96. *Rubber, Polyisoprenes, and Allied Compounds. Part II. The Molecule-linking Capacity of Free Radicals and its Bearing on the Mechanism of Vulcanisation and Photo-gelling Reactions.*

By Ernest Harold Farmer and Stephen E. Michael.

It is known that when dibenzoyl peroxide is heated with rubber at 140° interaction takes place and the rubber undergoes a species of vulcanisation. To elucidate the course of this reaction the behaviour of dibenzoyl peroxide towards a typical olefin, *cyclo*hexene, has been examined. Numerous products, including C_6- and C_{12}-hydrocarbons and benzoates of these, are formed, the reaction involving the thermal decomposition of the peroxide to give free phenyl and benzoate radicals. These radicals lead to (*a*) the interlinking of the olefin molecules, and (*b*) the formation of derivatives of both the simple and the " polymeric " olefins. The olefin molecules are attacked by the radicals principally at the α-methylene groups, but in part at the double bonds. The results described not only disclose an important reactivity of olefins but afford an explanation of numerous vulcanisation reactions which rubber undergoes, and also of certain photo-gelling reactions which are promoted by free-radical sources.

Ostromislensky (*J. Russ. Phys. Chem. Soc.*, **1915**, **47**, 1885) discovered that dibenzoyl peroxide when heated with rubber to 140° brought about a species of vulcanisation of the rubber, the chemical nature of which has been the subject of much conjecture and experimental investigation. It was at first thought that the process was essentially one of oxidation, and indeed, free benzoic acid derived from the peroxide was isolated by Ostromislensky from the reaction product; but van Rossem, Dekker, and Prawirodipoero (*Kautschuk*, 1931, **7**, 202, 220) found that, although much benzoic acid was liberated during the reaction, some became united with the rubber, and could afterwards be freed by saponification. Van Rossem and his collaborators, however, were unable to correlate the accumulated observations with the previously published generalisations of Gelissen and Hermans (*Ber.*, 1926, **59**, *B*, 662) concerning the nature of the reactions between dibenzoyl peroxide on the one hand and numerous substances, including alcohols, organic acids, and saturated and benzenoid hydrocarbons, on the other; nevertheless, they agreed with Gelissen and Hermans on one point, *viz.*, that to some extent cleavage of the peroxide with formation of benzoic acid probably occurred, and they suggested that the concomitant reaction was a dehydrogenation of the rubber, the latter possibly becoming cross-linked as the result ($2{\cdot}C_5H_8 + Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow {\cdot}C_5H_7{\cdot}C_5H_7{\cdot} + 2Ph{\cdot}CO_2H$). Subsequently, Ostromislensky (" Rubber Chemistry and Technology," 1937, p. 279), following useful observations by Bock (*Kautschuk*, 1931, **7**, 224), made a new examination of the reaction and concluded that it proceeded according to the equation :

$$(C_5H_8)_n + nPh{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow nPh{\cdot}CO_2H + (C_5H_7O{\cdot}COPh)_n$$

If this view is correct, the net result of the interaction must be the *substitution* of a benzoate group in each reacting isoprene unit of the rubber chain, presumably without materially decreasing the number of the original double bonds. Evidence that the reaction does indeed occur without substantial diminution in the original unsaturation had earlier been contributed by Fisher and Gray (*Ind. Eng. Chem.*, 1928, **20**, 294).

In view of recent developments relating to the formation of free radicals during the thermal decomposition of dry or dissolved dibenzoyl peroxide (cf. Hey and Waters, *Chem. Rev.*, 1937, **21**, 169), it appeared fairly certain that Ostromislensky's equation is an over-simplified representation of the phenomena involved. For further advance in the matter, however, it seemed desirable to examine in some detail the possibilities of reaction between dibenzoyl peroxide and some convenient simple olefin. That simple olefins readily react with dibenzoyl peroxide was effectively shown by Lippmann (*Monatsh.*, 1884, **5**, 562), who heated amylene with the peroxide at 100° and obtained definite (although doubtless incorrectly identified) products; * that the scope for the exercise of such reactivity is wide is already apparent from the ever-increasing list of condensations and " polymerisations " amongst olefinic substances which can be promoted by dibenzoyl peroxide or other peroxidic material. The simplest analogue of rubber is trimethylethylene, $H[CH_2{\cdot}CMe{:}CH{\cdot}CH_2]H$, but since in this hydrocarbon the α-methylene groups are somewhat modified in character by being incorporated in methyl groups, *cyclo*hexene was chosen for examination in its place.

When a *large excess* of *cyclo*hexene was heated with dibenzoyl peroxide to 140° in a closed vessel, all the peroxide disappeared, and most of its substance entered into combination with the *cyclo*hexene. Carbon dioxide was formed during the reaction, causing increase of pressure. The reaction product contained some benzoic acid but no significant proportion of any other acidic material. The neutral portion of the product consisted of a number of hydrocarbons of the C_6- and C_{12}-series, and various benzoates derived from these hydrocarbons.

