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α-METHYLENIC REACTIVITY IN OLEFINIC AND POLYOLEFINIC SYSTEMS.

THE COURSE AND MECHANISM OF AUTOXIDATION REACTIONS IN OLEFINIC AND POLYOLEFINIC SUBSTANCES, INCLUDING RUBBER.

IONIC AND RADICAL MECHANISMS IN OLEFINIC SYSTEMS, WITH SPECIAL REFERENCE TO PROCESSES OF DOUBLE-BOND DISPLACEMENT, VULCANISATION AND PHOTOGELLING.

α-METHYLENIC REACTIVITY IN OLEFINIC AND POLYOLEFINIC SYSTEMS.

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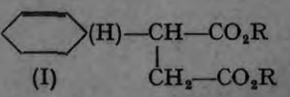
The most important reactions of olefins and olefinic systems have usually been considered to be additive ones. Recent work, however, has shown that substitutive reactions are likely to prove of equal importance, and attention is here drawn to a variety of substitutions which occur at the α-methylene groups of olefinic systems. Doubtless the reaction mechanisms of these processes differ from example to example, and it is of very considerable importance in respect to the utilisation of olefins, rubber, and drying oils that the exact nature of these mechanisms should be determined. Of particular interest is the influence on α-methylenic substitution of (1) reaction-conditions and (2) alkyl-substitution at the ethylenic carbon atoms. When chlorine reacts with an olefin in a polar solvent the halogen acts as an electrophilic reagent and the olefin as electron-donor, so that an ionic process of addition takes place; when, however, the reaction occurs in the gas phase, or in solvents of low polarity, it takes a more complicated course, involving chain processes and radical intermediates.[1] Also, in additions of ionic character, the presence of alkyl substituents on the ethylenic carbon atoms is well known to facilitate additive reaction, and to influence the direction of addition of reagents: it appears to do the same in α-methylenic substitutions, including (so far as present evidence gives an indication) even reactions which are fairly certainly radical reactions. Certain of the substitutions described below are liquid-phase reactions, which proceed apparently quite independently of photochemical activation, and in these especially, the relationship of substitution to addition in terms of the intrinsic reactivity of the system $—CH_2—CH{=}CH—$ needs to be defined.

The Maleic Anhydride Reaction.—Maleic anhydride combines readily with conjugated dienes (Diels-Alder reaction) in hydrocarbon media, in spite of the lessened unsaturation and greater activation energy of the ethylenic bonds due to resonance in the diene system; yet it will not similarly unite with mono-olefins or unconjugated polyolefins. This, together with the conclusion of Wassermann that for diene synthesis to be successful two-point contacts at the correct positions must be made by the colliding reactant molecules, suggests that reaction involves the radical form, $\cdot CH—CH{=}CH—CH\cdot$, of the diene. Reactions between olefins or unconjugated polyolefins and maleic anhydride (or maleic esters) can, however, be promoted,[2] provided an elevated temperature is used. Thus *cyclo*hexene, 1-methyl*cyclo*hexene, dihydromyrcene and rubber unite above 220° with methyl or butyl maleate. The reaction is a substitution at the α-methylene groups of the olefin, giving in the case of *cyclo*hexene first (I) and then a disubstitution product which is probably


(I)

mainly *cyclo*hexene-3 : 6-disuccinic ester. The reaction proceeds with particular ease in the system $—CH{=}CH—CH_2—CH{=}CH—CH_2—$ of drying oils, and the system $—CH_2—CMe{=}CH—CH_2—$ of rubber, and succeeds also if analogues of the maleic compounds (*e.g.* ethyl cinnamate) are used. What appears to be an analogous reaction occurs at moderate temperatures (around 100°) between the same reactants if a little peroxide is added as reaction-starter.

Peroxidation Reactions.—With little doubt peroxidation constitutes the first step in all autoxidations of olefins, although many or all of the peroxide groups formed may undergo decomposition before the end of reaction. The absorbed oxygen forms hydroperoxide groups which are attached substitutionally at the methylene groups adjacent to the olefinic double bonds; the point of entry at one α-methylene group or another seems to be greatly influenced by alkyl substituents in the carbon chain (*cf.* this vol., p. 350). It has been found that *cyclo*hexene,[3, 4, 5] 1-methyl*cyclo*hexene, 1 : 2-dimethyl*cyclo*hexene[4] and tetralin[5] give relatively

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[1] Stewart *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 2869 *et seq.*

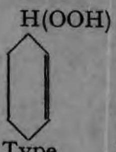
[2] Farmer and Farmer, *unpublished work.*

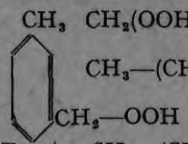
[3] Stephens, *J. Amer. Chem. Soc.*, 1928, **50**, 568.

[4] Farmer and Sundralingam, *J. Chem. Soc.*, 1942, 121.

[5] Criegee *et al.*, *Ber.*, 1939, **72**, 1799.

stable peroxides of type I by absorption of oxygen (without solvent) in U.V. light, whereas *m*- and *p*-xylene[6] and cymene[7] give hydroperoxides by substitution in the side chain (type II). Dihydromyrcene[8] gives relatively unstable mono- and di-hydroperoxides by substitution at one or other of the α-methylene groups in the chain (type III), while rubber[9] and other polyisoprenes[4] behave quite similarly, giving lightly or heavily peroxidised materials (multi-hydroperoxidic). Oleic acid[10] gives a mixture of relatively stable mono- and di-peroxides in which the hydroperoxide groups are found at C_8 or C_{11} (types IV and V) or at both.


Type I


Type II

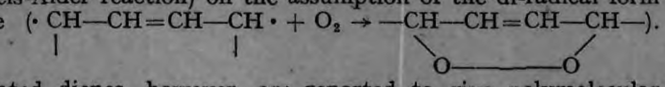
$CH_2(OOH){-}CMe{=}CH{-}CH_2{-}CH(OOH){-}CMe{=}CH{-}CH_3$ Type III

$CH_3{-}(CH_2)_6{-}CH(OOH){-}CH{=}CH{-}(CH_2)_7{-}CO_2Me$ Type IV

$CH_3{-}(CH_2)_7{-}CH{=}CH{-}CH(OOH){-}(CH_2)_6{-}CO_2Me$ Type V

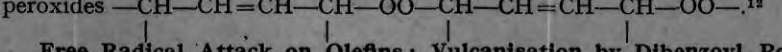
In all these hydroperoxidic autoxidation products the original double bonds remain intact, except in so far as the peroxidic groups have undergone secondary decomposition involving utilisation of their active oxygen for attack at the unsaturated centres. Such secondary decomposition proceeds side by side with peroxidation and is often well-nigh impossible to arrest; where this occurs the isolation of pure poly-hydroperoxides is impossible.

The foregoing remarks apply to mono- and unconjugated poly-olefins. In the case of cyclic conjugated dienes such as terpinene, 2 : 4-cholestadiene, ergosterol, dehydroergosterol, anthracene, rubrene, etc.[11] terminal addition of molecular oxygen seems to be possible, and this is probably dependent (as in the Diels-Alder reaction) on the assumption of the di-radical form of the diene



$$(\cdot\,\underset{|}{CH}{-}CH{=}CH{-}\underset{|}{CH}\,\cdot + O_2 \rightarrow \underbrace{{-}CH{-}CH{=}CH{-}CH{-}}_{O\text{———}O}).$$

Some conjugated dienes, however, are reported to give polymolecular peroxides



$${-}\underset{|}{CH}{-}CH{=}CH{-}\underset{|}{CH}{-}OO{-}\underset{|}{CH}{-}CH{=}CH{-}\underset{|}{CH}{-}OO{-}.$$[12]

Free Radical Attack on Olefins: Vulcanisation by Dibenzoyl Peroxide.—Dibenzoyl peroxide readily reacts with saturated and aromatic hydrocarbons, with alcohols, organic acids, etc., at temperatures above 100°. The peroxide decomposes thermally to give Ph• and Ph—CO—O• radicals,[13] and these are able to attack an organic substance RH with formation of new compounds and new free radicals:

(1) $Ph\cdot + RH \rightarrow PhR + H\cdot$
(2) $Ph\cdot + RH \rightarrow PhH + R\cdot$
(3) $Ph{-}CO{-}O\cdot + RH \rightarrow Ph{-}CO{-}OR + H\cdot$
(4) $Ph{-}CO{-}O\cdot + RH \rightarrow Ph{-}CO_2H + R\cdot$
(5) $R\cdot + RH \rightarrow R{-}R + H\cdot$, etc., etc.

The new free radicals are available for further attack on the molecules present, or, if their concentration permits, for intercombination. The fate of the various radicals formed must depend largely on the reaction conditions, since if the reactant RH is present in very large excess, the

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[6] Farmer and Narracott, *J. Chem. Soc.*, 1942, 185.
[7] Heilberger *et al.*, *Ber.*, 1939, **72**, 1643.
[8] Farmer and Sutton, *J. Chem. Soc.*, 1942, 139.
[9] Farmer and Sundralingam, *unpublished work.*
[10] Farmer and Sutton, *in the press.*
[11] Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367.
[12] Bodendorff, *Arch. Pharm.*, 1933, **271**, 1.
[13] Hey and Waters, *Chem. Rev.*, 1937, **21**, 169.

intercombination of free radicals must mainly give place to their attack on RH ; therefore potentially, at any rate, the action of the decomposing dibenzoyl peroxide is twofold, comprising a substituting agency (reactions 1 and 3) and a molecule-linking or " polymerising " agency (reaction 5).

