrm{CH(O}\underset{a}{\vdots}\mathrm{OH)}\underset{b}{\vdots}\mathrm{CH{:}CH}$, and (*b*) the purely oxidative scission of a double bond in a diene or olefin system by the action of external decomposing peroxido-groups as though by the action of an added reagent such as permanganate. Since active radicals appear generally to be immediate products of the thermal decomposition of peroxides (decomposition arising at the thermally sensitive ·OOH or ·OO· groups of these) it is perhaps not surprising that the ultimately isolable products of autoxidations carried out at temperatures around or above the decomposition points of the peroxides tend to be a good deal different from those obtained from the same materials at lower temperatures.

The Polymeric Tendency in Peroxide Formation.—As the product obtained by the addition of oxygen at one end of an olefinic double bond could achieve stabilisation by intermolecular as well as by intramolecular reaction it is not surprising that there is a strong polymeric tendency in peroxide formation.



$$\begin{array}{l}\cdot\mathrm{C{-}\overset{|}{C}{-}C{=}C}\cdot\\ |\\ \mathrm{OO}-\end{array} + \begin{array}{c}\cdot\mathrm{C{=}C{-}C{=}C}\cdot\\ +\\ \mathrm{O_2}\end{array} \longrightarrow \begin{array}{l}\mathrm{OO{\cdot}C{-}C{=}C{-}C}-\\ \diagdown\\ \quad\mathrm{C{-}C{=}C{-}C{-}OO}-\end{array}$$

All conjugated di- and tri- olefinic olefins which have so far been investigated appear to give as the main product mixtures of polymeric peroxides ranging from dimeric to hexameric or octameric complexity; moreover the yields of the simple dihydroxylated hydrogenation products obtained from these peroxides in favourable instances appear almost too good to

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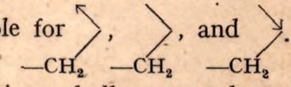
* The autoxidation of ethylene at higher temperatures yields ethylene oxide in addition to the expected scission product formaldehyde. This may conceivably arise by decomposition of the di-radical $*\mathrm{CH_2{-}CH_2{-}O{-}}\vdots\mathrm{{-}O}*$.

be accounted for by any means of stabilisation of the ends of the polymeric chains other than by hydroperoxidation or their direct union. Thus stable dimeric isoprene would be represented by

$$HOO\cdot[C_5H_8\cdot OO\cdot C_5H_8\cdot OO]\cdot H \quad \text{or} \quad \underbrace{C_5H_8\cdot OO\cdot C_5H_8\cdot OO}$$

This polymeric tendency does not disappear in the case of mono-olefins and unconjugated di- and poly-olefins, and in fact it seems to be general. Even in the characteristic examples of hydroperoxide-formation afforded by the cyclohexenes, there is always a polymeric fraction, and the yield of the fraction is likely to depend considerably on the constitution of the olefin and especially on the atoms or groups attached to the ethylenic carbon atoms. The mechanism by which the substituents affect the polymeric tendency may be connected with their efficiency is stabilising the electrical condition of the radical centre to which they are attached,† so that the diradical $\begin{matrix}R\\R'\end{matrix}\!>\!\underset{*}{C}-C(OO^*)\!<\!\begin{matrix}R''\\R'''\end{matrix}$ will be most stable (and therefore sufficiently long-lived to be able to give polymeric peroxides) where $\begin{matrix}R\\R'\end{matrix}\!>$ are aryl groups, and progressively less stable for