If the free-radical basis of the thermal decomposition of dibenzoyl peroxide as advanced by Hey and Waters is accepted, the radicals to be expected from the decomposed peroxide are Ph^- and $Ph{\cdot}CO{\cdot}O^-$, and these may be expected to react with the very abundant *cyclo*hexene molecules, either (*a*) extracting hydrogen atoms from them and so forming *cyclo*hexenyl radicals and radical hydrides RH (where R = Ph or $Ph{\cdot}CO{\cdot}O$),

$$(a)\ C_6H_{10} + R^- \longrightarrow C_6H_9^- + RH \qquad (b)\ C_6H_{10} + R^- \longrightarrow C_6H_9R + H^-,$$

or (*b*) expelling hydrogen atoms from them and themselves coupling with the resulting residues. Any olefin, however, which contains the grouping ${\cdot}CH_2{\cdot}CH{:}CH{\cdot}$ has two outstanding characteristics : (1) the exceptional ease with which α-methylenic hydrogen atoms can be detached (cf. Farmer and Sundralingam, this vol., p. 121, and forthcoming publications), and (2) the usual high reactivity of the double bond. The first characteristic is likely to ensure that, in spite of the general capacity of a free radical to displace a hydrogen atom from any saturated carbon atom in the *cyclo*hexene ring, the actual displacement will occur at one of the α-methylene groups. The second characteristic is of somewhat uncertain importance in the present connexion, since there is no very clear evidence to show how far attack by free radicals at the double bond in the manner (*c*) is likely to succeed, although recent investigations indicate that bromine *atoms* by adding at one end of an

$$(c)\ {\cdot}CH{:}CH{\cdot} + R^- \longrightarrow {}^-CH^-CHR$$

ethylenic bond can initiate the " abnormal " type of hydrogen bromide addition to olefins (Kharasch *et al.*, *J. Org. Chem.*, 1937, **2**, 288; *J. Amer. Chem. Soc.*, 1933, **55**, 2468, 2521, 2531), the *cis-trans*-rearrangement of stilbene (*idem, ibid.*, 1937, **59**, 1155; Taylor and Murray, J., 1938, 2078), and a species of oxygen addition to olefins (Bockemüller and Pfeuffer, *Annalen*, 1939, **537**, 178); also that sulphite radicals in a similar way can initiate the addition of sodium sulphite to olefins (Kharasch, *J. Org. Chem.*, 1938, **3**, 175), and likewise radical-molecules probably unite with olefin molecules and give by repetition of the process long macropolymeric chains (cf. Melville, J., 1941, 419).

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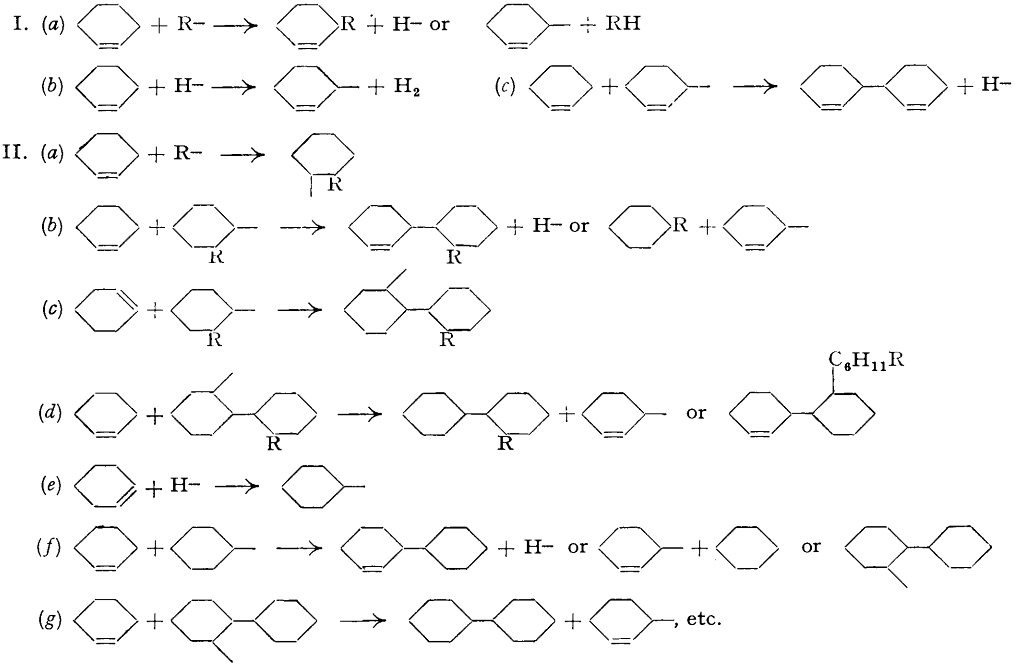
* Gelissen and Hermans' interpretation of the course followed by Lippmann's reaction (*Ber.*, 1925, **58**, 2396) is in our view erroneous.

If reaction according to (*c*) does occur to an appreciable extent, the number of possible products from dibenzoyl peroxide and *cyclo*hexene will be considerably increased, and the main lines of reaction are then likely to include the following specific reactivities,* in which R^- represents a free radical derived by decomposition of dibenzoyl peroxide.