This action is seen when RH is *cyclo*hexene, taken in large excess, so that the chance of encounter of phenyl or benzoate radicals from the peroxide with *cyclo*hexene molecules will be great, and that of their encounter with other free radicals will be small. Since *cyclo*hexene has two likely points of attack, *viz.* the α-methylene groups and the double bonds, it may be expected, if P represents either a phenyl or a benzoate radical derived from the peroxide, that the following types of reaction will occur :

(*a*) $C_6H_{10} + P\cdot \rightarrow PH + C_6H_9\cdot$ or $C_6H_9-P + H\cdot$
(*b*) $C_6H_{10} + C_6H_9\cdot \rightarrow C_6H_9-C_6H_9 + H\cdot$,

and also, by attack of the radicals at the olefinic double bonds :

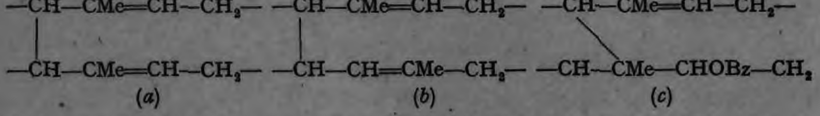
(*c*) $C_6H_{10} + P\cdot \rightarrow P—C_6H_{10}\cdot$
(*d*) $C_6H_{10} + P—C_6H_{10}\cdot \rightarrow C_6H_9—C_6H_{10}—P + H\cdot$, or $P—C_6H_{11} + C_6H_9\cdot$
(*e*) $C_6H_{10} + P—C_6H_{10}\cdot \rightarrow P—C_6H_{10}—C_6H_{10}\cdot$, etc., etc.

The products actually found are numerous,[14] but all agree with expectation according to the above scheme. Attack by the radicals at the α-methylene groups greatly exceeds their attack at the double bond, and molecule-linking is almost entirely confined to two-molecule linkings.

The vulcanisation of rubber by dibenzoyl peroxide at 140° was thought by its discoverer [15] to be substantially represented by the equation

$$(C_5H_8)_n + n\ Ph—CO—OO—CO—Ph \rightarrow n\ Ph—CO_2H + (C_5H_7—O—CO—Ph)_n.$$

Conformably with this view the unsaturation of the product is stated to be but little diminished,[16] but on the analogy of the *cyclo*hexene reactions, and bearing in mind the labilising action of the methyl groups in the rubber chain on the hydrogen atoms of adjacent methylene groups, the two processes of molecule-linking and substitution may be expected to give vulcanisates in which the rubber chains are extensively substituted at the α-methylene groups by benzoate and (to a lesser extent) by phenyl groups, and at the same time are in some degree cross-linked by bonds (intermolecular or intramolecular) joining the methylene groups of different rubber units (*e.g.* as shown in *a* and *b*), or bonds joining α-methylene groups to double bonds (as exemplified in *c*) :



(*a*) (*b*) (*c*)

Vulcanisation by dibenzoyl peroxide is therefore likely to be mainly a combination of cross-linking and substitution of the rubber chains, as distinct from cross-linking and double-bond addition as in sulphur vulcanisation.

Reaction of Quinones.—In the maleic anhydride reaction described above there is no tendency for three-carbon residues $(—\underset{|}{C}H—CH{=}CH—)$ and hydrogen *atoms* formed by dissociation of the olefin to unite at the oxygen-terminals of the system $O{=}\underset{|}{C}—CH{=}CH—\underset{|}{C}{=}O$ present in the

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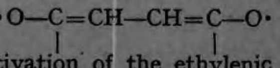
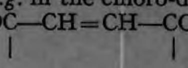
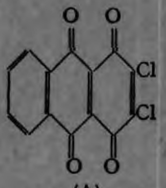
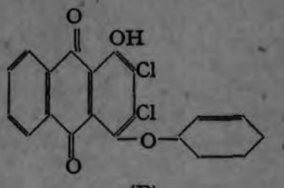
[14] Farmer and Michael, *in the press.*

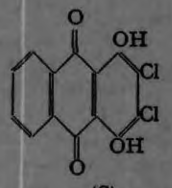
[15] Ostromislensky, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1885 ; *Rubber Chemistry and Technology*, 1937, 279.

[16] Fisher and Gray, *Ind. Eng. Chem.*, 1928, **20**, 294.

anhydride—possibly for lack of the resonance form  $\cdot O{-}\overset{|}{C}{=}CH{-}CH{=}\overset{|}{C}{-}O\cdot$ Successful reaction in this case depends on activation of the ethylenic bond of the anhydride. In the case of quinones the situation is different, and where the quinone is suitably substituted, *e.g.* in the chloro-diquinone (A), reaction at the terminals of the system  $OC{-}CH{=}CH{-}CO$ can be


(A)


(B)

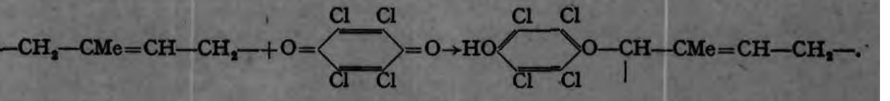

(C)

realised by heating the quinone with an olefin such as *cyclo*hexene or tetralin.[17] In this way the hydroquinone (B) from *cyclo*hexene, or an analogous compound from tetralin, is formed. At a higher temperature these hydroquinones of type (B) break down giving *cyclo*hexadiene (or 1 : 2-dihydronaphthalene) and the hydroquinone (C), so that the net result of the reaction carried out at high temperature is dehydrogenation of the olefin and reduction of the quinone.

Various halogenated quinones react with rubber causing a species of vulcanisation [18] (inferior for practical purposes to sulphur vulcanisation). Tetrachloroquinone (chloranil) is particularly successful, a part of it (stated to be ½) becoming reduced to the corresponding hydroquinone as a result. Since the latter can be re-oxidised to the quinone by including amongst the reactants a proportion of a suitable oxidising agent (*e.g.* PbO or HgO) the vulcanising agent can apparently function repeatedly. Although Ostromislensky has suggested a complicated reaction as occurring between the chloroquinone and the C_5H_8 rubber units, thus :

$$2\,QCl_4 + 3\,C_5H_8 \rightarrow H_2QCl_4 + C_5H_7{-}QCl_2{-}C_5H_7 + C_5H_8Cl_2 \quad (Q{=}C_6O_2),$$

the true course of reaction probably involves the process :



Since chloranil is now known to be a particularly effective dehydrogenating [19] agent for hydroaromatic compounds, some degree of dehydrogenation similar to that brought about by the above-mentioned diquinone may well enter into the rubber-chloranil reaction. The production of conjugated diene units in this way may well facilitate some cyclisation or some true polymerisation of the rubber molecules, and so contribute to the vulcanised character. There is, however, the possibility that the quinone may serve to greater or lesser extent as an oxidation-reduction system, and so lead to a more direct radical-linking of the rubber chains :

$$2\rangle C_5H_8 + QCl_4 \rightarrow 2\rangle C_5H_7\cdot + H_2QCl_4$$

$$2\rangle C_5H_7\cdot \rightarrow \rangle C_5H_7\cdot C_5H_7<$$

Vesterburg Reaction.—The earliest dehydrogenations of hydroaromatic substances were carried out by heating them with sulphur, whereupon

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[17] Criegee, *Ber.*, *B*, 1936, **69**, 2758.

[18] Fisher, U.S.P. 1,918,328.

[19] Arnold and Collins, *J. Amer. Chem. Soc.*, 1939, **61**, 1407.

hydrogen was removed as hydrogen sulphide. In the dehydrogenation of *cyclo*hexene, however, no *cyclo*hexenyl mercaptan (comparable with *cyclo*hexenyl hydroperoxide) is to be found in the reaction mixture: instead, the hydrogen sulphide generated adds, as would be expected,* to unused *cyclo*hexene to give *cyclo*hexyl mercaptan and to some extent di*cyclo*hexyl sulphide.[20] It appears, therefore, that the formation of an unsaturated mercaptan by a reaction exactly analogous to that cited above between Criegee's diquinone and *cyclo*hexene represents no essential stage in dehydrogenation by sulphur; instead, sulphur can probably function as hydrogen-acceptor by a direct mechanism.

Sulphur Vulcanisation.—When the Vesterburg reaction is applied to rubber at about 140° ordinary sulphur-vulcanisation ensues. This process has two main features, (1) the remarkable change in the physical properties (especially the solubility) of the rubber, and (2) the incorporation of sulphur in the rubber. Most authors have regarded the former as due to increase in the size of the rubber molecules arising from some kind of polymerisation promoted by sulphur, and the latter as due to addition of sulphur at the double bonds. It has most often been concluded that the chief function of sulphur in the vulcanisation process is to promote the formation of intermolecular links, usually considered to be sulphur bridges of one kind or another (sulphide, disulphide), but possibly to some extent direct C—C bonds. On the cross-linked structure the desirable physical properties of the sulphur vulcanisates are deemed to depend.

Two points have now become fairly clear, experimentally, *viz.* (1) that the desirable physical properties of the vulcanisates are conferred before any serious diminution in the unsaturation of the rubber has occurred, or any large proportion of sulphur has become chemically combined,[21] and (2) that after this stage (which is presumably the essential vulcanising or cross-linking stage) has been reached, chemical incorporation of sulphur sets in seriously and is attended by progressive decrease in the unsaturation.[22] In view of the fact that sulphur is not ordinarily an additive reagent for olefinic double bonds it is probably legitimate to deduce from (1) that the cross-linking essential to vulcanisation, whether this is by direct C—C links or by sulphur bridges, probably affects primarily and mainly the α-methylene groups, and from (2) that the extensive incorporation of sulphur at the later stages of sulphur-vulcanisation is a secondary process dependent on the attack at the methylene groups.

Photogelling of Rubber.—The photogelling of rubber dissolved in a mixture of carbon tetrachloride and acetone, or in various other halogenated solvents (with or without added ketones, and with or without added peroxide or oxygen as sensitising agents) has been described by Stevens.[23] The gelling proceeds fairly rapidly in sunlight and the intensity and duration of illumination affect very greatly the physical character of the gels. The process is found to involve the extensive chemical incorporation of fragments of the solvents in the rubber, and doubtless it also involves cross-linking of the rubber molecules or units; it appears to resemble closely the action of dibenzoyl peroxide on rubber, save that the free-radicals responsible for the interlinking of molecules and the attachment of organic fragments to the rubber chains are derived from the solvents by photochemical decomposition.

Halogenation Reactions.—The importance of α-methylenic reactivity is very evident in halogenation reactions. The results of Groll, Hearne

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* The addition of H_2S to olefins is, unlike that of sulphur, a normal reactivity; moreover, it is known to be catalysed by sulphur.

