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THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION

Publication No. 72

MODERN VIEWS ON THE CHEMISTRY OF VULCANIZATION CHANGES.

Part I. NATURE OF THE REACTION BETWEEN SULFUR AND OLEFINS.

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[Reprinted from Journal of Polymer Science, Vol. 1, No. 4, pp. 293–304, 1946.]

Modern Views on the Chemistry of Vulcanization Changes. I. Nature of the Reaction between Sulfur and Olefins*

E. HAROLD FARMER and F. W. SHIPLEY, *British Rubber Producers' Research Association, Welwyn Garden City, England*

Received May 20, 1946

Synopsis* — Whatever additional factors may be concerned in the production of good vulcanizates from natural rubber by the action of sulfur, there is no doubt that the action of sulfur on olefinic materials in general at the ordinary vulcanization temperature is a chemical one, the primary course of which is determined largely by the constitution of the olefin, and hence may be profitably studied by experimentation with olefins of different unsaturation patterns. Unaccelerated reaction between sulfur and simple monoolefins leads almost exclusively to cross linking of the separate olefin molecules, mostly in pairs, by groups of sulfur atoms. When, however, two or more olefinic units occur in the same molecule, as in the diisoprenic hydrocarbons, intramolecular cross linking, i.e., cyclization, at once becomes possible, and the result of sulfur action consists partly in the cross linking of separate molecules as with the monoolefins, but largely in cyclization of the individual olefinic chains, thereby forming sulfur-containing rings. These changes entail a certain loss of unsaturation, from which deductions can be made as to the mechanism of the reaction.

VULCANIZATION AND CROSS LINKING

AT THE PRESENT TIME it is taken for granted that in all kinds of linear high polymers, natural or artificial, true polymers or polycondensation products, the establishment of cross links between adjacent thread molecules is in itself sufficient to transform the physical properties of the material, producing a state which can be collated with the vulcanized state in rubber. Yet in most of these instances—and particularly in the case of the vulcanization of natural and synthetic rubbers by sulfur, by peroxides, and by other reagents—the idea that the vulcanized products with their characteristic toughness, swelling capacity, elasticity, etc., derive their special qualities from the mere formation (by one means or another) of connecting links between the original linear molecules still remains a matter of hypothesis. The sulfur-vulcanization process as applied to rubber presents many interesting and very elaborate features, especially those connected with its capacity for being accelerated by a host of similar and dissimilar organic substances, and for being retarded, reversed, delicately controlled, etc. Hence, it is of considerable interest to find out by experiment exactly what sulfur does to the rubber when the two are heated together (either alone or in the presence of different types of accessory reagents) and, thence, to discover whether the production of good *vulcanized* properties is in truth dependent on the production of chemical cross links, or

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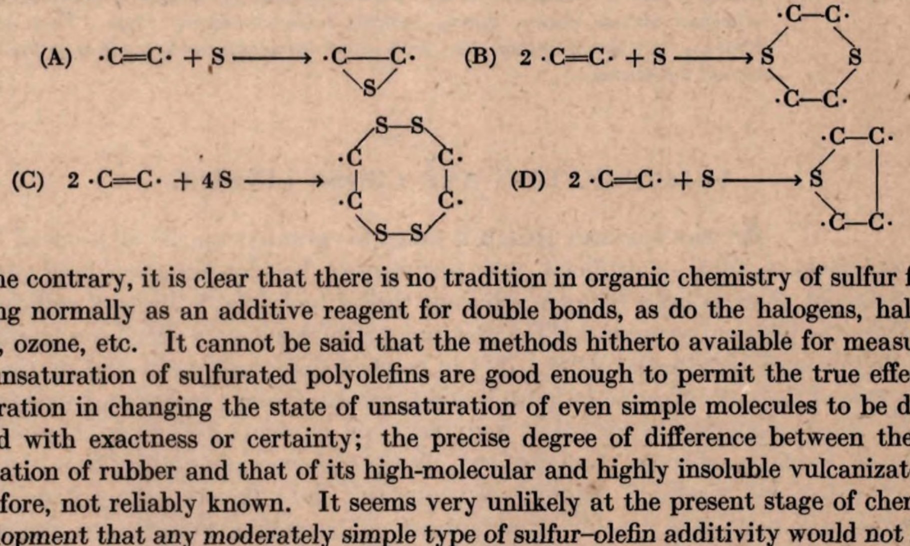
*** The work described in this series of papers forms part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The experimental details will be published formally at a later date.**

on certain kinds of chemical cross links, or on a judicious combination of cross linking and mere sulfuration (the latter possibly assisting the establishment of van der Waals' forces between molecules as an auxiliary factor); or whether, as some physical chemists have been inclined to allege, it results from a state of physical association between molecules which has little or nothing to do with cross linking. The present series of communications describes recent experimental advances in this subject; it is necessary to explain at the outset that the method of experimental approach adopted has of necessity (owing to the formidable molecular magnitude of even unvulcanized rubber) been by way of the response to vulcanization treatment of comparatively simple olefinic materials. This approach has thus involved in the first place a study of the chemistry of simple sulfur–olefin reactivity, which was previously never carried far.

SULFUR AND THE OLEFINIC BOND

Long observation by numerous workers of the chemical character of the sulfur vulcanizates of natural rubber has resulted in the generalization that (with fair exactness) one double bond of the hydrocarbon becomes saturated for each atom of sulfur which is chemically incorporated. This conclusion has rather naturally led to the *assumption* that the sulfur is essentially an additive reagent for double bonds, although no evidence has been adduced to show that simple additive courses, such as those represented in equations (A)–(D), are followed:



On the contrary, it is clear that there is no tradition in organic chemistry of sulfur functioning normally as an additive reagent for double bonds, as do the halogens, halogen acids, ozone, etc. It cannot be said that the methods hitherto available for measuring the unsaturation of sulfurated polyolefins are good enough to permit the true effect of sulfuration in changing the state of unsaturation of even simple molecules to be determined with exactness or certainty; the precise degree of difference between the unsaturation of rubber and that of its high-molecular and highly insoluble vulcanizates is, therefore, not reliably known. It seems very unlikely at the present stage of chemical development that any moderately simple type of sulfur–olefin additivity would not have been recognized and described, and it is perhaps not unreasonable to turn to that chemical analog of sulfur, oxygen, the high general reactivity of which toward olefinic materials has similarly resisted correlation with any simple scheme of double-bond additivity. Oxygen has, however, in recent years been shown to react with olefinic substances by a radical mechanism involving chain reactions, in which the first main step consists of the detachment of α-methylenic hydrogen atoms by oxygen ($\cdot CH_2 \cdot CH{:}CH\cdot + O_2 \rightarrow \cdot \underset{*}{C}H \cdot CH{:}CH\cdot + {}^*OOH$), and the second, of the addition of oxygen to the olefinic radicals so formed: $\cdot \underset{*}{C}H \cdot CH{:}CH\cdot + O_2 \rightarrow \cdot CH(OO^*) \cdot CH{:}CH\cdot \xrightarrow{\cdot CH_2 \cdot CH:CH}$

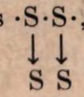
$$\cdot CH(OOH) \cdot CH{:}CH\cdot + \cdot \underset{*}{C}H \cdot CH{:}CH\cdot$$

> **It is quite likely that the reaction chains are started in all varieties of olefinic materials by a few additions of oxygen molecules at one end of double bonds, but these immediately set going the detachment of α-methylenic hydrogen atoms.[1]**

It seemed, at the outset of the work described here that sulfur—which like oxygen contains two unpaired electrons in its outer shell—might well behave in an essentially similar way to oxygen in initiating its attack on olefins ($\cdot CH_2\dot{\cdot}CH{:}CH\cdot + S_x \rightarrow \underset{*}{C}H\cdot CH{:}CH\cdot + S_xH$). If this conception is sound, it would account at once for the nonformation by sulfur of simple double-bond addition products and could probably also provide a guide to the lines of sulfur–olefin reactivity in general. The first experiments undertaken in this field gave the strongest support to the idea of radical reaction by sulfur (probably with very short reaction chains); the succeeding experiments revealed the existence of striking relationships and differences between the action of sulfur and that of hydrogen sulfide on the same olefinic materials.