Since $\text{R}^- = \text{Ph}^-$ or Ph·CO·O^-, the products according to (I) should be : *benzene, benzoic acid,* Δ^2-cyclo*hexenyl benzoate,* 3-*phenyl*-Δ^1-cyclo*hexene,* and $\Delta^{2'}$-cyclo*hexenyl*-Δ^2-cyclo*hexene,* whilst those according to (II) should be : 2′-phenyl*cyclo*hexyl-Δ^2-*cyclo*hexene, 2-$\Delta^{2'}$-cyclo*hexenyl*cyclo*hexyl benzoate,* phenyl*cyclo*hexane, cyclo*hexyl benzoate,* 1-phenyl-2-*cyclo*hexyl*cyclo*hexane, 2-*cyclo*hexyl*cyclo*hexyl benzoate, Δ^2-*cyclo*hexenyl-[*cyclo*hexyl-2′]-[*cyclo*hexyl-2″] benzoate, Δ^2-*cyclo*hexenyl-[*cyclo*hexyl-2′]-[*cyclo*hexyl-2″]-benzene, 3-*cyclo*hexyl*cyclo*hexene, *cyclo*hexane, *cyclo*hexyl*cyclo*hexane, etc.

The reaction products actually isolated, or otherwise identified, are shown in italics in the above list, but in addition to these, *cyclo*hexane and *cyclo*hexyl*cyclo*hexane, which would be difficult to recognise in the mixture, may well have been present in appreciable amount; phenyl*cyclo*hexane also may have been present in minor amount. The presence of *cyclo*hexyl*cyclo*hexene is doubtful. Tricyclic reaction products were not well represented, but in the highest-boiling fractions obtained from the reaction mixture the principal component (*cyclo*hexenyl*cyclo*hexyl benzoate) appeared to be admixed with appreciable proportions of tricyclic hydrocarbons (see p. 519). The substances which were found to be present in largest proportion were benzoic acid, *cyclo*hexenyl benzoate, *cyclo*hexyl benzoate, *cyclo*hexenyl*cyclo*hexene, and *cyclo*hexenyl-*cyclo*hexyl benzoate, but benzene, the yield of which could not be reliably determined, was probably also a major product.

A number of conclusions are to be drawn from the character and quantitative proportions of the chief reaction products. (1) The main bulk of the free radicals formed by decomposition of the peroxide attack the olefin molecules at the α-carbon atoms, although some not inconsiderable degree of attack apparently succeeds at the double bond. (2) It is clear that somewhere about half the Ph·CO·O· groups present in the peroxide (2 per molecule) survive in the form of benzoates, but it is not clear whether all the peroxide molecules decompose in the fashion (A) or whether some can decompose in the fashion (B). (3) The interlinking of hydrocarbon molecules, whether it occurs by the action of olefin or hydro-olefin free radicals on ordinary olefin molecules (*e.g.*, reactions I*c*, II*f*, II*g*), or of benzoate-substituted- or phenyl-substituted-hydro-olefin radicals on ordinary olefin molecules (*e.g.*, reactions II*b*, II*c*, II*d*), constitutes a very large proportion of the total reactivity observed. (4) Interlinking of olefin molecules is confined almost entirely to the " dimeric " stage of reaction, although a little phenyl-substituted " dimer " appears to have been formed. (5) *cyclo*Hexenyl-*cyclo*hexenyl benzoate, $C_6H_9{\cdot}C_6H_8{\cdot}O{\cdot}COPh$, occurs among the minor reaction products but does not appear in

$$\text{(A)}\quad \text{Ph·CO·O·O·COPh} \longrightarrow \text{Ph·CO·O·} + \text{CO}_2 + \text{Ph·}$$
$$\text{(B)}\quad \text{Ph·CO·O·O·COPh} \longrightarrow 2\text{Ph·CO·O·}$$

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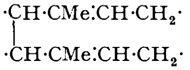
* In view of the large excess of *cyclo*hexene used, any direct union of free radicals to give R_2 is likely to be very small in amount and is neglected.

the schemes I or II; hence it is necessary to conclude that *cyclo*hexenyl*cyclo*hexene, $C_6H_9{\cdot}C_6H_9$, which is formed in considerable yield is subsequently attacked to some small extent by benzoate radicals.

In view of these results it is not surprising that the action of dibenzoyl peroxide on rubber consists largely in the attachment of numerous benzoate groups to the carbon chain (to a maximum of one benzoate group per unit) without material destruction of the original unsaturation of the rubber being caused. These groups doubtless become substitutionally attached at one or other of the α-carbon atoms of the isoprene units, but probably mainly at the α-methylene groups adjoining the methylated carbon atoms, thus :

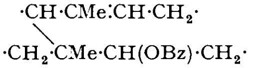
$$\cdot CH(OBz){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OBz){\cdot}CMe{:}CH{\cdot}CH_2\cdot$$

This substitution, however, will be only one of the *two* main results of the reaction with benzoyl peroxide, the second of which will involve the linking together of the rubber chains—probably largely at the α methylene groups (most usually the α-methylene groups adjoining the methylated carbon atoms) as in (*h*), but probably to some extent also at an ethylenic carbon atom in one of the interlinking units as in (*j*) or (*k*), and possibly to some minor degree in one of the other ways typified in the reactions II, (*a*)—(*g*). Some small degree of phenyl substitution in the unlinked chains according to reaction I(*a*) is also likely to have occurred.