[20] Meyer and Hohenemser, *Helv. Chim. Acta*, 1935, **18**, 1061.

[21] Hauser, *Ind. Eng. Chem.*, 1938, **30**, 1291; 1939, **31**, 1391.

[22] *Cf.* Spence and Scott, *Kolloid-Z.*, 1911, **8**, 304.

[23] Stevens, *Trans. Inst. Rubber Ind.*, 1940, **16**, 211.

et al.,[24] following earlier results of Stewart *et al.*,[25] and Deanesly,[26] in respect of olefins, and of McGavack[27] in respect of rubber, have shown that in certain circumstances α-methylenic substitution partly or wholly replaces double bond addition. There is often a second-order substitution at the ethylenic carbons.

Both substitution and addition occur when an olefin in gaseous form is mixed with chlorine at low or non-elevated temperatures. For substitution to become easy, however, and to compete successfully with addition, the lability of the α-methylenic hydrogen atoms requires enhancing either by structural modification of the normal olefinic chain or by using high temperatures. If an alkyl group is present at one of the ethylenic carbons of the normal chain as in $—\underset{a}{CH_2}—\underset{b}{CMe}=\underset{c}{CH}—\underset{d}{CH_2}—$ the substitutive capacity at *a* (or at *a* and *d*) is greatly increased, and some small degree of substitution occurs also at *c*. If a higher alkyl group than methyl is employed, the ease of substitution seems to be increased, and the evidence indicates that in the system $R_1R_2C=CR_3R_4$ the well-known rules regarding the inductive efficiency of alkyl groups in promoting and directing the course of ionic addition reactions are valid here also.* The substitutive reaction is found to be a liquid-phase reaction, occurring in liquid films on the walls of the vessel, and proceeds at about the ordinary pressure (low or moderate temperature) in the absence of light and without other catalyst than the walls of the vessel. At a suitable rate of gas-flow *iso*butylene (1 mol.) gives with chlorine (1 mol.) :

$$\underset{0{\cdot}87\ \text{mol.}}{CH_2Cl—\overset{(a)}{C}Me=CH_2} + \underset{0{\cdot}03\ \text{mol.}}{CH_3—\overset{(b)}{C}Me=CHCl} + \underset{0{\cdot}01\ \text{mol.}}{\overset{(c)}{CMe_3Cl}\dagger} + \underset{0{\cdot}06\ \text{mol.}}{CH_3—CMeCl—\overset{(d)}{C}H_2Cl} +$$

$$\underset{0{\cdot}02\ \text{mol.}}{\text{Satd. Dichlorides}} + \underset{0{\cdot}01\ \text{mol.}}{\text{Trichlorides}}$$

and the ratio of the yield (%) of (*a*) to that of (*b*) changes little with varying conditions from *ca.* 97/3. Tertiary amylene ($CMe_2=CHMe + CH_2=CMeEt$) gives comparable results.

For the promotion of a good degree of substitutive halogenation in normal-chained olefins it is necessary to rely on the provision of suitable experimental conditions. High temperatures (300°-600°, according to the olefin and halogen concerned) are effective, and propylene gives at 600°–650° at least 85·5 % of chloropropenes which comprise $CH_2Cl—CH=CH_2$ (96 %), $CH_3—CCl=CH_2$ (3 %) and $CH_3—CH=CHCl$ (1 %). When bromine is used to react with propylene, the substitutive tendency is even more marked, for although at 200° addition predominates, at 300° the product consists of substitutively-formed mono-bromides ; moreover at either temperature the substitutive tendency is more pronounced for bromine than it is for chlorine. The temperature which must be reached before addition gives place to substitution is higher for ethylene than for unbranched alkyl ethylenes, and very much higher for ethylene than for branched olefins.

The chlorinations which occur at elevated temperatures, whether substitutive or additive, appear to be mainly (not exclusively) of radical character, and the incidence of the specific reaction-chains is very dependent on the experimental conditions.[28] The role of oxygen during chlorination

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[24] *Ind. Eng. Chem.*, 1939, **31**, 1239, 1413, 1530.

[25] *J. Amer. Chem. Soc.*, 1930, **52**, 2869 ; 1931, **53**, 1121 ; 1935, **57**, 2036 ; 1936, **58**, 98 ; 1937, **59**, 1765.

[26] *Ibid.*, 1934, **56**, 250.

[27] *Ind. Eng. Chem.*, 1923, **15**, 961 ; *cf.* Bloomfield and Farmer, *J. Soc. Chem. Ind.*, 1934, **53**, 43T.

* This seems to apply also to the relative capacities for substitution of the ethylenic hydrogen atoms in $R—CH=CH_2$.

† Hydrogen chloride addition product.

[28] Rust and Vaughan, *J. Org. Chem.*, 1940, **5**, 472.

is unexpected, in that whereas small concentrations of oxygen catalyse strongly the substitutive reaction, especially at the higher temperatures, considerable concentrations of oxygen suppress both reactions below 300° ; above 300° the addition which occurs in presence of oxygen is probably of gas-phase, bimolecular type. Radicals containing an ethylenic linkage seem to be more stable to oxygen than those which have only single C—C bonds.

Lead Tetracetate Reactions.—Criegee [29] found that lead tetracetate reacts directly with *cyclo*hexene to give not only 1 : 2-diacetoxyl*cyclo*hexane but mono- and diacetoxyl-*cyclo*hexenes. This means that acetoxyl groups add at the double bond of the olefin, and also substitute one or both of the α-methylene groups to give 3-, 3 : 6- and 3 : 3-derivatives. Since both the substitutive and additive reactions consist in transfer of acetoxyl groups from reagent to olefin, it appears that reaction is of free-radical rather than ionic type in spite of the fact that reaction is sometimes conveniently conducted in presence of glacial acetic acid (to arrest hydrolysis of the reagent). The essential reaction is then the thermal decomposition : $Pb(OAc)_4 \rightarrow Pb(OAc)_2 + 2\,AcO\cdot$, the acetoxyl radicals thus formed attacking the double bond or an α-methylene group of the olefin as in the dibenzoyl peroxide reaction above. It is of interest that further acetoxyl-radical attack can occur, as perhaps might be anticipated, at the CH_3-groups of ingoing acetoxyl groups (to give $\cdot O{-}CO{-}CH_2{-}OAc$). Lead tetrabenzoate, tetrapropionate, etc., will serve in place of the acetate, the ingoing benzoyloxy-groups from the former not being subject to subsidiary attack by $Ph{-}CO{-}O\cdot$ radicals.

Selenium Dioxide Reactions.—Selenium dioxide behaves with extraordinary regularity in attacking olefins, aldehydes and ketones at the α-methylene groups. As indicated in the succeeding paper the point of attack in the case of olefins is very precisely determined by alkyl substitution in the chain. The reaction is carried out by heating the olefin or carbonyl compound with powdered selenium dioxide, whereupon the *methylene groups attacked are oxidised to carbonyl groups,* unless the reaction is carried out in presence of a fatty acid, in which case the fatty acid ester of the corresponding alcohol is obtained ($>CH_2 \xrightarrow[AcOH]{SeO_2} >CH\cdot OAc$) The reaction strongly resembles autoxidation, and can be applied to the oxidation of the alkyl groups of alkyl-aromatic compounds ; the condition of the reagent is not without importance, old samples having been found to favour formation of bimolecular (*e.g.* ketol) reaction products.[30] The exact course of reaction, which does not appear to be normally of ionic type, is as yet undetermined.

Ozonised Oxygen Reactions.—Oxidative attack at α-methylene groups by ozonised oxygen has been reported to occur in α-pinene,[31] α-hydrindene,[32] and dodecahydrophenanthrene,[33] and seems from the nature of the decomposition products to occur to a minor extent in rubber.[34] Possibly this attack ought to be attributed to the oxygen of the reagent rather than to ozone, especially as ozone is reported [35] to catalyse oxidation by oxygen.

Attack by Oxidising Agents.—The hydrogen atoms of α-methylene groups which stand between two double bonds are especially labile, and it is not surprising to find that certain oxidising agents, including perbenzoic acid [36] and chromic acid,[37] are reported to attack these active groups

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[29] *Annalen*, 1930, **481**, 263.

[30] Kaplan, *J. Amer. Chem. Soc.*, 1941, **63**, 2654.

[31] Spencer, Weaver *et al.*, *J. Org. Chem.*, 1940, **5**, 610.

[32] Long and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2670.

[33] Dorland and Adkins, *ibid.*, 1939, **61**, 429.

[34] Pummerer *et al.*, *Ber.*, *B*, 1936, **69**, 170.

[35] Briner *et al.*, *Helv. Chim. Acta*, 1932, **15**, 201.

[36] Bauer and Bähr, *J. prakt. Chem.*, 1929 (ii), **122**, 201 *et seq.*

[37] Scheller, *Ber.*, *B*, 1939, **72**, 1917.

in linoleic and linolenic acids and in *cyclo*pentadiene, although they attack the double bonds in oleic, elaidic and ricinoleic acids. The character of the reactions and of the products is, however, unknown. The α-methylene groups in *cyclo*hexene, 1-methyl*cyclo*hexene and in 6-dodecyne are oxidised to carbonyl by chromic acid.[38]

Thermal Polymerisations of Olefins.—In many low-molecular polymerisation processes amongst olefins it has been assumed that hydrogen separates from an ethylenic carbon atom of one molecule and adds at the double bond of another. This assumption is unnecessary in low-molecular processes which are catalysed by hydrion (*cf.* Whitmore's hypothesis), and probably also in most photochemical or radical-initiated polymerisations. In the case of purely thermal polymerisations of alkylethylenes it seems not unlikely that dissociation of hydrogen *atoms* from the α-methylene groups of some monomeric molecules leads in many examples to the addition of the residual hydrocarbon radicals (*e.g.* $\underset{\cdot}{\mathrm{C}}\mathrm{H{-}RCH{=}CHR'}$) at the double bonds of other (undissociated) molecules, so giving eventually low-molecular polymerides.