SULFURATION OF MONOOLEFINS

Effective attack by sulfur on olefinic materials begins ordinarily at temperatures around the usual vulcanization temperature (140°) employed for rubber. When the two reactants are heated together at 140° for several hours, progressive, but not very rapid, reaction sets in, and there are generally produced bimolecular sulfo derivatives of the olefin, having the composition $R\cdot S_x\cdot R'$, where R and R′ are radicals derived from the olefin by loss or gain of a hydrogen atom, and x varies in magnitude from one to five according to the proportion of sulfur taken up and the duration of heating. Thus, cyclohexene, C_6H_{10}, with sulfur gives a mixture of sulfurated materials of varied boiling point and viscosity in which (*a*) the H/C ratio characterizing the original hydrocarbon survives unchanged in the sulfo compound at the value 10/6, and (*b*) the average composition of the mixture can be expressed by the formula $C_6H_9\cdot S_x\cdot C_6H_{11}$. The last statement does not preclude the presence, to some small or large extent, of equal amounts of $C_6H_9\cdot S_x\cdot C_6H_9$ and $C_6H_{11}\cdot S_x\cdot C_6H_{11}$ in place of the *average compound* $C_6H_9\cdot S_x\cdot C_6H_{11}$. The mixture can be separated into mono-, di-, tri-, etc. sulfides by high-vacuum (molecular) distillation, but it is highly essential that the temperature not be allowed to rise above the original vulcanization temperature, since the fractionated materials are highly sensitive to temperatures 10° or so higher, or even to very prolonged heating at the vulcanization temperature. The higher temperatures or the prolonged heating cause severe *cracking* of the products with evolution of hydrogen sulfide and mercaptans, and when this degradation sets in, the task of distinguishing primary from secondary products of reaction becomes impossible. In the *separated* mono-, di-, tri-, etc. sulfo derivatives, the average composition, $C_6H_9\cdot S_x\cdot C_6H_{11}$, appears to be tolerably well maintained, but evidence is not lacking that for mono-, di-, tri-, etc. sulfides all three types of compound—$R_{satt.}\cdot S_x\cdot R'_{unsat.}$, $R_{sat.}\cdot S_x\cdot R_{sat.}$, and $R_{unsat.}\cdot S_x\cdot R_{unsat.}$—are to be found, the radical $R_{unsa.}$ containing one double bond. The question of whether those members of the polysulfide group, S_x, in which $x > 2$ consist of sulfur chains or are partly co-ordinated assemblages of sulfur atoms, such as $\cdot\underset{\substack{\downarrow\\ S}}{S}\cdot\underset{\substack{\downarrow\\ S}}{S}\cdot$, is considered later.



$$\cdot\underset{\substack{\downarrow\\ S}}{S}\cdot\underset{\substack{\downarrow\\ S}}{S}\cdot$$

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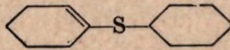
[1] E. H. Farmer, *Trans. Inst. Rubber Ind.*, **21**, 122 (1946); *Trans. Faraday Soc.*, **42**, 228 (1946).

These observations appear to preclude entirely the possibility that sulfur reacts with the olefin merely by a dehydrogenation mechanism, thereby producing hydrogen sulfide which immediately constitutes itself the effective cross-linking instrument by combining in turn with two molecules of the original olefin to give a saturated sulfide:

$$C_6H_{10} + S \longrightarrow C_6H_8 + H_2S$$

$$C_6H_{10} + H_2S \longrightarrow C_6H_{11}\cdot SH \xrightarrow{C_6H_{10}} C_6H_{11}\cdot S\cdot C_6H_{11}.$$

Jones and Reed[2] have reported that the interaction of cyclohexane and sulfur at the rather high temperature of 180° yields as main products cyclohexyl mercaptan and dicyclohexyl sulfide, apparently formed according to these equations. Meyer and Hohenemser[3] working at 150° have also reported the formation of the same two products, suggesting that unsaturated compounds,  and , may be formed initially, these subsequently becoming saturated—possibly by taking hydrogen atoms from mercaptan groups; the latter correspondingly become oxidized to disulfide groups. Neither set of authors considers the significance of the accompanying high-boiling products in relation to the possibility that the saturated mercaptan and sulfide are purely secondary products.

If this is the actual course of reaction there must be formed, concurrently with the hydrogen sulfide, a corresponding amount of cyclohexadiene (or more probably, benzene), whereas in practice the amount which is found at the end of the operation is trivial. It is true, however, that if cyclohexadiene (but not benzene) and hydrogen sulfide were indeed formed in a substantial degree, the latter might perhaps unite with the former in preference to uniting with cyclohexene; it would thereby be used up in the formation of an unsaturated mercaptan, $C_6H_9\cdot SH$, which might then conceivably combine with cyclohexene to produce the *average* observed product, $C_6H_9\cdot S_x\cdot C_6H_{11}$ (rather than the wholly saturated sulfide shown in the above equation) and so serve to maintain the overall H/C ratio at the value 10/6 appropriate to the original olefin. But even if hydrogen sulfide is thus generated in quantity and immediately used up in the formation of sulfides ($R\cdot S\cdot R'$) there is no likelihood that the latter could then (by secondary reaction) yield polysulfides, $R\cdot S_x\cdot R'$, the commonly obtained products of sulfuration (the amount of monosulfide in the polysulfide mixture invariably appears to be small). Experiment shows clearly that when hydrogen sulfide is caused to react with monoolefins (see Part II, p. 305) the products, even when free sulfur is available, provided the addition is of *normal* type (see Part II), are monosulfides almost entirely, not polysulfides.

When 1-methylcyclohexene-1 (which contains the polyisoprenic unit, $\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot$) is employed in place of cyclohexene, the reaction with sulfur becomes, as would be expected, easier, as is shown by the improved yields of sulfo derivatives. The products obtained, however, are strictly analogous to those from cyclohexene. There is but a mere trace of hydrogen sulfide, no recognizable yield of mercaptan, $R\cdot SH$, and but little monosulfide, $R\cdot S\cdot R$ or $R\cdot S\cdot R'$. The main products (as isolated by molecular distillation) are the di-, tri-, tetra-, and pentasulfides, $R\cdot S_x\cdot R'$ and/or $R\cdot S_x\cdot R$, and the residue—as with the cyclohexene sulfuration product—consists of a quantity of highly sulfurated, undistillable material. The experimentally determined H/C ratio of the isolated sulfides remains very close to the value, 12/7, characterizing the original hydrocarbon, thus agreeing with the *average* formulation, $C_7H_{13}\cdot S_x\cdot C_7H_{11}$, but not precluding the presence of equivalent amounts of $C_7H_{13}\cdot S_x\cdot C_7H_{13}$ and $C_7H_{11}\cdot S_x\cdot C_7H_{11}$.

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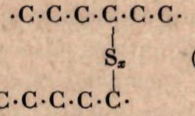
[2] S. O. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938).

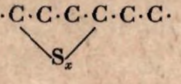
[3] K. H. Meyer and W. Hohenemser, *Helv. Chim. Acta*, **18**, 1061 (1935).

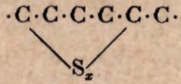
Quite similarly the sulfuration of isobutylene at 140° gives mainly distillable products which have proved to be di-, tri-, and tetrasulfides having (an average) monoolefinic unsaturation, and agreeing in average composition with the formula, $CHMe_2 \cdot CH_2 \cdot S_x \cdot CH_2 \cdot CMe{:}CH_2$.

SULFURATION OF DIOLEFINS

In passing from a monoolefin to an isoprenic diolefin the scope for complexity of reaction increases, because the olefin-coupling capacity characteristic of the former can take place intramolecularly, as well as intermolecularly, with the latter. Thus a diolefin possessing the polyisoprenic ($\Delta^{1,5}$-) unsaturation pattern, $\cdot C{:}C \cdot C \cdot C \cdot C{:}C \cdot$, may reasonably be expected to give either a dimolecular sulfide, such as is shown without unsaturation details in (E), or a cyclic sulfide with a (presumably) five- or six-membered ring, as indicated in (F) and (G):


(E)


(F)


(G)

The formation of an episulfide (thioepoxide) containing the ring has never been reported to occur by the action of free sulfur on olefins, and no compound of this structure has been found in the present investigations.

Experiment shows clearly that the diisoprenic hydrocarbon dihydromyrcene, $CH_3 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH \cdot CH_3$, gives two main products. The first of these (about half the total) is a mercaptan-free, and necessarily cyclic, unsaturated monosulfide, $C_{10}H_{18}S$, which retains the original H/C ratio unchanged: this cannot then be formed by double-bond addition of hydrogen sulfide—derived by sulfur dehydrogenation of part of the hydrocarbon—to the remaining hydrocarbon, for the mercaptan ($C_{10}H_{19} \cdot SH$) first formed could only yield, by subsequent addition of its $\cdot SH$ group to the remaining double bond, a *saturated* cyclic sulfide ($C_{10}H_{20}S$) of *changed* H/C ratio. The second product is a mixture of polysulfides, derived by cross linking of dihydromyrcene molecules, and largely consisting of polysulfides, $R \cdot S_x \cdot R'$, which are strictly comparable with those derived from monoolefins. A second isoprenic diolefin, geraniolene, $CH_3 \cdot CMe{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe{:}CH_2$, which lacks one of the terminal methyl groups characterizing dihydromyrcene, was found to behave similarly, in that it gave with sulfur a mercaptan-free, cyclic monosulfide, $C_{10}H_{16}S$, as well as a roughly equal amount of an easily decomposable, high-boiling mixture of sulfides of general type $R \cdot S_x \cdot R'$.

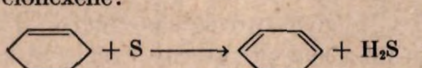
It is obvious, of course, that cyclization in these examples is only a special (intramolecular) case of cross linking, but if all the sulfur uptake in polyolefins occurred intramolecularly, effective vulcanization according to the cross-linking hypothesis would be impossible. Experiment shows that, in the simpler polyolefins, the amount of cyclization tends to exceed that of recognizable cross linking.