as-Diphenylethylene, as shown by Staudinger gives wholly, or nearly so, high-polymeric peroxides, and among the rubbers the effect of autoxidation on the physical character of the rubber (e.g. as seen in milling) is not a uniform one of mere softening brought about by chain scission. The constitution of the polymers formed from the hydroperoxides of simple olefins or of rubber is likely to be somewhat variable. Experiment with autoxidised rubber has shown that much of the combined oxygen survives in the form of ether links, and similar experiment with the *cyclohexenes* has shown that stable peroxide groups (doubtless of type $R\cdot OO\cdot R'$) are to be found together with ether links in the polymeric portion of the autoxidation products. Since, in the case of the simple olefins, polymers which contain both types of oxygen linking can be formed from the peroxides at will, doubtless they arise by direct decomposition of the hydroperoxide-groupings (i.e. $R\cdot OOH + R'\cdot OOH \longrightarrow R\cdot O\cdot R' + R\cdot OO\cdot R'$).‡ In this way rubber chains may be joined by oxygen links at the same time that they are undergoing scission elsewhere. In addition, some peroxido-links between rubber chains, or between different parts of the same chain, may possibly be formed independently of this decomposition by union of the $R\cdot OO^*$ radicals produced in the early stage of peroxide-formation with external double bonds ($R\cdot OO^* + \cdot C=C\cdot \longrightarrow R\cdot OO\cdot C-C^* \xrightarrow{H^*} R\cdot OO\cdot C-CH\cdot$). On the whole, the tendency to polymer-formation will probably be much smaller than with simpler substances, but even a few cross-links in a large molecule will have a marked effect on the properties of the rubber.

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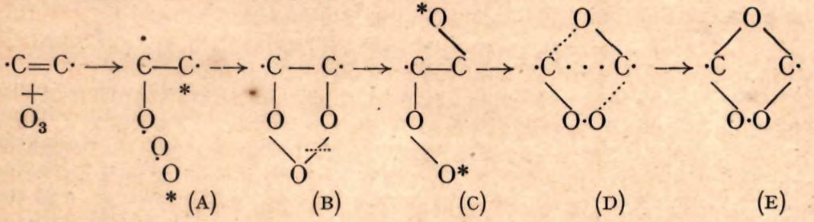
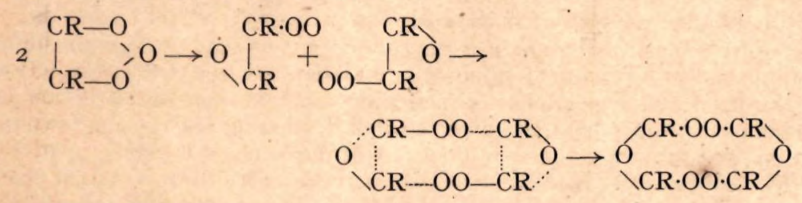
† The *cis* or *trans* configuration at the double bond may have some influence.

‡ Bolland has recently shown that the thermal decomposition of methyl linoleate hydroperoxide leads immediately to loss of water between ·OOH groups.

Analogies from Ozonide-formation.—The evidence of recent years leaves but slight doubt that all organic ozonides capable of isolation contain the peroxido-acetal type of grouping formed by addition of ozone at olefinic double bonds. (Rieche, Meister and Southoff, *Annalen*, 1942, **553**, 187). If the addition be considered to follow stages somewhat similar to those discussed above for peroxidation, then thermal scission of the oxygen chain at stage (C)

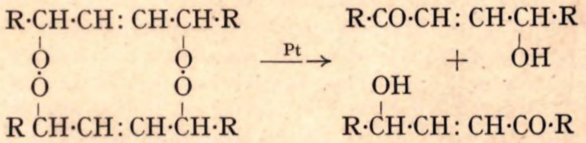


may well be followed by establishment of new ·O—C· and ·OO—C links (stage D) with contemporaneous weakening and ultimate breaking, of the original ·C—C· bond (stage E). The interesting point is that ozonide-formation, like peroxide-formation, shows a strong polymeric tendency, and most ozonides are mixtures of low-molecular polymers. In the case of the polymer the establishment of the new ·OO—C— link must be intermolecular, e.g. for a dimeride:



The ease of hydrolysis of ozonides is, however, superior to that of polymeric peroxides, since the ·C—O· link is much more susceptible to hydrolytic action than the ·C—OO· link; also the little that is known of the manner of thermal degradation of ozonides has distinct resemblance to that of the thermal degradation of peroxides.