Double-bond Displacement.—Hydrogen can be displaced as an ion from the α-methylene groups of olefinic chains, when strong caustic alkali is used as reagent at a sufficiently high temperature. The conditions need to be more drastic than are required for the αβ, βγ-change in unsaturated acids. The possibility of such displacement was first shown by Moore[39] in the case of the (unconjugated) triene-chain of linolenic acid, the product being a conjugated isomeride of linolenic acid.

The examples of methylene reactivity discussed briefly above are doubtless only representative instances, but they serve to show the considerable substitutive reactivity of olefinic systems, and especially of polyolefinic materials such as rubber.

The British Rubber Producers' Research Association,
48 *Tewin Road, Welwyn Garden City, Herts.*

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[38] Whitmore and Pedlow, *J. Amer. Chem. Soc.*, 1941, **63**, 785.

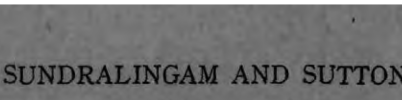
[39] *Biochem. J.*, 1937, **31**, 138; 1939, **33**, 1635; see also Kass and Burr, *J. Amer. Chem. Soc.*, 1939, **61**, 3292.

THE COURSE AND MECHANISM OF AUTOXIDATION REACTIONS IN OLEFINIC AND POLYOLEFINIC SUBSTANCES, INCLUDING RUBBER.

BY E. H. FARMER, G. F. BLOOMFIELD, A. SUNDRALINGAM AND D. A. SUTTON.

Received 22nd April, 1942.

The tendency of olefins to absorb molecular oxygen increases rapidly with increase in unsaturation. In mono-olefins absorption is usually very slow unless it is actively promoted by irradiation, by the use of temperatures above room-temperature, or by chemical catalysts; in dienes and trienes it usually becomes quite considerable in diffused daylight; and in the higher polyenes it tends to occur unpreventibly and excessively. The strong tendency towards oxidation shown by polyenes appears to be shared by unconjugated and conjugated substances alike, although the precise courses of reaction in the two cases are probably somewhat different. In the present paper attention is focussed mainly on mono-olefinic and unconjugated polyolefinic materials.

The Primary Autoxidation Reaction.—Although in the autoxidation of many different olefinic substances little peroxidic material survives at the end of reaction, there is no reason to doubt that the first stage in every such autoxidation is the formation of peroxide groups. Rubber hydrocarbon, for example, after vigorous autoxidation involving high oxygen-intake gives a product containing only traces of peroxidic material, but when the oxidation is conducted cautiously the bulk of the ingoing oxygen (80 % or more) is found in the early stages of reaction to be in peroxide form. It has usually been assumed, following the Engler-Bach hypothesis, that the oxygen is absorbed molecule by molecule, and adds at the olefinic centres, so that the *primary* reaction is in fact held to be a *simple additive reaction:*  $—CH=CH— + O_2 \rightarrow —\underset{|}{C}H—\underset{|}{C}H—$ ($O—O$). This view cannot be maintained: the disappearance of olefinic unsaturation rarely keeps pace with the incorporation of oxygen, although under usual conditions of reaction severe diminution of unsaturation due to secondary reactions often occurs. In all the (*unconjugated*) olefinic systems examined by the authors the oxygen appears to enter at the methylenic carbon atoms in the α-positions to the double bonds, and there forms hydroperoxide groups:

$$—CH_2—CH=CH— + O_2 \rightarrow —CH(OOH)—CH=CH—.$$

Each hydroperoxide group thus formed contains one atom of active oxygen and one atom of active hydrogen, but the introduction of the group leaves the olefinic unsaturation intact.

Intrinsic Stability of Hydroperoxides.—All hydroperoxides decompose comparatively readily, but some are sufficiently stable to permit of their isolation in tolerably pure form. The hydroperoxides of *cyclo*hexene, 1-methyl*cyclo*hexene, 1 : 2-dimethyl*cyclo*hexene and methyl oleate can thus be obtained by fractionally distilling the autoxidation product at reduced pressure, but with most polyolefins decomposition of the —OOH groups takes place unavoidably side by side with their formation, so that after the early stages of oxygen-absorption secondary reaction products begin to accumulate, and thus no pure hydroperoxide or polyhydroperoxide can be isolated in quantity. The polyisoprenes, *e.g.* dihydromyrcene, $H(CH_2—CMe=CH—CH_2)_2H$, and rubber, $(—CH_2—CMe=CH—CH_2—)_n$, and doubtless the drying-oil acids, *e.g.* linoleic acid,

$$C_5H_{11}—CH=CH—CH_2—CH=CH—(CH_2)_7—CO_2H,$$

and linolenic acid,

$$C_2H_5—CH=CH—CH_2—CH=CH—CH_2—CH=CH—(CH_2)_7—CO_2H,$$

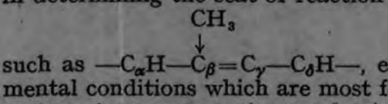
as well as the unconjugated polypene fish-oil acids, *e.g.* eicosatetraenoic acid and docosahexaenoic acid,† all belong to the latter category. In the fish-oil acids the intake of oxygen (in peroxidic form) in diffused daylight at room temperature is astonishingly rapid, but decay is rapid also.

Conditions of Hydroperoxide-formation and decay.—Absorption of oxygen is promoted by sunlight or U.V. light and by numerous chemical catalysts, both organic and inorganic; within the limits of present observation absorption is usually facilitated by raising the reaction temperature above the room temperature. The decomposition of —OOH groups is strongly promoted by elevated temperatures, apparently also by prolonged illumination, and by certain chemical catalysts such as iron salts, which can play a dual role as peroxidation-promoters and peroxide-destroyers. For the successful photochemical preparation of hydroperoxides in quantity, experience indicates that it is advisable to curtail

† The hydroperoxidic character of the peroxide groups in the diene- and polyene-acids has not yet been formally proved.

the duration of oxidation by operating with good illumination at the highest temperature which the intrinsic stability of the particular peroxide will allow.

Point of Entry of Hydroperoxide Groups ; Inductive Effects.—Experiments have indicated (*cf.* preceding paper) that inductive influences in olefinic chains have an important effect both in facilitating reaction, and in determining the seat of reaction (*e.g.* as between C_α and C_δ) in systems such as $—C_\alpha H—\overset{\overset{CH_3}{\downarrow}}{C_\beta}=C_\gamma—C_\delta H—$, even though the structural and experimental conditions which are most favourable to autoxidation are not such as to point to a reaction-mechanism of ionic type. Thus, although any methylene group (less easily a CH_3— or $>$CH-group) which is adjacent to an ethylene bond is a potential seat of reaction, autoxidation appears in practice more likely to occur at C_α in the above system rather than at C_δ. The most complete evidence of the effectiveness of alkyl groups in determining the seat of reaction is seen in the oxidising action of selenium dioxide in the presence of acetic acid,* where oxidation occurs preferentially at the precise points to be expected on the basis of the inductive influences present. Thus in the following systems [1] attack occurs first at the points marked * :



$\dot{C}H_3—CMe=CHMe$, $CH_3=\dot{C}H_2—CMe=CH_2$, $\dot{C}H_3—CPr=CHMe$, $\dot{C}H_3—CMe=CHEt$,

$CH_3—\dot{C}H_2—CPh=CHMe$, $CH_3—\dot{C}H_2—CH=CHMe$, $\dot{C}H_2R—CEt=CH—CH_2R$.

In the case of polyisoprene hydrocarbons, including rubber, present information indicates that peroxidation occurs not only at C_α in the system $C_\alpha—C_\beta=C_\gamma—C_\delta$, but extensively at C_δ also. In all the polyene drying-oil acids peroxidation seems to occur with exceptional facility at methylene groups situated between double bonds, just as ionic reactivity is very great in the methylene groups of the system $—CO—CH_2—CO—$ and $—CH=CH—CH_2—CO—$.

There are, however, other peroxidisable substances besides olefins (*e.g.* dialkyl ethers [2] and chloroform [3]) in which inductive influences seem to be potent. Thus the inductive influence of oxygen in the *n*-dialkyl ethers, and in di-isopropyl ether $[R—CH[H]\rightarrow OR \longrightarrow R—CH[OOH]—OEt]$, as also that of chlorine in chloroform $[Cl_3\leftarrow C[H] \longrightarrow CCl_3—OOH]$, doubtless renders oxidation easier than it is in saturated hydrocarbons, where usually high temperatures, catalysts, or irradiation are necessary to make a hydrogen atom detachable, and in consequence attack by molecular oxygen possible of initiation. Where, however, the structure of a substance and the ionising capacity of the medium in which it is placed favour ionic dissociation of hydrogen, the course of autoxidation may not involve the formation of an organic hydroperoxide at all. Thus in the case of α-ketols, α-aminoketones and α-methoxyketones, autoxidised in presence of alkali, the reaction probably consists purely in the oxidation by molecular oxygen of the enolic anion derived from the ketol, etc.,[4] *i.e.* in an oxidation-reduction change, *e.g.*

$$—C(\bar{O})=C(\bar{O})— + O_2 \rightarrow —CO—CO— + \bar{O}—\bar{O} \rightarrow 2—CO\bar{O}.$$

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* The free-radical character of the mechanism in this reaction requires confirmation.

[1] Guillemonat, *Ann. Chim.*, 1939, **11**, 143.

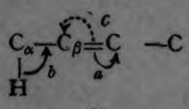
[2] Clover, *J. Amer. Chem. Soc.*, 1924, **46**, 419 ; *cf.* Mardles, *Nature*, 1931, **128**, 116.

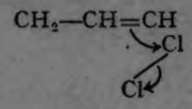
[3] Clover, *J. Amer. Chem. Soc.*, 1923, **45**, 3133 ; Chapman, *ibid.*, 1934, **56**, 818 ; 1935, **57**, 419.

[4] James and Weissberger, *ibid.*, 1937, 2040 ; *J. Chem. Soc.*, 1935, 226.

Mechanism of Peroxidation.