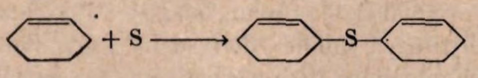
The totally undistillable material which is ordinarily obtained by sulfuration of di- and polyolefins may possibly be derived from the cross linking of three or more molecules of hydrocarbon by sulfur, or may be partly cyclized and partly cross linked multimolecular material. Generally speaking, however, the sulfur content of the high-boiling residues (freed as far as possible from uncombined sulfur) appears to be high.

If this condition still holds for such very high-molecular polyolefins as rubber, it becomes necessary to envisage the production by vulcanization of more sulfide rings in the carbon chains than sulfide cross links. The quality of the vulcanizates might then be expected to vary considerably as the proportion of cyclization to cross linking could by one device or another be induced to alter; also the scant relationship ordinarily existing between the physical properties of the vulcanizate and the total proportion of combined sulfur (which is especially noticeable when accelerated and unaccelerated vulcanizates are compared) might conceivably be the result of variation in the relative amounts of cyclization and cross linking.

MECHANISM OF REACTION

It is necessary to recognize at the outset that the behavior of di- and polyolefins possessing the rubber unsaturation pattern (*i.e.*, possessing $\Delta^{1,5}$- and $\Delta^{1,5,9,\mathrm{etc.}}$- unsaturation) is bound to be different in certain respects from that of olefins having other unsaturation patterns. Of the four olefinic groups to be considered, two (comprising $\Delta^{1,4}$-, $\Delta^{1,4,7,\mathrm{etc.}}$-, and conjugated olefins) are left for future consideration. One of us suggested earlier[4] that attack by sulfur at the α-methylenic groups adjacent to double bonds probably plays an important part in sulfur–olefin chemistry in general. This means that it may be expected to play a part in sulfur vulcanization also, since the latter is likely to be a mere extension to long-chain polyolefins of the chemistry of simpler systems. Now it appears fairly certain from the foregoing results that neither a simple (Vesterburg) dehydrogenation reaction (H) followed by hydrogen sulfide addition, nor a purely α-methylenic coupling (I), represents the main result of sulfur attack on cyclohexene or 1-methylcyclohexene:


(H)


(I)

On the contrary it would appear from the fairly close maintenance of the original H/C ratio and the usual diminution in the original unsaturation that a combination of substitutive and additive functions is in question. Also, since sulfur does not show any very plain tendency to act simply as an ordinary polar reagent, but on the contrary, by reason of its compliance with certain of the criteria of radical reaction (no less than from its elemental analogy with oxygen), gives some positive indication that it enters reaction with olefinic substances by a *nonpolar* mechanism, one may postulate provisionally that attack by sulfur begins by displacement of α-methylenic hydrogen atoms (*i.e.*, begins substitutively) and ends additively by attachment of a *sulfo radical* at one end of a double bond, with subsequent stabilization of the resulting radical by capture (or less usually, by loss) of a hydrogen atom, thus:


(1)


(2)


(3)

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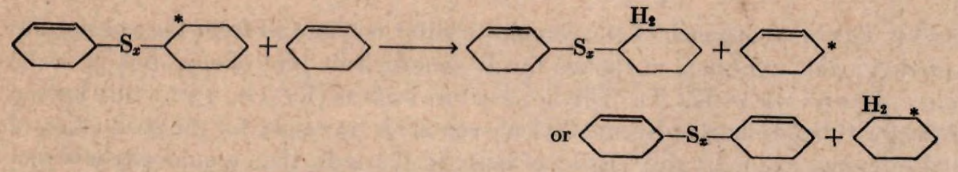
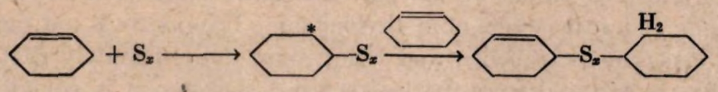
[4] E. H. Farmer, *Trans. Faraday Soc.*, **38**, 340, 356 (1942).



(4)

This does not necesssarily mean, any more than it does for oxygen attack, that the *initiation* of reaction chains does not occur by addition of relatively few sulfur molecules (chain starters) at double bonds (see pp. 294 and 295).

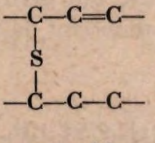
Conceivable alternative procedures are (*a*) the addition of sulfur molecules at one end of the double bonds of two olefin molecules, with subsequent stabilization by disproportionation as shown in (5):



(5)

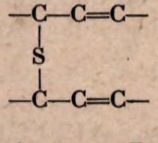
and (*b*) the polar addition to the olefin of the mercaptan or sulfohydride molecules formed by the radical mechanisms shown in (1), (2), and (3*b*) above, which would mean that the formation of sulfo rings starts as a radical reaction and ends as a polar one. Both of these alternative procedures would leave undisturbed the original H/C ratio and, on the average, reduce the original unsaturation by half; but it is clear that all three procedures could conform with the hitherto current notion regarding unsaturation loss in rubber vulcanizates (that one double bond is lost for each atom of sulfur incorporated), only provided that the cross links in rubber vulcanizates are almost entirely monosulfide links or alternatively that a very high degree of homogeneous α-methylenic linking, such as is shown in (E) above (and, correspondingly little double-bond addition), is exercised in place of the substitutive-additive attack represented in reactions (1) to (5). It is particularly to be emphasized that no evidence of direct carbon-to-carbon linking of olefins (whether di-α-methylenic or substitutive-additive) has been obtained by use of sulfur. Moreover, in all those examples in which desulfuration of the sulfurated products has been successfully accomplished by the action of hydrogen adsorbed on Raney nickel (following the method of Mozingo *et al.*[5]), only monomolecular hydrocarbons—not di- or polymolecular forms produced by cross linking—have been obtained.

Certain recent observations have a bearing on the foregoing formulation of the sulfur–olefin reaction as proceeding partly by a di-α-methylenic coupling. The first mechanism would give rise to the characteristic allyl alkyl sulfide type of grouping (J) and the second to the diallyl sulfide type (K). Thus Selker and Kemp[6] have shown that



$$\begin{array}{l}-C-C{=}C-\\ \ \ |\\ \ \ S\\ \ \ |\\ -C-C-C-\end{array}$$

(J)



$$\begin{array}{l}-C-C{=}C-\\ \ \ |\\ \ \ S\\ \ \ |\\ -C-C{=}C-\end{array}$$

(K)

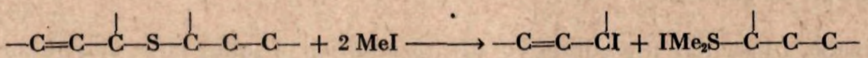
vulcanized natural rubber reacts with methyl iodide to give crystalline trimethylsulfonium iodide in a manner which is characteristic of diallyl sulfide (and, as more recent work shows, of several other simple diallylic sulfides):

$$(CH_2{:}CH\cdot CH_2)_2S + CH_3I \longrightarrow (CH_2{:}CH\cdot CH_2)SMeI \xrightarrow{2\ MeI} 2\ CH_2{:}CH\cdot CH_2I + Me_3SI$$

[5] R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

[6] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **36**, 16 (1944).

Their results suggest that much of the combined sulfur is removed from the vulcanizate by the methyl iodide treatment as though the di-α-methylenic type of cross linking is the major one. But it is clear that if a diallylic structure such as (K) (*i.e.*, a structure having both of the S—C bonds flanked by an ethylenic center) is necessary for the production of trimethylsulfonium iodide by the scission of both S—C bonds, then a monoallylic structure such as (J) might be expected to undergo scission at only one C—S bond, leaving the sulfur attached to the carbon skeleton:



$$-C{=}C-\overset{|}{C}-S-\overset{|}{C}-C-C- + 2\,\text{MeI} \longrightarrow -C{=}C-\overset{|}{C}I + IMe_2S-\overset{|}{C}-C-C-$$

Investigation shows that the two simple sulfides of type (J), allyl propyl sulfide and cyclohexenyl cyclohexyl sulfide, do not part with their sulfur in the form of trimethylsulfonium iodide under the action of methyl iodide. The matter is not quite simple, for although the experiments of Selker and Kemp show quite definitely that much of the combined sulfur is removed from the hydrocarbon skeleton, it is not established with certainty that the sulfur so removed is all from linkages of type (K); it is also known[7] that methyl iodide is not without the ability to bring about sulfur fission even in the case of dialkyl polysulfides, and presumably, therefore, allyl alkyl polysulfide also. Hence the proportion of type (K) linkages is probably not so high as the experiments with methyl iodide indicate. The production of α-methylenic links to sulfur is indicated by Armstrong *et al.*[8] by the oxidation with ozone of the sulfides and disulfides (both considered to be of allylic type) derived by the action of sulfur on certain simple open-chain olefins. No clear evidence of any very high yield of *di*-α-methylenic linking of type (K) is provided, however, although the existence of some is demonstrated. It is of great interest in connection with the radical hypothesis of sulfuration, that the methylbutene, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_3$, can give (owing to resonance in the allylic radical) a sulfo grouping, $—S{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, and that its isomer, $CH_3{\cdot}CMe{:}CH{\cdot}CH_3$, can give a sulfo-grouping, $CH_2{:}CMe{\cdot}CHMe{\cdot}S—$.