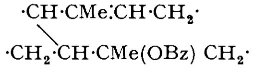
$$\begin{array}{l}\cdot CH{\cdot}CMe{:}CH{\cdot}CH_2\cdot\\ |\\ \cdot CH{\cdot}CMe{:}CH{\cdot}CH_2\cdot\end{array}$$

(*h*)



$$\begin{array}{l}\qquad\cdot CH{\cdot}CMe{:}CH{\cdot}CH_2\cdot\\ \qquad\diagdown\\ \cdot CH_2{\cdot}CMe{\cdot}CH(OBz){\cdot}CH_2\cdot\end{array}$$

(*j*)



$$\begin{array}{l}\qquad\cdot CH{\cdot}CMe{:}CH{\cdot}CH_2\cdot\\ \qquad\diagdown\\ \cdot CH_2{\cdot}CH{\cdot}CMe(OBz)\ CH_2\cdot\end{array}$$

(*k*)

As regards the widespread use of dibenzoyl peroxide and other peroxides for promoting the chemical aggregation, " polymerisation " or " condensation " of many different types of molecules, there is every reason to believe that free radicals from the decomposing peroxide initiate the cross linking, which can be continued by chain reactions.

It might be anticipated that other compounds which break down either spontaneously or on heating to give free radicals would have an action on olefins (and particularly on rubber) precisely analogous to that of dibenzoyl peroxide. It is not surprising therefore to find that diazo-compounds, whose strong tendency to break down to give free radicals and gaseous nitrogen is now well recognised (Hey and Waters, *loc. cit.*; Waters *et al.*, J., **1937**, 2007 *et seq.*), are active vulcanising agents (Buizov, *J. Russ. Phys. Chem. Soc.*, 1921, **53**, 166) for rubber. Buizov worked with diazoaminobenzene, but later Levi (*Gomma*, 1937, **1**, 4) found that all diazo-amino-compounds of the constitution $R{\cdot}N{:}N{\cdot}NXR'$, where R is an aryl group, R′ is an aryl-, aralkyl- or aryl-amino-group, and X is hydrogen, a metal, an alkyl-, acyl-, aryl- or aralkyl-group, are vulcanising agents. Also Levi observed that diazo-compounds which were effective vulcanising agents evolved nitrogen when they were heated to the usual vulcanisation temperature (*ca.* 140°),* and oxidation played no part in the vulcanising reaction. The reality of the active participation of free radicals is to be deduced from Levi's observation that diazoaminobenzene when heated alone at 150° gave 1 mol. of nitrogen and both *o*- and *p*-aminodiphenyl, a decomposition which may be represented :

$$NPh{:}N{\cdot}NHPh \longrightarrow Ph- + NHPh-$$

$$Ph- + NHPh- \longrightarrow Ph{\cdot}C_6H_4{\cdot}NH- + H- \longrightarrow Ph{\cdot}C_6H_4{\cdot}NH_2$$

Furthermore, Fisher (*Ind. Eng. Chem.*, 1939, **31**, 1381) has found, not only that 2 : 4 : 6 : 2′ : 4′ : 6′-hexa-chlorodiazoaminobenzene readily vulcanises rubber, but that some of the reagent (which presumably means fragments of the reagent molecules) adds to the rubber giving some hexachlorodiphenylamine as a by-product.

The symmetrically substituted diphenyl- and tetraphenyl-hydrazines are known to decompose readily into free radicals and these are found to produce a " stiffening " effect on rubber when kneaded into it. On the contrary, monosubstituted alkyl- and aryl-hydrazines, as well as *as*-diphenylhydrazines, act as softeners of rubber (Williams and Smith, *Ind. Eng. Chem.*, 1935, **27**, 1317), from which it may be deduced that they are promoters of oxidation, presumably functioning for this purpose in a similar manner to pyridine (cf. Farmer and Sundralingam, this vol., p. 128).

Perhaps, however, the most interesting example of an effective vulcanising agent is tetramethylthiuram disulphide, $CHMe_2{\cdot}CS{\cdot}S{\cdot}S{\cdot}CS{\cdot}CHMe_2$, which is a close sulphur analogue of dibenzoyl peroxide. The capacity of this substance to yield free radicals spontaneously or on heating has, so far as we are aware, not been demonstrated, but it is remarkable that this disulphide is not only by itself an excellent vulcanising agent for rubber, but is a first-rate accelerator of sulphur vulcanisation. The method of action of accelerators has never been determined, but it seems not unlikely that the effectiveness of at least some of them is due to their capacity to yield free radicals spontaneously or on heating, either when used in the form of their zinc salts (*e.g.*, dithio-carbamates, $R_2N{\cdot}CS{\cdot}SH$; thiolbenzthiazole, $C_6H_4{<}\overset{N}{\underset{S}{}}{>}C{\cdot}SH$) or when used directly [*e.g.*, tetramethyl-thiuram disulphide; di(benzthiazolyl) disulphide, $C_6H_4{<}\overset{N}{\underset{S}{}}{>}C{\cdot}S{\cdot}S{\cdot}C{<}\overset{N}{\underset{S}{}}{>}C_6H_4$].