(*a*) **Relation of Substitution to Addition in Olefins.**—The system responsible for the varied substitutive reactions described in the preceding paper is (I). The reactivity most commonly expected of such a simple


(I)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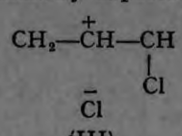
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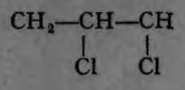
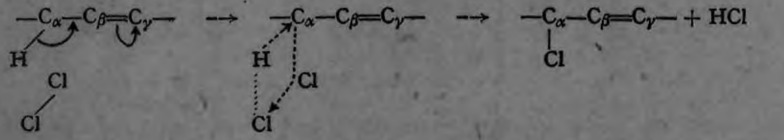

(IV)

olefinic system is addition at the double bond. The activating polarisation *a* creates at C_γ a point of relatively high electron density, so that electrophilic reagents, whether these be positive as in the case of HCl or incipiently positive as in Cl_2, are enabled to attack the system there, and reaction proceeds through the well-known stages as shown for Cl_2-addition in (II)-(IV). The normal mechanism of olefinic addition is thus an ionic one, and according to the usual electronic principles an alkyl group attached to system (I) at C_β assists by its inductive action the polarisation *a* (at the expense of the alternative *c*), and so both facilitates additive reaction and influences the direction of addition at the double bond. But it is clear from the examples quoted in the preceding paper that the system (I) possesses in addition to its additive properties a marked tendency to undergo substitution at C_α (or C_δ), and the mechanism of this substitutive reactivity is of considerable interest and practical importance.

Lability of a methylenic hydrogen atom is *normally* to be expected in the systems —CH[H]—C=O, —CH[H]—CH=CH—C=O, —CH[H]—CH=CH—CH=CH—C=O, etc., provided a basic catalyst (usually —OH or —OEt ions) is present to detach the hydrogen as proton. Also in the reinforced (conjugated) olefinic systems present in *cyclo*pentadiene, fluorene, diphenylmethane, etc., detachment of a hydrogen atom from the α-methylene group is possible provided a basic catalyst is present to remove it as an ion. But in the three-carbon system $—CH_2—CH=CH—$, as it occurs in an olefin, ionic separation of methylenic hydrogen in the absence both of a basic reagent and of an ionising medium is ordinarily * unknown and not to be expected. In order, therefore, to explain the substitutive halogenation of an olefin by chlorine or bromine on an *ionic* basis it would be necessary to envisage a reaction similar to that of aromatic substitution, in spite of the fact that the characteristic nuclear structure is absent :



In its form, however, the α-methylenic substitution in question resembles *side-chain* substitution rather than nuclear substitution, and hence a radical type of mechanism is to be expected ; also there is no obvious reason why an electrophilic reagent should attack the olefin preferentially at C_α (thus enforcing substitution) when a point of higher electron density (C_γ) is available. It is not surprising, therefore, that substitutional halogenation has proved to be dependent on radical-formation rather than on

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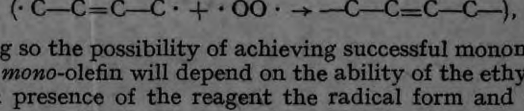
* The ionic separation of methylenic hydrogen from the olefinic three-carbon system can be effected by action of a strong base at a suitably high temperature (*cf.* succeeding paper). It occurs with much greater facility, however, in the system $—CH=CH—CH_2—CH=CH—$.

bimolecular reaction. In the case of the peroxidation of olefins the general efficacy of light and of radical-producing catalysts, etc., in promoting reaction, and the ease with which peroxidation occurs in olefins (in non-polar media) point to the same conclusion.

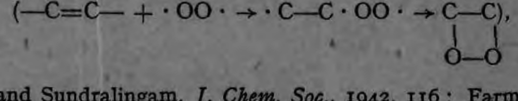
As noted above, the evidence available at present suggests that inductive effects due to alkyl groups attached to the ethylenic carbons of olefins assist substitutive as well as additive reaction, and serve to determine the point of substitutive as well as of additive attack; also there is some experimental indication that this holds for peroxidation reactions.[5] If, then, the separation of hydrogen in the substitutive reaction is not ionic, the conclusion must be drawn that the inductive effects are able to assist the symmetrical (free-radical) separation of the electron pair in the methylenic C—H bond, and it is common experience that such separation is promoted by non-ionising rather than ionising media. Waters[6] has pointed out that internal inductive effects in complex molecules produce great changes in the electrostatic bond-energy, and also that the probability that bond-fission processes at a bond A—B will take the unsymmetrical course $A{-}B \rightarrow A^+ + B^-$ (to yield two ions) and not the symmetrical course $A{-}B \rightarrow A^\bullet + B^\bullet$ (to yield two neutral radicals) becomes greater as the ionic resonance energy of the bond increases. The ionic character then of a bond such as C—H, which has only low resonance energy, is likely to be considerably inferior to the free-radical character. Waters further points out that the electrostatic energy needed to create a single gaseous ion is greater than the thermal energy needed to dissociate a co-valent bond into *two* neutral radicals, but the dielectric effect of a solvent in reducing the energy of ion-formation is very great. Hence it appears that at least those α-methylenic substitution reactions which are conducted in the undiluted hydrocarbon or in media of low dielectric constant are likely to be based on symmetrical dissociation of the C—H bond; furthermore it is to be inferred that the C=O group in the system —CH—C=O enhances the tendency to ionic dissociation (rather than radical dissociation) of the adjacent C—H bond, since otherwise it is surprising that autoxidation in oleic and similar acids and esters occurs at the CH_2-groups α- to the ethylenic double bonds, and not at those adjacent to the carboxyl groups.

Now although olefins when they are submitted to the action of chlorine or bromine can show both the additive and the substitutive reaction, under suitable experimental conditions, the evidence is not yet clear as to whether a corresponding *additive* reaction can be achieved when oxygen is the reagent. Certain cyclic conjugated dienes (but not so far as is known open-chain ones) can add oxygen terminally,[7] but here, presumably, owing to the paramagnetic character of the oxygen, and the easily assumed free-radical phase of the diene, the addition is not ionic, but of radical type



$$(\cdot\,\mathrm{C{-}C{=}C{-}C}\,\cdot + \cdot\,\mathrm{OO}\,\cdot \rightarrow \overset{\mathrm{O{-}O}}{-\mathrm{C{-}C{=}C{-}C}-}),$$

and this being so the possibility of achieving successful monomeric additive reaction in a *mono*-olefin will depend on the ability of the ethylenic carbons to assume in presence of the reagent the radical form and to make two simultaneous or nearly simultaneous links with oxygen



$$(-\mathrm{C{=}C}- + \cdot\,\mathrm{OO}\,\cdot \rightarrow \cdot\,\mathrm{C{-}C}\,\cdot\,\mathrm{OO}\,\cdot \rightarrow \underset{\mathrm{O{-}O}}{\mathrm{C{-}C}}),$$

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[5] Farmer and Sundralingam, *J. Chem. Soc.*, 1942, 116; Farmer and Sutton, *ibid.*, p. 139.

[6] *Ibid.*, 153.

[7] Bodendorff, *Arch. Pharm.*, 1933, **271**, 1; Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367.

either of which courses is for steric reasons hardly likely to be easily accomplished. There is as yet no clear evidence that this *additive* peroxidation has ever been achieved, but with respect to the *general* possibility of forming peroxides additively from mono-olefins, three cases may be cited: first, certain olefins which contain no α-methylene group, and notably *as*-diphenylethylene,[8] appear to be capable of giving under illumination polymeric peroxides

$$\text{—E—OO—E—OO—E—OO—} \quad (\text{E}=\text{Ph}_2\text{C}_2\text{H}_2),$$

presumably formed by polymerisation of the monomer —E—OO— * secondly, other similar olefins (*e.g.* styrene [9]) give with oxygen polymers of the *olefin* which contain but little peroxidic oxygen; and thirdly, certain olefins add oxygen readily after they have first been attacked by halogen atoms [10] *e.g.*

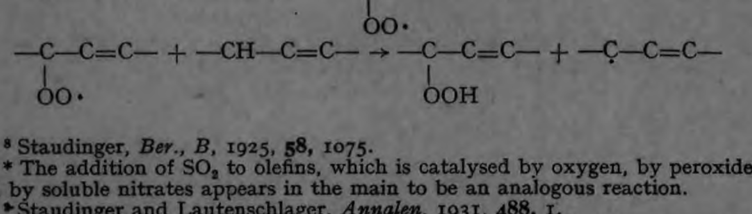
$$[2\ \text{CH}_2\text{=CH—CH}_2\text{Br} \xrightarrow{\text{Br}\cdot} 2\ \text{CH}_2\text{Br—}\dot{\text{C}}\text{H—CH}_2\text{Br} \xrightarrow{\text{O}_2} (\text{CH}_2\text{Br})_2\text{CH—OO—CH}(\text{CH}_2\text{Br})_2].$$

With regard to the relative ease of radical-attack at the α-methylene group and at the double bond, recent experiments [11] indicate that in *cyclo*hexene phenyl- and benzoate-radicals (from dibenzoyl peroxide) attack most successfully at the methylene group.

(*b*) **Photoperoxidation.**—Both oxygen and peroxides (especially the latter) have been found by Kharasch and his co-workers [12] to be generally efficacious in starting reaction-chains in hydrogen halide additions, presumably owing to the assistance which the paramagnetic character of the former and the radical-yielding (or possibly the co-ordinative power) of the latter lend to the formation of halide atoms

$$(\text{HX} + \cdot\text{OO}\cdot \rightarrow \text{HOO}\cdot + \text{X}\cdot;\ \text{R}\cdot + \text{HX} \rightarrow \text{RH} + \text{X}\cdot).$$

In view of the remarkable ease with which (in the absence of inhibitors) peroxidation succeeds in diffused light in the case of rubber and the drying oils, in comparison with the comparative immunity of mono-olefins from oxidative attack, it seems at first sight that the feature which predisposes towards oxidation is the inherent structural lability of the hydrogen atoms, which is at its maximum in the α-methylenic groups. In the polyolefins the appropriate atoms might then be considered to be labile enough to permit of their being detached by oxygen sufficiently readily and frequently to start enough reaction-chains to sustain a reasonably rapid rate of oxidation. Such a process might be expected to be initiated more easily by introduction of a little already-formed peroxidic material (probably providing radicals), than by oxygen alone. The course of reaction would then be:



$$\text{—CH—C=C—} + \cdot\text{OO}\cdot\ (\text{or R}\cdot) \rightarrow \text{—}\underset{\cdot}{\text{C}}\text{—C=C—} + \cdot\text{OOH (or RH)}$$

$$\text{—}\underset{\cdot}{\text{C}}\text{—C=C—} + \cdot\text{OO}\cdot \rightarrow \text{—}\underset{\text{OO}\cdot}{\underset{|}{\text{C}}}\text{—C=C—}$$

$$\text{—}\underset{\text{OO}\cdot}{\underset{|}{\text{C}}}\text{—C=C—} + \text{—CH—C=C—} \rightarrow \text{—}\underset{\text{OOH}}{\underset{|}{\text{C}}}\text{—C=C—} + \text{—}\underset{\cdot}{\text{C}}\text{—C=C—}$$

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[8] Staudinger, *Ber.*, *B*, 1925, **58**, 1075.

