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

By Ernest Harold Farmer.

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$^\gamma$). Thus in *p*-methylbenzyl bromide the suggested function of the methyl group (dotted arrows in (I)) permits additional electron-release
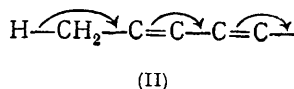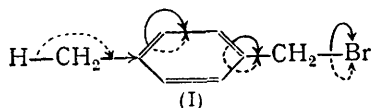
at the C—Br bond, and so facilitates the anionisation of the bromine. Baker and Nathan suggest that the electrons of the duplet constituting

[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 $-CH\overset{\curvearrowright}{}CH\overset{\curvearrowleft}{=}\overset{*}{C}H$. This conclusion has, if correct,
$|$
H

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 $\left(-\!\!\!\mid\!\!-C\!-\!C\!=\!C\!-\!C\!-\!\!\!\mid\!\!-\right)$; 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 *.
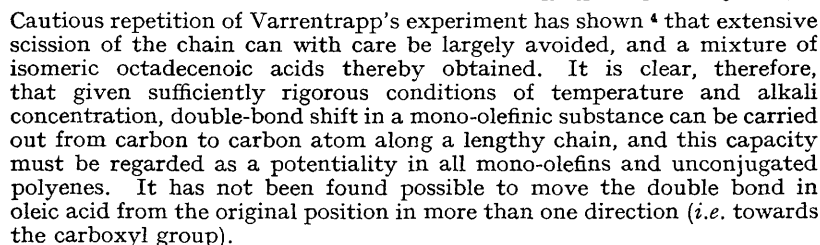
Ionic Double-bond Displacement.

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 $\alpha\beta$- or $\beta\gamma$-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

[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 linoleic 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

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 $C\alpha$ by the
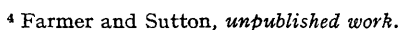
[4] Farmer and Sutton, *unpublished work*.   [5] *Annalen*, 1840, **35**, 196.

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 $-CH_2-\overset{11}{C}H=\overset{10}{C}H-\overset{9}{C}H_2 \to \overset{\delta+}{(CH_2)_6} \to CO_2^-$ 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)
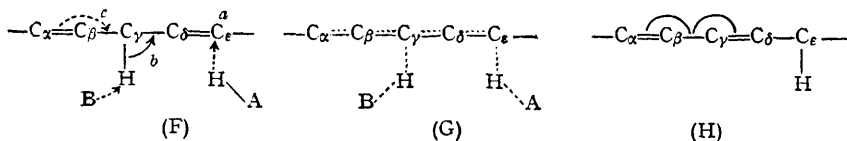
and since a condition of complete conjugation of the double bonds finally ensues, the resonance energy corresponding to this condition reduces the energy of the system (say by Y), so that the degree of conjugation in the transition state will be less than in the final state, *i.e.* $y < Y$.† But it is 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 [6] compound is scrupulously freed from its autoxidation products. Rubber also shows the same anomaly. Whether these exaltations are significant and refer

[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.
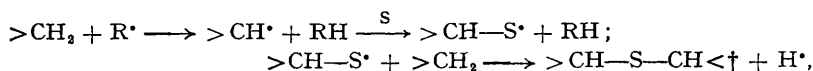
Vulcanisation.

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,

$$Me_2N\text{—}CS\text{—}SS\text{—}CS\text{—}NMe_2,$$

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 :—

$$>CH_2 + R\cdot \longrightarrow >CH\cdot + RH\,;\ >CH\cdot + >CH_2 \longrightarrow >CH\text{—}CH< + H\cdot,$$

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

$$>CH_2 + R\cdot \longrightarrow >CH\cdot + RH \xrightarrow{S} >CH\text{—}S\cdot + RH\,;$$
$$>CH\text{—}S\cdot + >CH_2 \longrightarrow >CH\text{—}S\text{—}CH<† + H\cdot,$$

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

$$2>CH_2 + S \longrightarrow >CH\text{—}CH< + H_2S.$$
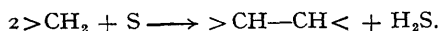
With regard, however, to the mechanism by which sulphur becomes steadily and extensively incorporated in rubber during the later stages of reaction, with concurrent loss of the unsaturation of the latter, it would

[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

$$[-CH(OO^{\bullet})-CH{=}CH- \text{ or } -CH(OOH)-CH{=}CH-]$$
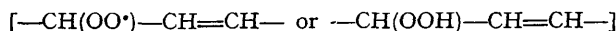
and then by secondary reaction attacks and saturates (inter- or intramolecularly) a near-by double bond.

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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