Comparable with the breaking of S—C links by methyl iodide is their reductive scission by nascent hydrogen. Diallylic sulfides of type (K) undergo scission at one or both of the S—C bonds to give mercaptans and hydrogen sulfide (together with hydrocarbon), whereas allyl alkyl sulfides of type (J) undergo scission only at the allylic S—C links to give mercaptan (together with hydrocarbon), but no hydrogen sulfide. Dialkyl sulfides do not reduce at the S—C bonds, but episulfides, like diallylic sulfides, do, at one or both of the bonds, yielding mercaptan and hydrogen sulfide. It is especially significant that the cyclic sulfides derived, respectively, by the action of sulfur on dihydromyrcene and geraniolene, both undergo *partial* reduction to mercaptan, but give no hydrogen sulfide; hence it appears that groupings of type (J) are fairly abundant, but not so those of type (K).

CONSIDERATIONS AFFECTING THE FORMATION OF CYCLIC SULFIDES

One of us earlier advanced the hypothesis that the production of conjugated systems from $\Delta^{1,4}$ and $\Delta^{1,4,7,\text{etc.}}$ olefins by autoxidative action is due to the momentary production of radicals ($\cdot CH{:}CH{\cdot}\underset{*}{C}H{\cdot}CH{:}CH\cdot$, $\cdot CH{:}CH{\cdot}\underset{*}{C}H{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH$, etc.)

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[7] P. C. Ray and N. Adhikari, *J. Indian Chem. Soc.*, 7, 297 (1930).

[8] R. T. Armstrong, J. R. Little, and K. W. Doak, *Ind. Eng. Chem.*, 36, 628 (1944).

which pass by resonance into their conjugated counterparts ($\cdot CH{:}CH\cdot CH{:}CH\cdot \underset{*}{C}H\cdot$, $\cdot\underset{*}{C}\cdot H\cdot CH{:}CH\cdot CH{:}CH\cdot$, $\underset{*}{C}\cdot H\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot$, etc.).[9] The same kind of resonance applies to all mono- and polyolefinic systems (including the $\Delta^{1,5}$ and $\Delta^{1,5,9,\text{etc.}}$ systems of the terpenes and rubber) from which α-methylenic hydrogen atoms have become detached in the course of oxidative, thermal, and photochemical processes. If, then, reaction by sulfur ordinarily takes place by a radical mechanism it may reasonably be expected that double bond shifts analogous to those promoted by autoxidation will be realized in the sulfur–olefin reaction also. In the case of the $\Delta^{1,5}$, $\Delta^{1,5,9,\text{etc.}}$ systems of polyisoprenes, the detachment of a hydrogen atom is possible at three points in each isoprenic C_5H_8 unit, although existing evidence suggests that it tends to occur at *a* in preference to *b*, and *b* in preference to *c* in $\cdot CH_2\cdot \underset{a}{C}(CH_3){:}\underset{c}{C}H\cdot \underset{b}{C}H_2\cdot$. Also it must be borne in mind that most isoprenic materials of natural origin appear on good evidence to contain quite appreciable components in which the ordinary isoprenic unit is replaced by its isomeric (methylenic) form: $\cdot CH_2\cdot C({:}CH_2)\cdot CH_2\cdot CH_2\cdot$. These complications increase considerably the number of the possible radical forms obtainable from even diisoprenic materials such as dihydromyrcene and geraniolene, so that the prospect for the formation of a homogeneous cyclic monosulfide from either is remote—although one form may predominate in each product and certain of the others appear only in traces. There is, however, the further complication that the cyclic monosulfides consist possibly of mixtures of isomers containing 6-, 5-, and even 4-membered rings. Experimental examination of the cyclic monosulfides obtained disclosed their marked heterogeneity and afforded slight prospect of isolating even the principal components in tolerably pure condition, or of identifying the different components by crystalline derivatives or directly by spectroscopic means. Since, however, it was unlikely that all the possible isomeric forms could be produced in any example, it was desirable to look for a simplifying factor that would restrict the number of forms to be taken into consideration. With regard to substitutive attack by sulfur (at the α-methylenic centers) the reaction possibilities are universally those given above—which cannot be further simplified; with respect to additive processes, however, a distinction may be drawn between those proceeding by a radical and those by a polar mechanism.

If for substituted ethylenes of the two types, $CRR'{:}CH_2$ and $CRR'{:}CHR''$ (R, R', R'' = hydrocarbon groups), it may be assumed that the *polar* addition of ionizable addenda of type HX (*e.g.*, $HS\cdot R$) occurs uniquely in conformity with the Markovnikov rule, whereas *radical* addition occurs uniquely by union of the active center at the more hydrogenated carbon atom of the ethylenic pair (*i.e.*, in the manner opposed to the Markovnikov rule), then, provided the sulfuration process has a truly radical mechanism, the number of cyclic monosulfides that can be formed is greatly reduced. There are accordingly three cases for consideration: (*1*) Sulfuration involves radical reaction throughout, beginning substitutively at an α-methylene group and ending additively at a double bond. (*2*) Sulfuration begins substitutively as a radical reaction, but each of the sulfo radicals thereby formed abstracts a hydrogen atom from the α-methylene group of a neighboring olefinic center to form a mercaptan ($RH \xrightarrow{-H^*} R^* \xrightarrow{S} RS^* \xrightarrow{RH} R\cdot SH$), the latter adding in polar fashion to an adjacent double bond to form a cyclic sulfide). (*3*) Sulfuration, in spite of the above-mentioned indications to the contrary, is wholly polar, giving first a more unsaturated (conjugated) olefin by dehydrogenation, then a mercaptan by

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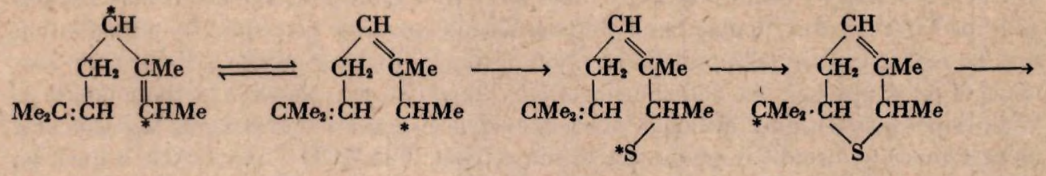
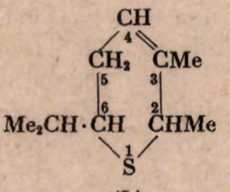
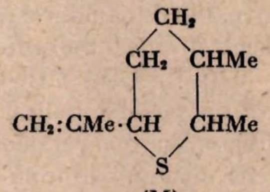
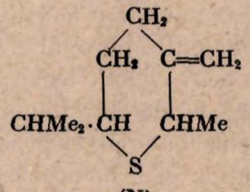
[9] E. H. Farmer, D. A. Sutton, and H. P. Koch, *J. Chem. Soc.*, **1943**, 541.

addition of the liberated hydrogen sulfide to one of the double bonds, and finally a cyclic sulfide by addition of the —SH group to one of the remaining double bonds. Thus, for dihydromyrcene, if consideration is limited to the production of 6-membered cyclic sulfides, reaction according to (*1*) may reasonably be expected to proceed as follows to give (L). (Analogous consequences will result if cyclization leads to the formation of 5-membered sulfide rings.):

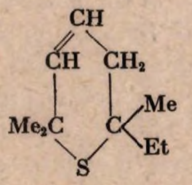


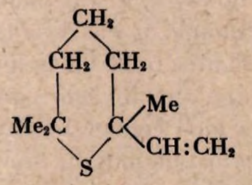

(L)

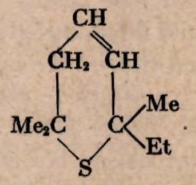

(M)


(N)

By comparable attack (in minor degree) at other α-methylenic groups in the original olefin molecule, two other 6-membered sulfides, (M) and (N), can be formed. Similarly reaction according to (*2*) would be expected to yield (O) and (P), and reaction according to (*3*), (Q) only. Geraniolene would be expected to give cyclic sulfides differing from


(O)


(P)


(Q)

those obtained from dihydromyrcene only by the absence of the methyl group on the second carbon atom.