Ostromislensky's reaction between dibenzoyl peroxide and rubber appears to involve two distinct features, *viz.*, the interlinking of rubber units (which process may be inter- or intra-molecular and so take the form of cross linking of molecules or cyclisation reactions), and the addition of fragments to the rubber chain. This

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* Curiously enough, diazonium chlorides, $R{\cdot}N_2Cl$, in spite of their decomposability at vulcanisation temperatures, were found not to serve as vulcanising agents.

dual type of reaction probably extends also to sulphur vulcanisations, and to vulcanisations in which the action of sulphur is assisted by an organic accelerator. The exact course of reaction in either of these cases is uncertain, but in both cases the production of a satisfactory vulcanised structure as determined by a physical test (the tensile strength *) is but little dependent on the loss of original unsaturation in the rubber. Thus Brown and Hauser (*ibid.*, 1938, **30**, 1291; 1939, **31**, 1225) have found that the optimum (physical) state of vulcanisation of rubber obtained when tetramethylthiuram disulphide is the vulcanising agent (*i.e.*, when no free sulphur is used) occurs when $<2\%$ of the original rubber-unsaturation has been lost, and an average of 0·25 atom of sulphur per C_5H_8 unit has been incorporated in the rubber chain. At this point chemical incorporation of sulphur in the rubber stops, and if heating at the vulcanisation temperature (141°) is continued, it causes little further diminution in the unsaturation. When the vulcanising agent is sulphur, used in conjunction with a small proportion of active accelerator, the loss of unsaturation on vulcanisation appears in most examples to amount only to several units % at the point of optimum vulcanisation; but often chemical incorporation of sulphur continues beyond this point, and concurrently the unsaturation usually continues to decrease, although the amount of this decrease varies considerably from accelerator to accelerator. For sulphur used alone as vulcanising agent a larger decrease in unsaturation than the foregoing value was observed at the point of optimum vulcanisation, and both the incorporation of sulphur and the decrease in unsaturation continued rapidly beyond this point. The best vulcanisates over the range of experiments were obtained when the proportion of combined sulphur at the point of optimum vulcanisation amounted to *ca.* 2 atoms per double bond lost, and not to 1 atom as has previously been supposed. It appears, therefore, from these observations that the incorporation of sulphur, and the concurrent saturation of double bonds can continue (especially if sulphur alone is used) after the essential work of vulcanisation is completed, and this reactivity may perhaps be considered as a side reaction which, although having an effect on the properties of the vulcanisates, is subsidiary to the basic process of vulcanisation.

Such subsidiary saturation of the double bonds could conceivably be caused by the direct addition of hydrogen sulphide, if sufficient of this reagent were generated in the vulcanisation reaction (for which there is little direct evidence), or alternatively it might result from a secondary reaction following after the primary reaction at the α-methylene carbon atoms; on the other hand, it is quite unlikely, in view of the usual incapacity of sulphur to act as an addendum for olefins, to be caused by the direct addition of sulphur at the double bonds. The fact that sulphur reacts readily with unconjugated di- and poly-olefinic substances such as linoleic and linolenic esters and glycerides (these substances showing a marked tendency for the ordinary olefinic additivity to be replaced by an α-methylenic substitutive tendency) suggests that the initial attack by sulphur in the sulphur-vulcanisation reaction may occur (like that of oxygen) at the α-methylene groups, and may possibly be succeeded (somewhat comparably with secondary autoxidation processes) by one or several types of secondary reaction which cause saturation of the double bonds. Such α-methylenic attack by sulphur may well be initiated by extraneous free radicals formed under vulcanisation conditions, or possibly by free radicals formed by direct thermal dissociation of α-methylenic hydrogen atoms. The precise course of reaction, however, remains to be determined.

Another phenomenon which appears to involve the production of a vulcanised structure in which the incorporation of foreign atoms or fragments in the hydrocarbon chains plays a part is the photo-gelling of dissolved rubber. The absolute dependence of this phenomenon on sunlight or ultra-violet light, its entire independence of any concurrent autoxidation process,† and also its promotion by acetone, acetophenone, benzophenone, etc., and by certain halogenated solvents (carbon tetrachloride, ethylene dibromide, chloroform, chloro- and dichloro-benzene, dichloro- and trichloro-ethylene, in order of decreasing efficiency) which not only are themselves prone to undergo photochemical decomposition with formation of free radicals, but can contribute these radicals (alkyl groups formed from the ketones, and chlorine atoms and chlorinated fragments from the halogenated solvents) to the interlinking hydrocarbon units or molecules, all suggest that the gelling takes a course closely analogous to those represented above for *cyclo*hexene and dibenzoyl peroxide. Stevens (*Trans. Inst. Rubber Ind.*, 1940, **16**, 211) has described the progress of gelling with the above-mentioned and other promoters, one or more of these usually acting as solvents for the rubber. Mixtures of acetone and carbon tetrachloride are particularly effective as promoters, and ethyl ether containing peroxides or acting in the presence of such peroxides as barium peroxide is also successful. Benzoyl peroxide in carbon tetrachloride–acetone acts very slowly in the dark, but more effectively under illumination to give extensively chlorinated gels, thus suggesting that, although in general free-radical decomposition of peroxides promoted by light can initiate the gelling reaction, yet a slow thermal decomposition similar to that which occurs in Ostromislensky's reaction at 140° can also feebly initiate gelling in conjunction with carbon tetrachloride–acetone. The gels produced differ in consistency, according to the efficiency of the promoters used, from tenuous gels, which oxidise readily in the presence of air and light to regenerate liquids, to tough materials easily cut by scissors. The dried rubbers recovered from the gels by evaporation of the solvent differ correspondingly in physical properties, but the extent to which the gelling promoters have become incorporated is shown by the large increases in weight, and in the case of halogenated promoters by the substantial halogen contents, most of which remain after treatment of the materials by boiling alcoholic potash. As would be expected, the physical

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* This is only one, although a very important one, of the usual criteria of satisfactory vulcanisation.

† Oxygen, if present, delays gelling.

properties of the dried halogenated photo-gels obtained from rubber by means of dibenzoyl peroxide dissolved in carbon tetrachloride–acetone differ considerably from those of rubber vulcanised by Ostromislensky's procedure.