* The addition of SO_2 to olefins, which is catalysed by oxygen, by peroxides, and by soluble nitrates appears in the main to be an analogous reaction.

[9] Staudinger and Lautenschlager, *Annalen*, 1931, **488**, 1.

[10] Bockemuller and Pfeuffer, *ibid.*, 1939, **537**, 178; *cf.* Dickinson and Leermakers, *J. Amer. Chem. Soc.*, 1932, **54**, 3852.

[11] Farmer and Michael, *in the press.*

[12] *Cf.* Mayo and Walling, *Chem. Rev.*, 1940, **27**, 351.

and the role of such catalysts as cobalt and copper salts in initiating reaction could be represented

$$\text{—CH—C=C—} + Cu^{++} \rightarrow \text{—}\underset{\cdot}{\text{C}}\text{—C=C—} + Cu^{+} + H^{+}.$$

But Morgan and Naunton[13] have found that the rate of thermal oxidation of rubber in the early stages of reaction is independent of oxygen pressure (so confirming earlier results of Williams and Neal[14]) and thus indicating that a course of reaction dependent on bimolecular collision between oxygen and the hydrocarbon is unlikely. They suggest that the autoxidation of rubber involves a chain-mechanism, and they advance the scheme.

$$R \rightleftharpoons R^* ;\ R^* + O_2 \rightarrow RO_2^* ;\ RO_2^* + R \rightarrow RO_2 + R^* ;\ RO_2^* \rightarrow RO_2,$$

where R^* is an activated rubber double bond, RO_2^* a rubber peroxide, and RO_2 the product of rubber oxidation. This scheme is difficult to reconcile with the experimental findings cited above respecting the unsaturated peroxidic character of the first-formed rubber photo-oxidation products, since reaction is made dependent on acceptance of the double bond as the necessary point of initiation and the subsequent seat of peroxidation; also the rubber peroxide seems to be regarded as having only a transient existence. An alternative to both of the foregoing schemes is that initiation of peroxidation depends on the prior dissociation of the olefin at the α-methylenic C—H bond

$$(\text{—CH—C=C—} \rightarrow \text{—}\underset{\cdot}{\text{C}}\text{—C=C—} + H\cdot)$$

under the influence of light. No direct evidence can, however, be advanced for this course of reaction. The kinetics of olefinic autoxidation are at present the subject of examination.

Somewhat similar problems arise with regard to the polymeric addition of SO_2 to olefins and the polymeric peroxidation of olefins. Here reaction would superficially appear to begin as the result of bimolecular interaction between oxygen and olefin, in contrast to the oxygen- or peroxide-induced "abnormal" addition of HBr to olefins, in which the attack of the oxygen- or peroxide-catalyst is directed to the additive reagent. Whether in the polymerisation reactions the first step necessarily takes place at a methylene group and never at a double bond is not clear.

Secondary Autoxidation Reactions.—Except with the most stable hydroperoxides, and then only under optimum conditions of operation, peroxide decay occurs side by side with new peroxidation. Thus in polyenes—especially long-chain polyenes such as rubber—hydroperoxide groups and their oxygeno-derivatives inevitably occur in the same molecule. This mixing of peroxidic and secondary groupings is aided by the usual very uneven distribution of oxidative attack over the olefinic molecules present. The principal, and doubtless the most invariable, feature of secondary autoxidative changes is that the hydroperoxide groups themselves revert to hydroxyl groups (in some circumstances to keto groups) and concurrently the active oxygen is used in oxidising either the adjacent or some remote double bond—the latter perhaps in another molecule. This oxidative action may proceed as far as chain-scission *at the double bonds*, or may oxygenate and so saturate the double bonds without severing them. Chain-scission reactions can occur with embarrassing facility in rubber after even slight oxygenation; in a less serious degree they occur unavoidably in the polyene fish-oil acids and the shorter polyisoprenes. It is impossible at present to distinguish between thermal and photochemical secondary decompositions. The basic reactions, so far as they are at present known, seem to be the following :—

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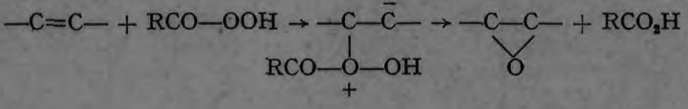
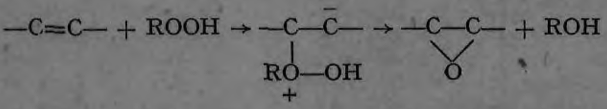
[13] *Proc. Rubber Technology Conference*, 1938, p. 599.

[14] *Ind. Eng. Chem.*, 1930, **22**, 874.

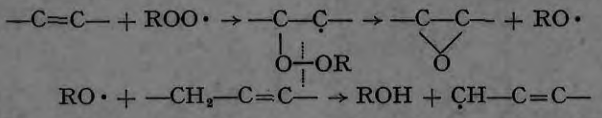
1. Interaction of a hydroperoxide group with a double bond, giving a hydroxyl group at the former and an epoxy group at the latter. This reaction is in part comparable with the action of an organic peracid at an ethylenic bond (equation *a*), and since it can be brought about at will by heating an olefin hydroperoxide with an olefin, may be represented as in (*b*). But since the change appears to occur with greater facility during the actual autoxidation reaction than subsequently by thermal decomposition of the isolated hydroperoxide, it may possibly be brought about during the autoxidation in a more direct way, *e.g.* by the interaction of a radical peroxide with a double bond as shown in (*c*). This reaction is of " intermolecular " type, occurring between a peroxide group in one molecule and either a double bond in another molecule, or a remote double bond in the same molecule.

(*a*)


$$-\mathrm{C}{=}\mathrm{C}- + \mathrm{RCO{-}OOH} \rightarrow -\underset{\mathrm{RCO{-}\underset{+}{O}{-}OH}}{\mathrm{C}}{-}\overset{-}{\mathrm{C}}- \rightarrow -\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C{-}C}}- + \mathrm{RCO_2H}$$

(*b*)


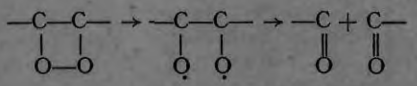
$$-\mathrm{C}{=}\mathrm{C}- + \mathrm{ROOH} \rightarrow -\underset{\mathrm{R\underset{+}{O}{-}OH}}{\mathrm{C}}{-}\overset{-}{\mathrm{C}}- \rightarrow -\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C{-}C}}- + \mathrm{ROH}$$

(*c*)


$$-\mathrm{C}{=}\mathrm{C}- + \mathrm{ROO}\cdot \rightarrow -\underset{\mathrm{O{\vdots}OR}}{\mathrm{C}}{-}\underset{\cdot}{\mathrm{C}}- \rightarrow -\underset{\diagdown\mathrm{O}\diagup}{\mathrm{C{-}C}}- + \mathrm{RO}\cdot$$

$$\mathrm{RO}\cdot + -\mathrm{CH_2}{-}\mathrm{C}{=}\mathrm{C}- \rightarrow \mathrm{ROH} + \underset{\cdot}{\mathrm{C}}\mathrm{H}{-}\mathrm{C}{=}\mathrm{C}-$$

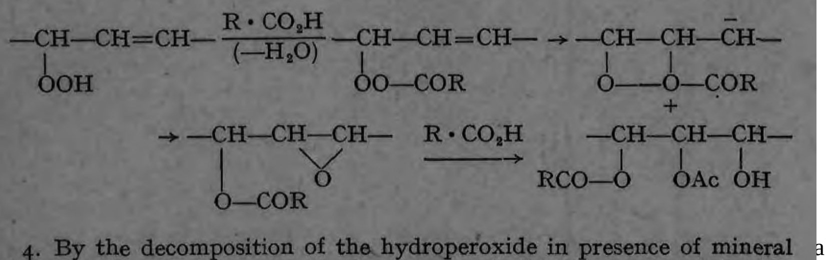
2. Scission of the carbon chain at the double bond occurs with considerable ease, both during the autoxidation reaction (*i.e.* perhaps as the result of irradiation), and subsequently by thermal decomposition. The precise mechanism of this change in either case remains still to be determined. There is insufficient evidence at present for rejecting finally the possibility that in some very small degree scission can occur during the original autoxidation by momentary formation and immediate decomposition of a cyclic peroxide, thus :



$$-\underset{\mathrm{O{-}}}{\mathrm{C}}{-}\underset{\mathrm{O}}{\mathrm{C}}- \rightarrow -\underset{\underset{\cdot}{\mathrm{O}}}{\mathrm{C}}{-}\underset{\underset{\cdot}{\mathrm{O}}}{\mathrm{C}}- \rightarrow -\underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\!\!{\Vert} + \underset{\mathrm{O}}{\mathrm{C}}\!\!{\Vert}-$$

but this mechanism cannot apply to thermal decompositions of the hydroperoxide.