It is to be noted that the products thus expected to arise when the reaction is partly or wholly polar, as in (*2*) and (*3*), would all be identical after they had been hydrogenated, but would be different from the (single) product which would be obtained by hydrogenation of the forms (L), (M), and (N) derived by the homogeneous radical reaction. There remains, however, a further contingency to be considered, *i.e*,. the possibility that neither radical nor polar addition to double bonds is to be relied on to occur *uniquely* in the direction (*abnormal* or *normal*) appropriate to each in systems of the type $CRR':CHR''$ and $CRR':CH_2$ if departure from the rigid rule would, for purely steric reasons, considerably assist addition—and this applies particularly to cyclizing addition—in the inappropriate direction. Clearly the first necessity for narrowing the lines of progress in the cyclizing attack by sulfur is to determine the precise course of reaction when hydrogen sulfide is caused to add to the same olefins under conditions which promote, respectively, *normal* and *abnormal* addition at the double bonds. The results of this investigation are described in Part II, but it can be said at once that the cyclic sulfides derived by the sulfur reaction closely resemble in certain structural features those derived by hydrogen sulfide addition, which are in the main 6-membered (*i.e.*, thiopyrane) rings.

OLEFIN POLYSULFIDES

The structure of organic polysulfides, such as those obtained above, present certain difficulties. Patrick[10] regards the tri- and tetrasulfides derived by the action of organic dihalides on sodium tetrasulfide as being basically disulfides with easily removable coordinated sulfur ($R\cdot \underset{\substack{\downarrow \\ S}}{S}\cdot S\cdot R'$, $R\cdot \underset{\substack{\downarrow \\ S}}{S}\cdot \underset{\substack{\downarrow \\ S}}{S}\cdot R'$), and other authors have supposed that analogous compounds are obtainable. Various syntheses, however, of chain polysulfides up to the penta- and hexa-compounds have been reported by various authors (*e.g.*, tetrasulfides from sulfur monochloride and organic mercaptides, $2\ R\cdot SM + S_2Cl \rightarrow R\cdot S\cdot S\cdot S\cdot S\cdot R + 2\ MCl$), and in view of the closed-chain 8-atom structure ordinarily attributed to crystalline sulfur there is nothing improbable in the constitutions assigned. With the tri- and tetrasulfides derived by the action of sulfur on the various olefins examined, however, the extent to which combined sulfur can be removed by the action of caustic soda (the reagent used by Patrick), or sodium sulfite (the reagent used by Parker[11]), amounts only to a few units per cent of the whole. In contrast, the ethyl tetrasulfide derived by interaction of ethyl mercaptan and sulfur monochloride, as well as that derived by interaction of sodium tetrasulfide and ethyl iodide, loses nearly half its sulfur by stripping.

An investigation of the constitution of organic polysulfides is in progress, the results of which will be reported later. For the present it is not possible to say whether (judged by the criterion of stripping liability) the sulfur in the olefin polysulfides is present wholly, or nearly so, in uncoordinated chain form. Presumably the closed chains of atoms of elementary sulfur are opened at the moment of reaction and more or less broken down into shorter chains having active radical ends. There is no special reason to suppose that these latter become rearranged (to give coordinated chains) before reacting with olefins, or otherwise unite with the olefin molecules at their own nonterminal atoms. It is clear from the fact that the cyclic sulfides formed from olefins are all monosulfides that any open chain of sulfur atoms which may become joined at one of its ends to an olefin molecule can only form a second link with the same olefin molecule to produce a cyclic monosulfide if it sheds all but one of its sulfur atoms, *i.e.*, the one linked to carbon. This presumably must mean, having regard to the nature of the electronic system concerned ($—C{=}C—C—C—C—\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}\cdot$) and the fact that in monoolefin–sulfur reactions the polysulfide chains largely survive, that the break *precedes* cyclization but is not independent of it.

THERMAL DEGRADATION OF POLYSULFIDES

At temperatures above 140° the polysulfides derived from diolefins break down progressively with formation of hydrogen sulfide, mercaptan, and monosulfide. The

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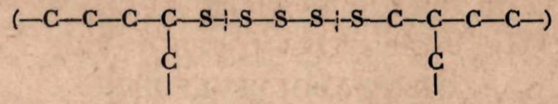
[10] J. C. Patrick, *Trans. Faraday Soc.*, **32**, 347 (1936).

[11] L. F. C. Parker, *India Rubber J.*, **108**, 387 (1945).

precise course of decomposition is uncertain but it would seem that the weakest points in the polysulfide molecules are always the S—S links:



$$(\text{—C—C—C—}\underset{\substack{|\\ \text{C}\\ |}}{\text{C}}\text{—S}\vdots\text{S—S—S}\vdots\text{S—C—}\underset{\substack{|\\ \text{C}\\ |}}{\text{C}}\text{—C—C—})$$

so that mercaptyl radicals are formed which then give rise to mercaptan and cyclic sulfide molecules. The source of the hydrogen sulfide, possibly resulting from simple dehydrogenation by liberated sulfur, is as yet undetermined.

[Reprinted from Journal of Polymer Science, Vol. 1. No. 4, pp. 305–11, 1946.]

Modern Views on the Chemistry of Vulcanization Changes. II. Role of Hydrogen Sulfide*

RALPH F. NAYLOR, *British Rubber Producers' Research Association, Welwyn Garden City, England*

Received May 20, 1946

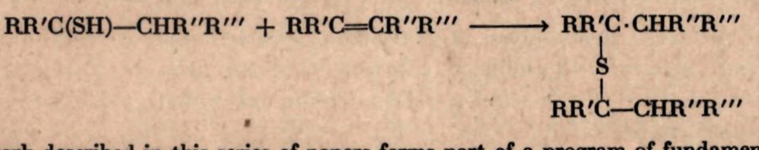
Synopsis—*Hydrogen sulfide has often been thought to play an important role in the sulfur vulcanization of natural rubber. A study has therefore been made of the reaction of hydrogen sulfide with olefins, including polyisoprenes, with special reference to the capacity of the reagent to react with olefins in the presence of free sulfur. Comparison of the products so obtained with those derived* (a) *by light-catalyzed reaction of hydrogen sulfide and* (b) *by reaction of free sulfur with polyisoprenes has greatly assisted the understanding of the course of sulfur reaction in vulcanization processes.*

INTRODUCTION

IT HAS OFTEN been considered that hydrogen sulfide might play a considerable part in the reactions involved in the vulcanization of rubber; H. L. Fisher[1] has gone so far as to suggest that the whole process may be explained on the basis of the initial formation and subsequent reaction of hydrogen sulfide. Such a hypothesis must, however, be regarded as an oversimplification in view of the difficulty usually experienced in effecting satisfactory reaction of hydrogen sulfide with olefins. However, hydrogen sulfide is known to be liberated to some relatively small extent during the sulfur vulcanization of rubber, so that it is of interest to consider its reactivity toward olefins, particularly in the presence of sulfur. The information which has now been derived by a close study of the reactions occurring between hydrogen sulfide and mono- and polyolefins (including rubber) has led to a better understanding of the role that hydrogen sulfide may be expected to play in the vulcanization process and (what is possibly more important) to the elucidation of cyclization reactions, which are probably the reason for the relatively poor qualities of unaccelerated vulcanizates.

In the reaction of hydrogen sulfide with olefins there are two main steps to be considered: (*1*) the initial addition of a molecule of hydrogen sulfide to a double bond to form a mercaptan, and (*2*) the subsequent reaction of this mercaptan with a further double bond, resulting in the formation of a dialkyl sulfide.

$$\mathrm{RR'C{=}CR''R''' + H_2S \longrightarrow RR'C(SH){-}CHR''R'''} \qquad (1)$$



$$\mathrm{RR'C(SH){-}CHR''R''' + RR'C{=}CR''R''' \longrightarrow \begin{array}{l} \mathrm{RR'C{\cdot}CHR''R'''} \\ \quad | \\ \quad \mathrm{S} \\ \quad | \\ \mathrm{RR'C{-}CHR''R'''} \end{array}} \qquad (2)$$

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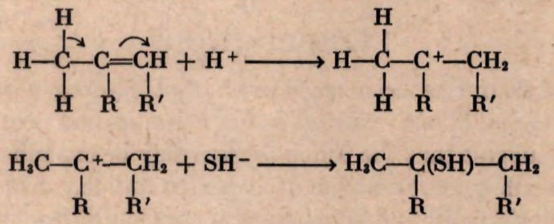
* The work described in this series of papers forms part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The experimental details will be published formally at a later date.

[1] H. L. Fisher, *Ind. Eng. Chem.*, **31**, 1386 (1939).