The profound difference between the result of irradiating rubber in presence of a potential source of free radicals such as acetaldehyde, first in strict absence of oxygen, and then in presence of oxygen, is clear from experiments of Spence and Ferry (*J. Soc. Chem. Ind.*, 1939, **58**, 345; *J. Amer. Chem. Soc.*, 1937, **59**, 1468). Under the first conditions vulcanisation or " polymerisation " occurs in the manner described above, and in the second, rapid autoxidation of the rubber sets in with oxidative scission of the hydrocarbon chains and " depolymerisation " of the rubber. The acetaldehyde in the latter conditions acts as a powerful autoxidation catalyst (see this vol., p. 144; Bloomfield and Farmer, *J. Soc. Chem. Ind.*, 1934, **53**, 121T).

EXPERIMENTAL.

Action of Benzoyl Peroxide on cyclo*Hexene*.—The peroxide (50 g.; 1 mol.) and *cyclo*hexene (200 c.c.; 9·6 mols.) were heated together in a stainless-steel autoclave or in sealed glass tubes at 140° for 6 hours. Carbon dioxide was produced and caused a small increase above atmospheric pressure in the cooled vessel. The resulting clear, slightly yellow liquid was shaken several times with 2N-sodium hydroxide, then with water, and finally it was dried over anhydrous sodium sulphate. The combined alkaline and aqueous washings were acidified, and the precipitated acid filtered off; it proved to be benzoic acid, m. p. 121° (equiv., 122), uncontaminated by any other acid.

The main reaction product was fractionally distilled : at atmospheric pressure, a forerun (I) (102 g.), consisting mainly of unchanged *cyclo*hexene, passed over, leaving a liquid residue which was divided into the following fractions by distillation at 0·1 mm. pressure : (II) (*a*) b. p. 70—74° (7·2 g.), (*b*) 74—110° (1·0 g.); (III) (*a*) 112—116° (33 g.), (*b*) 116° (2·0 g.), (*c*) residue in still (16·8 g.). The distillates were colourless liquids, the earlier ones mobile, the later ones viscous liquids. The residue was divided by distillation from a molecular (batch) still into the fractions : (IV) (*a*) bath-temperature 146—148° (12·9 g.), (*b*) bath-temp. 150—180° (1·1 g.), (*c*) yellow, very viscous, oily residue (2·8 g.), probably somewhat decomposed. This procedure was carried out numerous times with new batches of the reactants, but in the later experiments the re-fractionation of fraction (IV) was omitted.

Fraction (I). The forerun, although consisting mainly of *cyclo*hexene, was not homogeneous. The likely adulterants were *cyclo*hexane and benzene, but these were present in too small proportion to permit of their separation by careful fractional distillation, either directly, or after conversion of the *cyclo*hexene component into its dibromide; indeed, no satisfactory method of demonstrating the presence of a little *cyclo*hexane in the forerun was discovered. Spectroscopic examination, however, of the forerun showed unmistakably that a benzenoid compound was present. The absorption curves for (*a*) benzene in *cyclo*hexane, and (*b*) *cyclo*hexene in *cyclo*hexane at dilutions of 2½% and below show sufficiently marked differences to permit the presence of benzene to be distinguished at concentrations greater than 0·1%, and the presence of *cyclo*hexene at concentrations above 2%. When both benzene and *cyclo*hexene are present in *cyclo*hexane the former cannot be detected with certainty if the concentration of *cyclo*hexene is above *ca.* 3%, and the latter cannot be detected if the concentration of the benzene exceeds 0·1%; consequently, unless the concentration of benzene in the mixture is less than 1/30 of that of the *cyclo*hexene and itself exceeds 0·05%, its characteristic absorption will be masked by that due to the *cyclo*hexene. The absorption curves for (i) dilute solutions of benzene and *cyclo*hexene (together) in *cyclo*hexane, and (ii) dilute solutions of the forerun in *cyclo*hexane were found to be closely similar, but when solutions in *cyclo*hexane of the hydrogenated forerun (*i.e.*, forerun which had been hydrogenated as fully as possible at room temperature in presence of Adams's catalyst in order to convert *cyclo*hexene into *cyclo*hexane) were examined, the presence of benzene became unmistakable, and its concentration in the forerun was estimated to be 2·5%.

Fraction (II)(*a*). This fraction was an impure hydrocarbon of the C_{12}-series containing about 1% of oxygen and $|\overline{1}{\cdot}74$ (Found : C, 88·05, 87·9, 88·15; H, 10·95, 11·05, 10·95; iod. val., 272. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%; iod. val., 313).

A portion of this fraction (1 g.) was heated with powdered selenium (2 g.) at about 300° for 100 hours. The product was extracted with ether, the ether distilled, and the oily residue heated for a time over sodium. The liquid residue was freed from a little solid inorganic matter by dissolving it in ether, filtering, and removing the solvent; afterwards it was distilled. The bulk (0·5 g.) distilled at 98—108°/12 mm., and appeared to be unchanged hydrocarbon, but the succeeding portion distilled when the bath reached 200°, and solidified in the receiver. This solid was diphenyl, m. p. 69° (mixed m. p. 68—69°) (Found : C, 93·1; H, 6·75. Calc. for $C_{12}H_{10}$: C, 93·5; H, 6·5%).