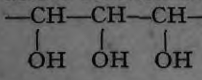
3. In the presence of organic acids or their anhydrides autoxidation occurs readily. This may be represented for the free acid :



$$-\underset{\mathrm{OOH}}{\mathrm{CH}}{-}\mathrm{CH}{=}\mathrm{CH}- \xrightarrow[(-\mathrm{H_2O})]{\mathrm{R\cdot CO_2H}} -\underset{\mathrm{OO{-}COR}}{\mathrm{CH}}{-}\mathrm{CH}{=}\mathrm{CH}- \rightarrow -\underset{\mathrm{O}{-\!-}}{\mathrm{CH}}{-}\underset{\mathrm{\underset{+}{O}{-}\underset{\cdot}{C}OR}}{\mathrm{CH}}{-}\overset{-}{\mathrm{C}}\mathrm{H}-$$

$$\rightarrow -\underset{\mathrm{O{-}COR}}{\mathrm{CH}}{-}\underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH{-}CH}}- \xrightarrow{\mathrm{R\cdot CO_2H}} -\underset{\mathrm{RCO{-}O}}{\mathrm{CH}}{-}\underset{\mathrm{OAc}}{\mathrm{CH}}{-}\underset{\mathrm{OH}}{\mathrm{CH}}-$$

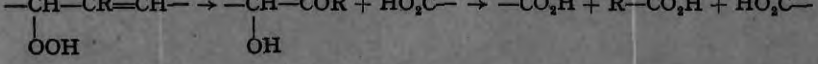
4. By the decomposition of the hydroperoxide in presence of mineral acid a reaction analogous to the foregoing and yielding a saturated triol,



$$-\underset{\mathrm{OH}}{\mathrm{CH}}{-}\underset{\mathrm{OH}}{\mathrm{CH}}{-}\underset{\mathrm{OH}}{\mathrm{CH}}-$$

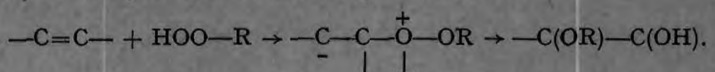
, occurs.

5. Subsidiary scission can occur between an ethylenic bond and an α-carbon atom :



$$-\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{CH}}-\mathrm{CR{=}CH}- \rightarrow -\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\mathrm{COR} + \mathrm{HO_2C}- \rightarrow -\mathrm{CO_2H} + \mathrm{R{-}CO_2H} + \mathrm{HO_2C}-$$

6. Polymerisation occurs by the interaction of —OOH groups and double bonds. This appears to give mainly *dimerides* of ether type, possibly to be represented as involving the reaction



$$-\mathrm{C{=}C}- + \mathrm{HOO{-}R} \rightarrow -\underset{-}{\mathrm{C}}-\underset{|}{\mathrm{C}}-\overset{+}{\underset{\substack{|\\ \mathrm{H}}}{\mathrm{O}}}-\mathrm{OR} \rightarrow -\mathrm{C(OR){-}C(OH)}.$$

In addition, radical forms, RO·, produced by thermal (or possibly photochemical) dissociation of the hydroperoxides, and radical forms, ROO·, produced in the primary peroxidation reaction, probably take part in the process by reacting with other olefinic systems present.

7. In the presence of iron salts, and in some cases as the result of spontaneous or violent thermal decomposition, hydroperoxides give unsaturated ketones. This is comparable to the spontaneous formation of esters from the peroxides of ethers [$\mathrm{RCH(OOH){-}OR'} \rightarrow \mathrm{RCO{-}OR'} + \mathrm{H_2O}$].

8. In the presence of alkalies extensive hydrolysis of the hydroperoxide groups occurs ($\mathrm{ROOH} + \mathrm{H_2O} \rightarrow \mathrm{ROH} + \mathrm{H_2O_2}$) with concomitant oxidative degradation of the double bonds by the hydrogen peroxide liberated.

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IONIC AND RADICAL MECHANISMS IN OLEFINIC SYSTEMS, WITH SPECIAL REFERENCE TO PROCESSES OF DOUBLE-BOND DISPLACEMENT, VULCANISATION AND PHOTO-GELLING.

BY ERNEST HAROLD FARMER.

Received 29*th April*, 1942.

The α-methylenic reactions discussed in the two preceding papers recall a series of interesting observations by Baker and Nathan [1] which indicate that a *p*-methyl substituent attached to the benzene nucleus can permit electron-release to the nucleus in a manner that appears only in lesser degree in higher alkyl groups and may be absent in some (*e.g.* Bu^{γ}). Thus in *p*-methylbenzyl bromide the suggested function of the methyl group (dotted arrows in (I)) permits additional electron-release

(I)

(II)

at the C—Br bond, and so facilitates the anionisation of the bromine. Baker and Nathan suggest that the electrons of the duplet constituting

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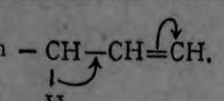
[1] *J. Chem. Soc.*, 1935, p. 1847 ; see also *ibid.*, 1942, p. 191.

the C—H bond of the methyl group are less localised than those in a similarly placed C—C bond, and hence that a methyl group attached to the necessary conjugated unsaturated system is capable of electron-release by a mechanism similar to the tautomeric effect (II). They make clear, however, that the new mechanism functions *in addition to* the generally-accepted inductive (+ I) effect of alkyl groups, and they find experimentally that the efficiency of representative alkyl groups is in the order Me > Et > Pr^{β} > Bu^{γ}, and that the suggested electron-release must be of mesomeric rather than of tautomeric type. The phenomenon noted by Baker and Nathan seems to be part of a much wider phenomenon which applies to unconjugated (as well as to conjugated) polyolefines, and even to mono-olefins which contain the system $—CH_2—CH{=}CH—$, and it appears likely that in general the three-carbon system exists in a mesomeric state corresponding to the electron-shifts in  $-\underset{\displaystyle H}{\underset{|}{CH}}—CH{=}CH$. This conclusion has, if correct, certain consequences with respect to the ionic reactivity and physical properties of olefinic substances: these consequences are exemplified in the following two sections. In addition, however, the mesomeric condition as here conceived appears to lie at the root of the well-known "cracking" rule of diene polymers (as it is illustrated in the cracking of rubber to isoprene, the reversal of the diene synthesis, etc.), whereby the links which brerk, *i.e.* the weakest links, are never the C—C links adjoining the double bonds $\left(—\vdots—C—C{=}C—C—\vdots—\right)$; also it appears to exert a marked influence on the tendency of the α-methylenic C—H bond to dissociate symmetrically. Such observations as have been made in the latter respect indicate that alkyl substituents attached to the ethylenic carbon atoms do indeed appear to facilitate the symmetrical dissociation; nevertheless it is difficult at present to disentangle the purely inductive effect of the alkyl groups from the mesomeric effect in a system such as $R—\overset{*}{C}H_2—C(\overset{*}{C}H_3){=}CH—\overset{*}{C}H_2—R'$, characteristic of the polyisoprenes and rubber. The available evidence suggests that dissociative reaction does not occur principally at the methyl groups, but it is too fragmentary to distinguish quantitatively between the three C—H bonds marked *.

Ionic Double-bond Displacement.

Double-bond displacement induced by the action of alkali is well known under the name of three-carbon or prototropic change and is a common property of αβ- or βγ-unsaturated fatty acids, ketones, nitriles, etc. The same type of change has been observed in the case of the aryl-olefins, β-phenylpropylene, eugenol and Δ^2-dihydronaphthalene in which the aryl group replaces >CO or —CN as an activating group, but until recently was unknown in olefinic chains in which the double bond was remote from all activating groups of the usual types. Moore,[2] however, found that linolenic acid, $C_2H_5—(CH{=}CH—CH_2)_3—(CH_2)_6—CO_2H$, when heated with alkali passed slowly into an isomeric conjugated form. Linoleic acid and linoleyl alcohol similarly pass into conjugated forms,[3] and it is undoubtedly a

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[1a] *Cf.* Schmidt, *Ber. B.*, 1936, **69**, 1885; Scheller, *ibid.*, 1939, **72**, 1917.

[2] *Biochem. J.*, 1937, **31**, 139; 1939, **33**, 1635.

[3] Kass and Burr, *J. Amer. Chem. Soc.*, 1939, **62**, 1796.

common property of 1 : 4-diene hydrocarbon systems to pass with moderate facility into one or both of the forms $—CH{=}CH—CH{=}CH—CH_2—$ and $—CH_2—CH{=}CH—CH{=}CH—$ when the substances containing them are heated with caustic alkali at elevated temperatures. The question then arises as to whether displacement also occurs in the 1 : 5-diene system, $—CH{=}CH—CH_2—CH_2—CH{=}CH—$, or generally in mono-olefinic systems, $—CH_2—CH{=}CH—CH_2—$, in which the double bond is remote from carbonyl or similar activating groups.

In the case of the 1 : 5-diene system as it is represented by the linked isoprene units $—CH_2—CMe{=}CH—CH_2—$ of squalene, dihydromyrcene and rubber, prolonged treatment with alkali under the conditions which are successful with linolenic and lineoleic acids has been found to cause no recognisable degree of bond shift.[4] With regard to the simple mono-olefinic system there is on record the early statement of Varrentrapp [5] that oleic acid when fused with caustic alkali gave a considerable yield of palmitic and acetic acids, as though by hydrolytic fission of Δ^2-octadecenoic acid :

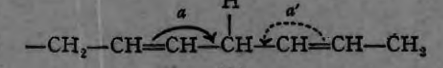
$$C_8H_{17}—CH{=}CH—(CH_2)_7—CO_2H \longrightarrow [C_8H_{17}—(CH_2)_7—CH{=}CH—CO_2H] \longrightarrow C_{15}H_{31}—CO_2H + CH_3—CO_2H.$$

Cautious repetition of Varrentrapp's experiment has shown [4] that extensive scission of the chain can with care be largely avoided, and a mixture of isomeric octadecenoic acids thereby obtained. It is clear, therefore, that given sufficiently rigorous conditions of temperature and alkali concentration, double-bond shift in a mono-olefinic substance can be carried out from carbon to carbon atom along a lengthy chain, and this capacity must be regarded as a potentiality in all mono-olefins and unconjugated polyenes. It has not been found possible to move the double bond in oleic acid from the original position in more than one direction (*i.e.* towards the carboxyl group).