In each of these reactions it is theoretically possible for the hydrogen sulfide or mercaptan to add in one of two ways, according to which end of the double bond the mercapto group becomes attached. The type of addition which results in the hydrogen atom becoming attached to the carbon atom already carrying the greater number of hydrogen atoms (*e.g.*, $RCH{:}CH_2 + H_2S \rightarrow RCHMe{\cdot}SH$) is in accordance with the rule formulated by Markovnikov and is known as the *normal* reaction; the reverse mode of addition (*e.g.*, $RCH{:}CH_2 + H_2S \rightarrow RCH_2{\cdot}CH_2SH$) is termed *abnormal*. In the case of the very similar reaction of hydrogen bromide with olefins the two types of addition have been explained by assuming that the *normal* reaction is polar in character and the *abnormal* addition of a radical nature. There is evidence to indicate that a similar explanation is applicable to the reaction of hydrogen sulfide and mercaptans.[2] A study of the hyperconjugation which is intrinsic in the olefinic system, $\cdot C(CH_3){:}CH\cdot$, present in isoprenic compounds, shows that if in the polar reaction the initial attack is regarded as being by a proton (a view that is supported by the catalytic effect of acidic compounds on the addition of hydrogen bromide and of mercaptans), then the addition would be expected to follow the Markovnikov rule.[3]

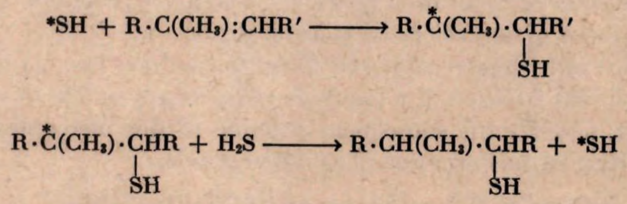
$$H_2S \longrightarrow H^+ + SH^-$$



$$H{-}\underset{H}{\overset{H}{C}}{-}\underset{R}{C}{=}\underset{R'}{CH} + H^+ \longrightarrow H{-}\underset{H}{\overset{H}{C}}{-}\underset{R}{C^+}{-}\underset{R'}{CH_2}$$

$$H_3C{-}\underset{R}{C^+}{-}\underset{R'}{CH_2} + SH^- \longrightarrow H_3C{-}\underset{R}{C(SH)}{-}\underset{R'}{CH_2}$$

On the other hand, in the abnormal addition, the action of a peroxide catalyst, or irradiation with ultraviolet light, gives rise to neutral free radicals (*Br, *SH, *SR, etc.); and it has been suggested[4] that consideration of the possibilities of resonance in the structures which would result from attack at either end of the double bond leads to the conclusion that the *abnormal* type of addition is energetically the more likely. The universal applicability of the argument is, however, open to some doubt.



$$^*SH + R{\cdot}C(CH_3){:}CHR' \longrightarrow R{\cdot}\overset{*}{C}(CH_3){\cdot}\underset{SH}{CHR'}$$

$$R{\cdot}\overset{*}{C}(CH_3){\cdot}\underset{SH}{CHR} + H_2S \longrightarrow R{\cdot}CH(CH_3){\cdot}\underset{SH}{CHR} + {^*SH}$$

Having discussed the mechanisms underlying the two modes of reaction of hydrogen sulfide and mercaptans with olefins, it can now be shown how conditions of reaction influence the appearance of polar and radical addition and how this study is related to the vulcanization of rubber.

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[2] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 387 (1940).

[3] G. L. Wheland, *The Theory of Resonance.* Chapman & Hall, London, 1944, p. 235.

[4] G. L. Wheland, *loc. cit.*, p. 239.

SULFUR-CATALYZED REACTION OF HYDROGEN SULFIDE WITH OLEFINS

Monoolefins. Jones and Reid[5] first reported that the reaction of hydrogen sulfide with olefins was positively catalyzed by elementary sulfur, and that the mode of addition was in accordance with Markovnikov's rule. However, the relatively large quantities of catalyst used in some of these experiments introduced a measure of uncertainty as to what extent the products had arisen by reaction of the hydrogen sulfide and to what extent by reaction of the sulfur catalyst with the olefins. Further examinations of the reaction of hydrogen sulfide with representative monoolefins, *e.g.*, with isobutylene and cyclohexene, has shown quite definitely that not only does sulfur catalyze the addition, but also that quite small amounts of sulfur are sufficient to promote a considerable degree of reaction at 140°C. The main products in each case are the mercaptan and a monosulfide that is formed by sulfur-catalyzed addition of a molecule of the mercaptan to a further olefin molecule. In the case of isobutylene the products are quite definitely tertiary butyl derivatives arising by *normal* addition:

$$\mathrm{CMe_2{:}CH_2 + H_2S \longrightarrow CMe_2(SH)\cdot CH_3}$$

$$\mathrm{CMe_2{:}CH_2 + CMe_2(SH)\cdot CH_3 \longrightarrow CH_3\cdot CMe_2\cdot S\cdot CMe_2\cdot CH_3}$$

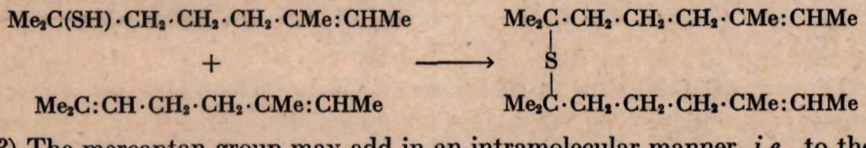
but with cyclohexene, owing to its symmetry, no differentiation between the products of normal and abnormal addition is, of course, possible. It is of considerable interest that a small amount of disulfide accompanies the other reaction products and that it arises even when air is excluded and in experiments where no sulfur is included (the reaction being then catalyzed to a small extent by the iron sulfide formed on the walls of the steel autoclave used in the experiments). As atmospheric oxidation of the initially formed mercaptan is excluded, it would appear that the oxidation must be associated with a complementary reduction (*i.e.*, hydrogenation) of the olefin.[6]

Polyisoprenes. The presence of the $\Delta^{1,5}$- diene system in polyisoprenic compounds considerably adds to the inherent possibilities of reaction with hydrogen sulfide. If the diisoprene, dihydromyrcene, is considered as a typical compound of this group ($\mathrm{CH_3}$-$\mathrm{CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe}$), it is found that, initially, one molecule of hydrogen sulfide adds *normally* to one or the other of the double bonds to give a monomercaptan. Four courses of reaction now remain open:

(*1*) A second molecule of hydrogen sulfide may add to the mercaptan giving a dimercaptan:

$$\mathrm{Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe \longrightarrow}$$
$$\mathrm{Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(SH)Me\cdot CH_2Me}$$

(*2*) The monomercaptan may add to a second molecule of dihydromyrcene or to the second double bond of a further molecule of monomercaptan to give a monosulfide or mercaptosulfide, which contains four $\mathrm{C_5}$ units:



$$\begin{array}{c} \mathrm{Me_2C(SH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe} \\ + \\ \mathrm{Me_2C{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe} \end{array} \longrightarrow \begin{array}{l} \mathrm{Me_2C\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe} \\ \quad\ \ \mathrm{|} \\ \quad\ \ \mathrm{S} \\ \quad\ \ \mathrm{|} \\ \mathrm{Me_2C\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe} \end{array}$$

(*3*) The mercaptan group may add in an intramolecular manner, *i.e.*, to the other double bond in the same molecule, giving a cyclic sulfide, containing a 6-membered ring:

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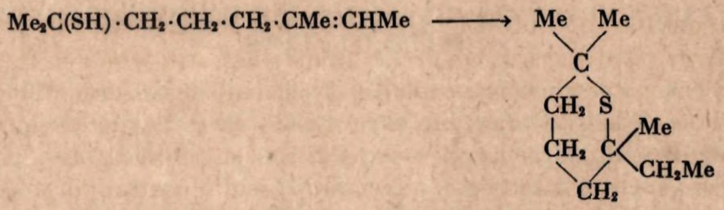
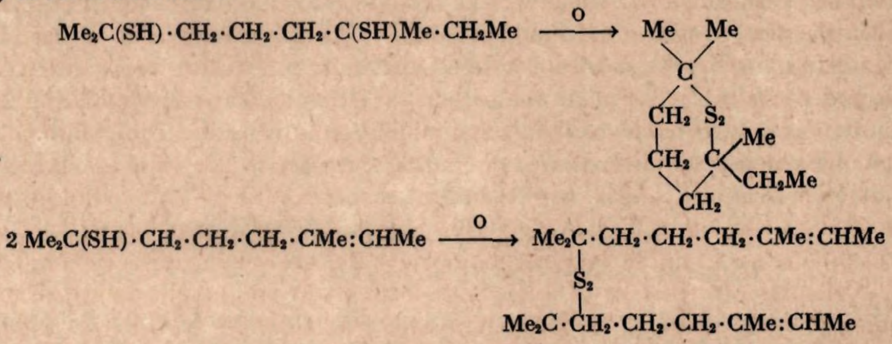
[5] S. O. Jones and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938).

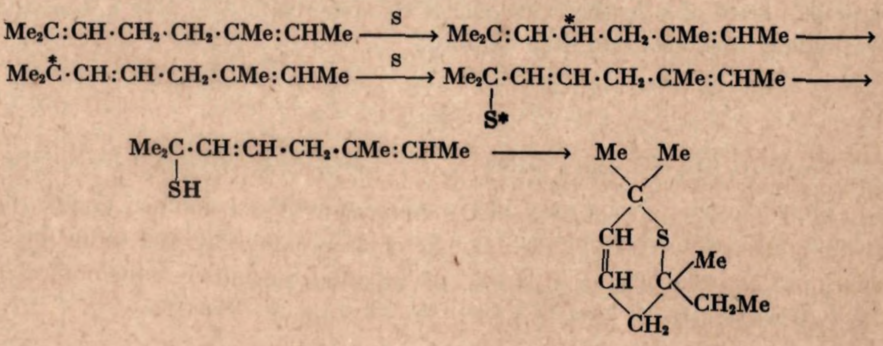
[6] E. C. Williams and C. C. Allen, U. S. Pat. 2,052,268; *C. A.*, **30**, 7122 (1936).