Thermal and Catalysed Decomposition of Peroxides.—This is perhaps the most important consideration in understanding the details of the autoxidative degradation of rubber and of other olefinic materials. Unfortunately, but little detailed experimental work has been done on the subject, and the more important lines of reaction can only be rather uncertainly discerned. Finely divided metals and some chemical reagents show a strong tendency to promote a disproportionated type of peroxide scission. Thus in attempted catalytic hydrogenation of peroxides the metallic catalyst frequently promotes extensively the direct decomposition of the peroxide rather than its hydrogenation. In this way polymeric methyl elaeostearate peroxide gives with platinum considerable amounts of a crystalline ketol ester, instead of the expected diol, e.g. for the dimer, which is here for convenience represented as stabilised by end-joining:



$$\begin{array}{c}\mathrm{R{\cdot}CH{\cdot}CH{:}\,CH{\cdot}CH{\cdot}R}\\ \mathrm{O}\qquad\qquad\mathrm{O}\\ \mathrm{O}\qquad\qquad\mathrm{O}\\ \mathrm{R\,CH{\cdot}CH{:}\,CH{\cdot}CH{\cdot}R}\end{array}\xrightarrow{\mathrm{Pt}}\begin{array}{c}\mathrm{R{\cdot}CO{\cdot}CH{:}\,CH{\cdot}CH{\cdot}R}\\ +\quad\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{R{\cdot}CH{\cdot}CH{:}\,CH{\cdot}CO{\cdot}R}\end{array}$$

In the case of monomeric olefin hydroperoxides the same process leads to the formation of ketones and the elimination of water:

$$\cdot\mathrm{CH{:}\,CH{\cdot}CH(OOH)}\cdot \xrightarrow{\mathrm{Fe^{\cdot\cdot}}} \cdot\mathrm{CH{:}\,CH{\cdot}CO}\cdot + \mathrm{H_2O}$$

Uncatalysed thermal scission appears to lead largely towards the severing of the O–O link of the peroxide groups, and this is followed by further decomposition of the resulting radicals, which may involve the breaking of some saturated C–C bonds. Polymeric *as*-diphenylethylene peroxide thus give some benzophenone and formaldehyde by dry-heating, and the formation of formaldehyde by the decomposition of $\beta\gamma$-dimethylbutadiene peroxide may, as indicated above, quite well be due to the breaking of the $\alpha\beta$-bond in $\cdot\mathrm{O}-\vdots-\mathrm{O{\cdot}CH_2}-\vdots-\mathrm{CMe{:}\,CMe{\cdot}CH_2{\cdot}O}-\vdots-\mathrm{O}\cdot$ Uncatalysed decomposition in the case of the polymeric peroxides is not very ready at temperatures around room-temperature, and apparently it is not very homogeneous as regards the course of reaction. In the case of hydroperoxido-rubber, although scission of the molecules occurs extensively at double bonds in the chains, a quite appreciable degree of subsidiary scission occurs at C–C bonds immediately adjoining the severed double bonds.

Influence of combined sulphur on chain-breaking.—Although high-sulphur vulcanisates are more prone to undergo deterioration by the action of oxygen than low-sulphur vulcanisates, observation of the action of oxygen on simple saturated and unsaturated sulphides has so far shown no strong tendency for the C–S bond to be broken oxidatively. On the other hand, Armstrong, Little and Doak (*Ind. Eng. Chem.*, 1944, **36**, 628) have recently shown that ozone causes fairly complete scission of C–S bonds in simple olefinic sulphides.

Softeners and Chain-degradation.—Phenylhydrazine, its salts and numerous accelerators of rather different types when milled into natural rubber cause softening of the mass. In a number of cases examined the molecular weight of the softened material has been found to have fallen substantially (by *ca.* 25 per cent.) as the result of the milling, and in the case of phenyl hydrazine the result appears to be genuinely due to the promotion of increased oxygen uptake (Farmer and Naylor, unpublished work). Auxiliary substances which are active at all may in general be expected to be effective either in promoting oxygen-uptake or in promoting the decomposition of peroxides in a particular way. Success in aiding oxygen uptake is presumably a question of the successful initiation of chain reactions (and likewise successful anti-oxidant activity of success in chain-stopping) but the effectiveness of both pro-oxidants and anti-oxidants is probably much affected by conditions of reaction. Concerning the influence of auxiliary substances on the decomposition of peroxides or peroxide radicals much remains to be discovered.

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