Hydrogenation of a portion (4·7 g.) of this fraction in 5 c.c. of alcohol at room temperature and pressure in presence of Raney nickel (1240 c.c. of hydrogen absorbed, corresponding to 95·4% of that required for $C_{12}H_{18}$) gave a colourless liquid hydrocarbon, quite saturated to alkaline permanganate, but having too high a C/H ratio for *cyclo*hexyl*cyclo*hexane (Found : C, 87·3, 87·15; H, 12·75, 12·75. Calc. for $C_{12}H_{22}$: C, 86·65; H, 13·35%). Spectroscopic examination of the hydrogenated hydrocarbon side by side with pure *cyclo*hexyl*cyclo*hexane revealed U.V. absorption for the former approximately 100 times as strong as was shown by the latter, and an absorption band for the former in the appropriate region for benzene derivatives (2400—2550 A.; $\log_m \xi = 2{\cdot}0$); no individual maxima could, however, be observed. The curve for the hydrogenated hydrocarbon was approximately a mean between those of *cyclo*hexyl*cyclo*hexane and diphenyl, but it has not been possible to make direct comparison with the curve for pure phenyl*cyclo*hexane. The succeeding experiments confirm that the bulk of fraction (II)(*a*) was *cyclo*hexenyl*cyclo*hexene; the contaminant was doubtless mainly phenyl*cyclo*hexene, with possibly a little phenyl*cyclo*hexane.

A further portion of fraction (II)(*a*) (9 g.) was dissolved in chloroform and treated gradually at 0° with excess of N/5-bromine in chloroform (2 mols. of Br_2 per mol. of $C_{12}H_{18}$). The excess of bromine and most of the chloroform were evaporated at reduced pressure, whereupon much crystalline bromide separated (65% yield). This formed colourless prisms, m. p. 159°, from chloroform and proved to be $\Delta^{2'}$-cyclo*hexenyl*-Δ^2-cyclo*hexene tetrabromide* (Found : C, 29·8, 29·9; H, 3·9, 4·05; Br, 66·25. $C_{12}H_{18}Br_4$ requires C, 29·9; H, 3·75; Br, 66·35%). The tetrabromide appears to be identical with that, m. p. 158°, obtained by Cogan and Marvel (*J. Amer. Chem. Soc.*, 1934, **56**, 1815) from a hydrocarbon which they thought was probably di-Δ^2-*cyclo*hexenyl.

A portion of the tetrabromide (9 g.) was debrominated by zinc dust in alcoholic solution, giving thereby the parent hydrocarbon $\Delta^{2'}$-*cyclo*hexenyl-Δ^2-*cyclo*hexene, but this was contaminated with a little bromide (Found : C, 86·3; H, 10·6%). The constitution of the hydrocarbon was established by ozonisation of a portion in chloroform, without further purification, the ozonide giving on decomposition with water, and further oxidation of the product with dilute alkaline permanganate at 0°, a tetracarboxylic acid, $C_8H_{14}(CO_2H)_4$, which separated from ether (in which it was sparingly soluble) as a white crystalline powder, m. p. 177°. This was n-*octane*-$\alpha\delta\epsilon\theta$-*tetracarboxylic* acid (Found : C, 49·8; H, 6·45; equiv., 72·3. $C_{12}H_{18}O_8$ requires C, 49·65; H, 6·25%; equiv., 72·5).

The bromide recovered from the mother-liquors was freed as far as possible from the crystalline bromide, by crystallisation of the latter from light petroleum, and the solvent then completely removed at reduced pressure. The residual bromide was a brown viscous liquid (Found : Br, 59·3%). In order to remove from this any unbrominated (non-olefinic) hydrocarbons of the C_{12}-series, the liquid bromide was partly distilled, at 0·05 mm. pressure, whereupon only a few drops (0·1 g.) of impure hydrocarbon (Found : C, 81·05; H, 9·05%) passed over, leaving a residue which from its bromine content appeared to consist largely of a dibromide. This was probably, in view of the foregoing spectroscopic evidence, derived from phenyl*cyclo*hexene; some proportion of the dibromide of *cyclo*hexyl*cyclo*hexene, may, however, have been present.

Fraction (II)(*b*). This consisted of a mixture of C_{12}-hydrocarbon and the material of fraction (III).

Fraction (III)(*a*). This colourless oil of strong odour consisted of a mixture of benzoates of C_6-alcohols. The analytical values, which differed little from preparation to preparation, taken in conjunction with the iodine and benzoyl values, show that the mixture consisted of *cyclo*hexenyl benzoate and *cyclo*hexyl benzoate in roughly the proportion of 3 : 10 (Found : C, 76·55; H, 7·65; Bz, 59·4; iod. val., 38·4. Calc. for $C_6H_5{\cdot}CO_2C_6H_9$: C, 77·3; H, 6·9; Bz, 60·0%; iod. val., 125. Calc. for $C_6H_5{\cdot}CO_2C_6H_{11}$: C, 76·5; H, 7·85; Bz, 59·4%; iod. val., 0). The benzoyl value was determined by refluxing portions (6 g.) of the mixed esters with N-methyl-alcoholic sodium hydroxide (100 c.c.) in a nitrogen atmosphere for 5 hours, and then titrating with N-hydrochloric acid.