(*4*) Two mercaptan groups, in the same or different molecules, may be oxidized (see above) to form a disulfide:



In actual practice, with both dihydromyrcene and geraniolene, it is found that by far the most important reaction is (*3*). Reactions (*1*) and (*4*) take place to a negligible extent, and reaction (2) occurs to give a very small yield of cross-linked sulfides. The importance of these observations in relation to the vulcanization of rubber is obvious, as it means that if such reactions play any considerable part in the vulcanization process, then, in the absence of adventitious materials (*e.g.*, zinc oxide, accelerators), a very high percentage of the total sulfur goes to form cyclizing links, which are valueless from the point of view of strengthening the molecular network of rubber. In this connection it is significant that, as far as present evidence goes, the cyclic products formed by reaction of sulfur with dihydromyrcene and geraniolene (see Part I, page 302) show a greater resemblance to the cyclic sulfides derived by polar (*i.e.*, sulfur-catalyzed) addition of hydrogen sulfide to these olefins than they do to those obtained by radical (ultraviolet-light-catalyzed) addition (see below) of hydrogen sulfide. This may possibly be explained—as indicated among the possibilities of sulfur reaction in Part I—by assuming that the mercaptan radical formed by sulfur attack preferentially captures a hydrogen atom to become a mercaptan of the same structure (apart from the incidence of unsaturation) as that obtained by polar addition of hydrogen sulfide; under the influence of sulfur this mercaptan adds *normally* in an intramolecular manner:



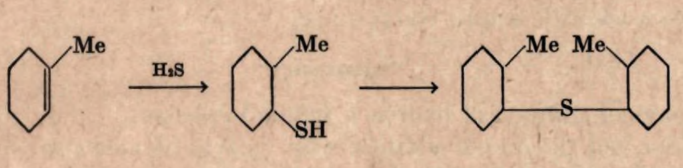
Such a hypothesis is consistent with the observed fact that addition of the monomercaptan is very effectively catalyzed by sulfur. In the sulfur-catalyzed reaction of hydrogen sulfide with polyisoprenes, monomercaptan and cyclic sulfide are formed in approximately the ratio of 1:8. When the reactions are repeated using aluminum sulfide instead of sulfur as a catalyst, although the over-all yields are not much reduced, this ratio is reduced to 1:2 or sometimes nearly 1:1. In addition some dimercaptan is formed, according to reaction (*1*) above, indicating that the speed of addition of hydrogen sulfide is now of the same order as that of the mercaptan.

Rubber. The high molecular weight of rubber renders impossible the separation and identification of individual reaction products in the manner that is feasible with simpler olefins. However, it has been shown that solid rubber does react with hydrogen sulfide under pressure at 140°C. in the presence of either sulfur or iron sulfide; the properties of the products indicate that some sulfide cross links are being formed. Dissolution of hydrogen sulfide in the rubber during the reaction gives rise to bubbles in the sheet when pressure is released, with the result that it is very difficult to obtain samples of the product which are suitable for tensile strength tests. Nevertheless, selected portions of products containing 2–3% of combined sulfur are capable of over 700% elongation. Although the reaction of diisoprenes with hydrogen sulfide indicates an overwhelming preponderance of *intra*molecular over *inter*molecular addition, it is probable that this is offset to some extent in the case of rubber by the purely physical intermolecular entanglements of the long rubber molecules.

ULTRAVIOLET-LIGHT-CATALYZED REACTION OF HYDROGEN SULFIDE WITH OLEFINS

It has been shown by Vaughan and Rust[7] that hydrogen sulfide becomes dissociated on irradiation by ultraviolet light and that the resulting mercapto radicals will attack olefins to give the *abnormal* products. As it is considered (see Part I) that the reaction of sulfur with olefins under vulcanization conditions is, in the initial stages at least, a radical reaction, it is of interest to study the radical addition of hydrogen sulfide to olefins.

Irradiation of mixtures of liquid hydrogen sulfide with such simple olefins as 1-methylcyclohexene, the latter containing the isoprenic unit, —$C(CH_3):CH$—, results in the formation of the corresponding alkyl mercaptan and dialkyl sulfide by abnormal addition.



The diisoprene, dihydromyrcene, reacts similarly with the formation of a monomercaptan, which then follows the reaction schemes (*1*), (*2*), and (*3*) for polyisoprenes enumerated in the section dealing with the sulfur-catalyzed reaction (p. 307). In this case it is found that about 50% of the monomercaptan remains as such, while most of the remainder reacts *intra*molecularly to give a cyclic sulfide; small amounts of dimercaptan

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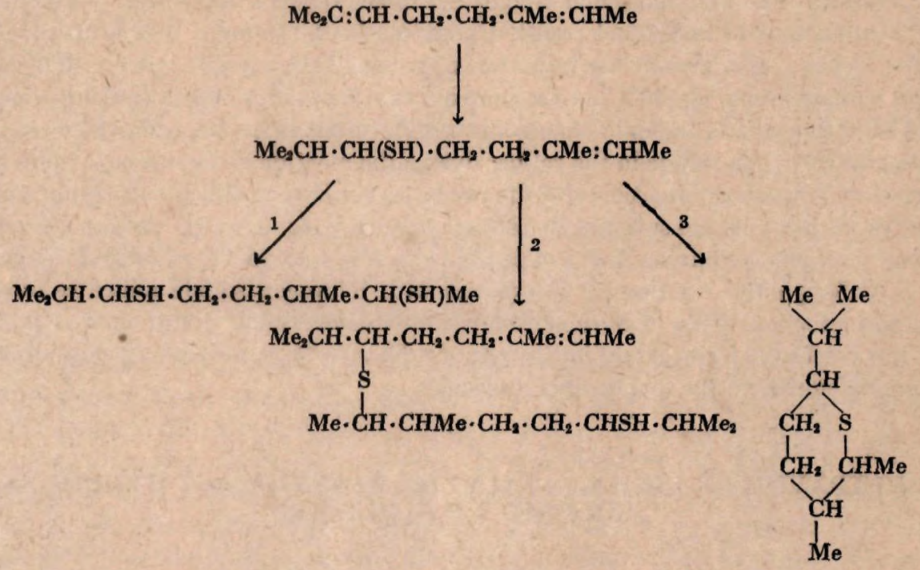
[7] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, 7, 472 (1942).

and of *inter*molecular sulfides are also formed. The persistence of much of the monomercaptan under conditions that are eminently suited to radical reaction lends support to the hypothesis that in the reaction of sulfur with polyisoprenes, the radical chain mechanism proceeds, in the main, only as far as the mercaptan and that the subsequent addition reaction is of a polar type. It will be noted that the *abnormal* reaction gives rise to products which are different from those obtained in the sulfur-catalyzed *normal* reaction and, although the cyclic sulfide obtained again contains a 6-membered ring, the substituents in the ring are now differently oriented.



It is thus possible to distinguish between products resulting from a radical addition and those from a polar addition of hydrogen sulfide and this comparison has been of value in examination of the cyclic sulfides arising by sulfur attack on polyisoprenes (see above).

Under the influence of ultraviolet irradiation, rubber itself reacts with hydrogen sulfide, either when its solution in a hydrocarbon solvent is saturated with the gaseous reagent, or when it is dissolved directly in liquid hydrogen sulfide (in which it is reasonably soluble). Although precise elucidation of the mode of reaction is not possible with the complicated rubber molecule, the nature of the products obtained does indicate that some of the sulfur atoms are utilized in forming cross links of the same types as have been identified in the work with simpler compounds.

Summary

1. The *normal* addition of hydrogen sulfide to olefins is catalyzed by very small amounts of sulfur, but the rate of addition is too slow to provide a satisfactory basis for the hydrogen sulfide-actuated mechanism of vulcanization.

2. The main products of the sulfur-catalyzed (polar) reaction of hydrogen sulfide with polyisoprenes are substituted pentamethylene sulfides, derived by intramolecular *normal* addition of the initially formed monomercaptans.

3. The main products of the ultraviolet-light-catalyzed (radical) reaction of hydrogen sulfide with polyisoprenes are monomercaptans and substituted pentamethylene sulfides, the latter derived by intramolecular *abnormal* addition.

4. The resemblance of the cyclic sulfides obtained by reaction of free sulfur with polyisoprenes to the products of polar hydrogen sulfide addition (as opposed to the products of the radical-type addition) supports the hypothesis that, in the sulfur–olefin reaction, the radical reaction chain is terminated by the capture of a hydrogen atom by an RS* radical, the mercaptan so formed adding intramolecularly in a polar reaction catalyzed by sulfur.

[Reprinted from Journal of Polymer Science, Vol. 1, No. 4, pp. 312–17, 1946.]