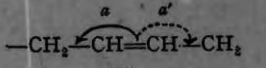
In view of the greatly superior ionising capacity of methylenic hydrogen in the systems

$$—CO—CH_2—CO— \quad \text{and} \quad —CH{=}CH—CH_2—CO—,$$

compared with that in the system $R—CH_2—CO—$, it may be concluded that the double-bond displacements most likely to occur (alternatively) in the system (A) are those indicated by *a* and *a′*, and these will appear concomitantly with detachment of a proton from the central methylene



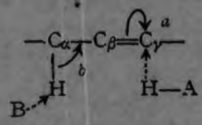
(A)



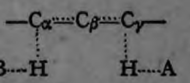
(B)

group (preferentially to detachment of a proton from either of the outer methylene groups). In the case of the system (B), the double-bond shift, under suitably drastic experimental conditions, may be either to left or to right, with corresponding ionisation of hydrogen from the adjoining methylene group on the left or on the right.

If we consider the three-carbon system (C) in terms of Ingold's conception of prototropic mechanism, the removal of a proton from Cα by the

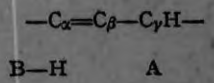


(C)



Transition state.

(D)



(E)

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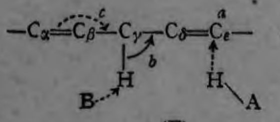
[4] Farmer and Sutton, *unpublished work.*

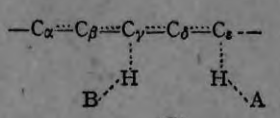
[5] *Annalen*, 1840, 35, 196.

base B and the complementary and concurrent supply of a proton to $C\gamma$ by some substance in the system together constitute a process with a definite activation energy (say E). This energy, equal to the difference in energy between the transition state (D) and the initial state C, may be considered to be reduced by a quantity x, due to the polarisations a and b, and representing resonance energy resulting from the electron distribution symbolised by a and b. *If* the process actually does occur, then the system becomes (E), *i.e.* the process necessitates a double-bond shift, which in the absence of an imposed external constraint and with an energy in the system after the change essentially the same as before it (as, *e.g.*, in a purely hydrocarbon system with only saturated carbon atoms beyond the three-carbon system) may be in either direction. But since in the case of oleic acid double-bond displacement not only succeeds, but apparently proceeds only in one direction (towards the CO_2^- group), it must be concluded both that the required activation energy $E - x$ is actually developed under the conditions of alkali fusion, and that the negative charge on the CO_2^- ion exercises a sufficient, albeit a very feeble, inductive influence through a chain of six saturated carbon atoms (or alternatively through the medium) to determine that a hydrogen atom is detached from C_8 in the system $\underset{11}{-CH_2}-\underset{10}{CH}=\underset{9}{CH}-\underset{8}{\overset{\delta+}{CH_2}}\rightarrow(CH_2)_6\rightarrow CO_2^-$ in preference to one from C_{11}, *i.e.* to ensure that a transition state involving the three-carbon system C_8—C_{10} rather than one involving the system C_9—C_{11} becomes operative.

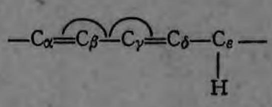
Turning to the diene system (F), the activation energy of the isomerisation which applies to the simple three-carbon system (*i.e.* $E - x$) will here be further reduced by a quantity, y, due to incipient conjugation resulting from the polarisation c, so that the activation energy is $E - (x + y)$



(F)



(G)



(H)

and since a condition of complete conjugation of the double bonds finally ensues, the resonance energy corresponding to this condition reduces the energy of the system (say by Y), so that the degree of conjugation in the transition state will be less than in the final state, *i.e.* $y < Y$.† But it is important to note that the process which gives rise to Y is that which in a less complete manner gives rise to y. The double-bond displacement then in the diene system is likely to be more easily achieved than in the mono-olefinic system, and, since the same (central) methylene group loses a proton whichever of the two three-carbon systems comes into play, the occurrence and direction of displacement are likely to be largely unaffected by polar groups terminating the carbon chain. From similar considerations it appears that double-bond displacement in rubber and the polyisoprene hydrocarbons is unlikely to occur with any facility under alkali-treatment, if at all.

It is of some interest that the polyisoprene hydrocarbon, squalene ($C_{30}H_{50}$), shows a persistent exaltation of the molecular refraction of 1·6 units and the normal-chained unconjugated fish-oil acid, docosahexaenoic acid ($C_{22}H_{32}O_2$; F6), one of 0·8 units[6] provided that each compound is scrupulously freed from its autoxidation products. Rubber also shows the same anomaly. Whether these exaltations are significant and refer

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† The author gratefully acknowledges a discussion of this matter with Dr. L. C. Bateman.

[6] Farmer and Sutton, *unpublished work*.

to an element of conjugation in the polyene chain analogous to that shown for the diene system in formula (G), which exists in spite of the fact that the double bonds are here separated by two methylene groups, remains to be tested by other methods.

Double-bond Displacement by Heat.

The above-mentioned optical anomalies were at first thought to be due to conjugation brought about by progressive heat-isomerisation during slow fractional distillation of the high-boiling materials; but this was not the case, since the anomaly appears in specimens which have not been heated above 100°. Prolonged heating of these latter specimens in entire absence of oxygen at temperatures a little below their decomposition points, has caused no changes in the absorption spectra which can be attributed to conjugation. Yet at high temperatures (above 270°, or possibly at somewhat lower temperatures in presence of a contact catalyst) olefinic hydrocarbons and the esters of vegetable oil acids give polymerised and cyclised products whose constitutions are such that conjugation can be fairly definitely concluded to have preceded polymerisation or cyclisation.[7] This isomerisation must be attributed to radical dissociation of α-methylenic hydrogen atoms.

Vulcanisation.

The process of vulcanisation is usually hastened by the use of organic accelerators, some of which can themselves act as efficient vulcanisers, even when no sulphur is present. The basis of the success of these self-sufficient compounds appears to be their capacity for decomposing thermally to give free radicals which then act precisely analogously to dibenzoyl peroxide[8] and bring about direct C—C linking of the rubber units at the α-methylenic carbon atoms; tetramethylthiuram disulphide,

$$\mathrm{Me_2N{-}CS{-}SS{-}CS{-}NMe_2},$$

one of the most efficient of these is a close sulphur-analogue of dibenzoyl peroxide, and polyalkyl-hydrazines, which are prone to decompose thermally to give radicals, have been found to have a vulcanising effect. Where sulphur alone, or sulphur together with an accelerator, forms the vulcanising agent, three processes of bridging seem to be possible, *viz.* (*a*) direct C—C linking at the α-methylene groups caused by radicals derived from peroxidic chain-starters contained in the rubber, or by radicals derived from the decomposing accelerator, or by atmospheric oxygen :—

$$>\mathrm{CH_2} + \mathrm{R^{\bullet}} \longrightarrow\ >\mathrm{CH^{\bullet}} + \mathrm{RH}\,;\ >\mathrm{CH^{\bullet}} + >\mathrm{CH_2} \longrightarrow\ >\mathrm{CH{-}CH}< + \mathrm{H^{\bullet}},$$

(*b*) sulphur bridging at the α-methylene group, initiated by chain-starters :—

$$>\mathrm{CH_2} + \mathrm{R^{\bullet}} \longrightarrow\ >\mathrm{CH^{\bullet}} + \mathrm{RH} \xrightarrow{\mathrm{S}}\ >\mathrm{CH{-}S^{\bullet}} + \mathrm{RH}\,;$$
$$>\mathrm{CH{-}S^{\bullet}} + >\mathrm{CH_2} \longrightarrow\ >\mathrm{CH{-}S{-}CH}<^{\dagger} + \mathrm{H^{\bullet}},$$

and (*c*) C—C linking brought about by sulphur functioning purely as a hydrogen-acceptor :—

$$2>\mathrm{CH_2} + \mathrm{S} \longrightarrow\ >\mathrm{CH{-}CH}< + \mathrm{H_2S}.$$

With regard, however, to the mechanism by which sulphur becomes steadily and extensively incorporated in rubber during the later stages of reaction, with concurrent loss of the unsaturation of the latter, it would

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[7] Farmer, *Trans. Faraday Soc.*, 1939, **35**, 1039.

[8] *Cf.* Farmer, preceding paper, p. 348.

† Or the corresponding disulphide-bridged compound.

be unprofitable without further investigation of sulphur-olefin reactions to attempt to formulate the precise sequence of events. There are, however, two possibilities of double-bond saturation in the vulcanisation reaction which do not necessitate recourse to postulation of the direct addition of sulphur in one or other of its known modifications at the double bonds. The first is addition at the double bonds of hydrogen sulphide generated by the attack of sulphur at the methylene groups (equation (*c*) above)—an addition which is known to be catalysed by sulphur, and the second a reaction analogous to that by which a molecule of oxygen becomes attached to an olefin at an α-methylene group

$$[\text{—CH(OO}^{\cdot}\text{)—CH=CH— or —CH(OOH)—CH=CH—}]$$

and then by secondary reaction attacks and saturates (inter- or intramolecularly) a near-by double bond.

The Photo-gelling of Rubber.

This phenomenon is one of a group of insolubilisation reactions which are of embarrassingly frequent occurrence in connection with the manipulation of rubber and its derivatives, and for which the exact cause usually remains obscure. Solutions of rubber containing such " sensitisers " as ketones, aldehydes, carbon tetrachloride, chloroform, peroxides, etc., undergo rapid gelling in sunlight, the best sensitisers being those which break down photochemically to give free-radicals, and the poorest comparatively stable substances such as pure petroleum fractions and benzene. The very considerable extent to which fragments from the sensitisers or photochemically-decomposing solvents enter into the composition of the photo-gels, leaves little doubt as to the radical nature of the reaction, and there seems to be no difference at all in reaction-principle between the type of combined cross-linking and radical-addition here encountered and that observed with rubber containing thermally-decomposing dibenzoyl peroxide molecules. The increasing toughness of the photo-gels with increasing degree of reaction (increasing cross-linking) is impressive.

The role of oxygen in the photo-gelling reactions seems from the observations of Stevens to be a mixed one. As in the case of the substitutional chlorination of olefins, traces of oxygen appear to function catalytically, although in this case the gelling promoted is very slow; larger amounts of oxygen on the contrary hinder oxidation, and serve to cause severe oxidative degradation of the gels.

The above paper and the two preceding ones relate to subjects forming part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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