The mixed alcohols from the hydrolysed ester fraction were obtained by distilling off, through a column, the methyl alcohol from the basified hydrolysis products, and then thoroughly extracting the residue with ether. The ethereal solution after being dried (anhydrous sodium sulphate), gave a colourless, viscous liquid of strong smell. This was a mixture (*ca.* 1 : 4) of *cyclo*hexen-3-ol and *cyclo*hexanol (Found : C, 72·35; H, 11·65; iod. val., 64. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%; iod. val., 258·8. Calc. for $C_6H_{12}O$: C, 71·9; H, 12·1%). A crude α-naphthylurethane prepared from the mixture gave after several crystallisations from ether the pure α-naphthylurethane of *cyclo*hexanol, forming colourless needles, m. p. 128° (mixed m. p. 128°) (Found : C, 76·0; H, 6·8; N, 5·4. Calc. for $C_{17}H_{19}O_2N$: C, 75·8; H, 7·1; N, 5·2%); the corresponding derivative of *cyclo*hexen-3-ol was not isolated in pure form. Acidification of the alkaline hydrolysis liquor gave at once benzoic acid, which melted after one recrystallisation from water at 121°; no other aromatic acid could be found.

On addition of N/5-bromine in chloroform to a solution of the mixed alcohols (0·8 g.) in chloroform at 0°, 0·3 mol. of bromine was decolorised, and the product gave on removal of the solvent at reduced pressure a liquid from which by distillation (*a*) 0·5 g. of crystallisable *cyclo*hexanol, b. p. 60—64°/12 mm., and (*b*) 0·5 g. of 1 : 2-dibromo*cyclo*hexan-3-ol (clusters of needles, m. p. 55°, from light petroleum; mixed m. p. with authentic specimen of m. p. 55°, 55°. Found : C, 27·8; H, 4·2; Br, 62·4. Calc. for $C_6H_{10}OBr_2$: C, 27·9; H, 3·9; Br, 62·0%) were isolated.

Fraction (IV). The sub-fractions (*a*)—(*e*) were entirely saponifiable. Each fraction was analysed and then hydrolysed by 5 hours' heating with N-methyl-alcoholic sodium hydroxide. The derived alcohols were also analysed. It was apparent that no satisfactory fractionation had been achieved. A much better result was obtained by hydrolysing batches of fraction (IV) directly (*i.e.*, without any distillation) and isolating and fractionally distilling the derived alcoholic material at *ca.* 0·3 mm. pressure. Numerous such fractions were obtained having somewhat different composition and unsaturation, but the bulk of the material fell into three rather well-defined fractions : (i) a small amount of mobile liquid, b. p. 80°/0·3 mm., (ii) a viscous liquid, b. p. 90—100°/0·5 mm., (iii) a very viscous liquid, b. p. 100—118°/0·1 mm. The sub-fraction (i) resembled in all characteristics the mixture of *cyclo*hexanol and *cyclo*hexenol obtained by hydrolysis of fraction (III), and was not further examined. The sub-fraction (ii) was a mono-olefinic dicyclic alcohol, $C_{12}H_{20}O$ [Found : C, 80·2; H, 11·15; iod. val., 112; * *M* (in benzene), 185. Calc. for $C_{12}H_{20}O$: C, 79·9; H, 11·1%; iod. val., 141; *M*, 180]. This probably consisted mainly of Δ^2-*cyclo*hexenyl*cyclo*hexan-2-ol, although some proportion of its isomeride, 1-*cyclo*hexyl-Δ^2-*cyclo*hexen-4-ol, may have been present. The sub-fraction (iii), which distilled only with difficulty at 0·1 mm., gave carbon and molecular-weight values well above those required for a dicyclic alcohol of the C_{12}-series. The composition varied somewhat from preparation to preparation [*e.g.*, Found : (*a*) C, 83·5; H, 11·6; *M*, 206. (*b*) C, 84·0; H, 10·7; *M*, 214. (*c*) C, 82·8; H, 10·8%], but the range of variation in the hydrogen values was comparatively small. The fraction appeared to consist of a mixture of the dicyclic alcohols appearing in fraction (ii) with a minor proportion of a tricyclic hydrocarbon such as phenyl*cyclo*hexyl*cyclo*hexane (Calc. : C, 89·2; H, 10·8%; *M*, 242·2) or phenyl*cyclo*hexyl*cyclo*hexene (Calc. : C, 89·9; H, 10·1%; *M*, 240·2).

The acid obtained by saponification of fraction (IV) was homogeneous benzoic acid.

Yields.—The following table shows approximately the recovery of Ph·CO·O· groups (contained originally in the dibenzoyl peroxide) in a typical run employing 100 g. of peroxide and 400 c.c. of *cyclo*hexene.

	Fraction.	Wt. (g.).	Wt. of Ph·CO·O· (g.).
(I)	Forerun	—	—
(II)	C_{12}-hydrocarbon	24	(*ca.*) 2
(III)	Benzoates of C_6-alcohol	51	30—32
(IV)	Benzoates of C_{12}-alcohol	31	12—13
	Free benzoic acid	15	12—15
		Total	54—62

This shows that between 38% and 46% by weight of the original Ph·CO·O· groups in the peroxide had broken down during reaction and must thus have given rise to phenyl radicals and carbon dioxide amounting to 12—14% and 7—8% respectively of the weight of the original peroxide.

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* The iodine values of all the sub-fractions derived by hydrolysis of Fraction (IV) were somewhat low. The corresponding hydrogen values were considerably lower still.