Modern Views on the Chemistry of Vulcanization Changes. III. Reaction of Sulfur with Squalene and with Rubber*

GEORGE F. BLOOMFIELD, *British Rubber Producers' Research Association, Welwyn Garden City, England*

Received May 20, 1946

Synopsis *— Squalene containing six isoprene units is more free of end-group effects and less limited in the range of space-distributional contortions of its carbon lchain than mono- and diolefins. Hence it is more comparable with rubber than the atter group where matters of chemical reactivity are concerned. Nevertheless, in its reaction with sulfur, squalene pursues a course very similar to that followed by the diisoprene, dihydromyrcene, in that intramolecular sulfide linkages as well as intermolecular polysulfide linkages are formed. Taking into consideration the amount of sulfur which would suffice for the establishment of some given number of the simplest possible intermolecular linkages (i.e., monosulfide linkages), the efficiency of sulfur as a cross-linking reagent during the vulcanization of squalene is seen to be of a rather low order; this condition might be expected to hold for rubber in the absence of auxiliary mechanisms. So far as can be determined by direct experiment the action of sulfur in forming cross links is not essentially different from that encountered with squalene, since there are indications that both intra- and intermolecular sulfide linkages are formed—the latter being of both dialkenyl and dialkyl sulfide type, and, possibly also of alkenyl alkyl type. Under the influence of small amounts of zinc oxide or of various nitrogen-containing organic accelerators, sulfur reacts with the thiol groups of organic mercaptans forming di- and polysulfides, together with hydrogen sulfide. In the presence of rubber the same reaction occurs without actual liberation of hydrogen sulfide and it thus appears that if any thiol groups are formed as intermediates in vulcanization reactions, they will undergo ready conversion into intermolecular di- and polysulfide linkages. This may well represent an important auxiliary mechanism of cross linking.*

INTRODUCTION

THE HEXAISOPRENE, squalene ($C_{30}H_{50}$), is a promising hydrocarbon for inclusion in a comprehensive survey of sulfur–olefin reactivity and the mechanism of rubber vulcanization, since its molecular complexity is such as to render it more closely comparable with long-chain polyisoprenes than is the diisoprene dihydromyrcene, while its molecular weight is still sufficiently low to enable molecular distillation of the sulfurated reaction product to be accomplished without recourse to unduly elevated temperatures. It has been shown elsewhere[1] that the behavior of squalene toward halogens rather more closely resembles that of rubber than does the behavior of dihydromyrcene. It is now found that the reaction of squalene with sulfur at the ordinary vulcanization tem-

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* The work described in this series of papers forms part of a program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association. The experimental details will be published formally at a later date.

[1] G. F. Bloomfield, *J. Chem. Soc.*, 1943, 289.

perature pursues a course very similar to that of dihydromyrcene (see Part I, p. 297) while at the same time showing a close resemblance to rubber–sulfur vulcanization.

REACTION OF SQUALENE WITH SULFUR

When squalene and sulfur were heated together at 140°, both monomolecular and bimolecular sulfurated products were formed, which were readily separable by molecular distillation. In neither portion of the reaction product was there any over-all change in the ratio of hydrogen to carbon from that of the original hydrocarbon. In the monomolecular product olefinic unsaturation had been destroyed in the proportion of one double bond per sulfur atom incorporated, but no mercapto groups were present; by analogy with dihydromyrcene it may reasonably be considered to be a cyclic sulfide. (A precise method for determining the olefinic unsaturation of soluble substances of low sulfur content has recently been described.[2]) The bimolecular product appeared to be a polysulfide of the over-all composition $C_{60}H_{100}S_6$. Of the squalene which entered into reaction with sulfur $\nless 24\%$ formed monomolecular cyclic sulfide and $\ngtr 10\%$ formed bimolecular polysulfide. Of the sulfur originally present, 37% entered into reaction, and of this at least a half formed the monomolecular product. The presence of mercaptobenzothiazole and zinc oxide during the reaction of squalene with sulfur increased the yields of both products but did not raise the proportion of the intermolecularly linked product at the expense of the intramolecular sulfide. An increase in the proportion of monosulfide at the expense of polysulfide has been reported with this accelerator in the reaction of sulfur with 2-methylbutene.[3]

RUBBER VULCANIZATION

The chief characteristics of the vulcanization of rubber with sulfur are: first, that there is no over-all loss of hydrogen relative to carbon in vulcanizates containing quite considerable proportions of combined sulfur, and, second, that there is a loss of unsaturation accompanying sulfur combination corresponding to one double bond per sulfur atom incorporated[2]; if zinc oxide or certain mixtures of zinc salts and accelerators are present the loss of unsaturation may be substantially less.

FORMATION OF HYDROGEN SULFIDE AND ITS INFLUENCE ON THE REACTION OF SULFUR WITH RUBBER

Small amounts of free hydrogen sulfide (containing a total of sulfur equivalent to 1–2% of that entering into combination with the rubber) can be detected during vulcanization even when the purest available fractionated rubber hydrocarbon ($N < 0.01\%$) is used. Hydrogen sulfide has, moreover (as already observed by Byzov and Popova[4]), a marked catalytic effect on rubber–sulfur combination, promoting combination of a proportion of sulfur considerably in excess of that which would be obtained even if all of the hydrogen sulfide present were added to the rubber. Experiment showed, however, that in the presence of the considerable proportion of sulfur normally used in vulcanization processes the amount of combined sulfur resulting from combination of hydrogen sulfide

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[2] G. F. Bloomfield, *J. Soc. Chem. Ind.*, **64,** 274 (1945).

[3] R. T. Armstrong, J. R. Little, and K. W. Doak, *Ind. Eng. Chem.*, **36,** 628 (1944).

[4] B. V. Byzov and M. K. Popova, *Rubber Chem. Tech.*, **8,** 473 (1935).

was not large, and over a fairly wide range of relative concentrations of rubber, sulfur, and hydrogen sulfide the following relationship was maintained:

$$\frac{\text{combined S contributed by H}_2\text{S}}{\text{combined S contributed by free S}} = \frac{\text{S present as H}_2\text{S}}{\text{S present as free S}}$$

This relationship indicated that addition of hydrogen sulfide to rubber might become appreciable if the amount of hydrogen sulfide present was greatly increased while the amount of sulfur present was suitably reduced; this has indeed been found to be so. Moreover, the sulfur content arising from the combined hydrogen sulfide then made a significant contribution to the physical properties of the resulting vulcanizate.

As might be expected from the foregoing considerations, the reaction between purified rubber and sulfur in a sealed evacuated tube is appreciably autocatalytic, contrary to the well-established linear rate of combination of sulfur with rubber observed in technical vulcanization. This difference in behavior can probably be attributed to oxygen, which is found to suppress appreciably the catalytic activity of hydrogen sulfide.

Ethyl mercaptan has a catalytic effect on rubber–sulfur combination comparable with that of hydrogen sulfide, but diethyl sulfide is entirely without effect. Diethyl disulfide slightly increases the sulfur content of a vulcanizate of which it is an ingredient, but the increase does not contribute to the physical properties of the vulcanizate and probably arises partially from combination of the disulfide itself with the rubber (see below).

Accelerated vulcanization exhibits rather different characteristics, since the rate of combination of sulfur decreases rapidly with time and the catalytic effect of hydrogen sulfide may be very much reduced or entirely absent according to the type of accelerator used.

When nonaccelerated vulcanization is conducted with rigid exclusion of oxygen, slightly higher sulfur contents are obtained in comparison with vulcanization conducted in the presence of quite limited amounts of oxygen, and there is a corresponding improvement in the physical properties of the vulcanizate. It cannot be stated with certainty, however, whether this effect is due to an inhibition of rubber–sulfur combination (as suggested by Armstrong *et al.*[3]) or to an inhibition of the autocatalytic effect of hydrogen sulfide.

NATURE OF THE SULFUR LINKAGE IN VULCANIZED RUBBER

The formation of trimethyl sulfonium iodide from vulcanized rubber and methyl iodide[5] can be accepted as a rigid proof of the presence of di-α-methylenic linkages only if alkyl alkenyl sulfides, polysulfides, and the cyclic sulfides formed from dihydromyrcene and squalene do *not* form trimethyl sulfonium iodide with methyl iodide. In the investigation described in Part I, no evidence of trimethyl sulfonium iodide formation from any of these compounds has been found; it must accordingly be accepted that some part of the sulfur in vulcanized rubber is present in di-α-methylenic linkages. Since there is no over-all reduction in the ratio of hydrogen to carbon, and since unsaturation is lost during vulcanization, it necessarily follows that there must be present a proportion of the fully saturated sulfur-linked material, $\mathrm{R—S}x\mathrm{—R'}$, equivalent to the amount of the di-α-methylenic sulfur linked component, $\mathrm{R}\,\lvert\!=_{1}\!\mathrm{—S}_x\mathrm{—R'}$.

The formation of a cyclic sulfide instead of an intermolecularly linked monosulfide appears to be common to both dihydromyrcene and squalene; with rubber the

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[5] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, 36, 20 (1944).

extensive formation of cyclic sulfides may perhaps be rendered more difficult by the lower order of mobility in the rubber system, in which cross linking is simultaneously occurring by intermolecular reaction.

Polysulfide Formation in Rubber. Treatment of vulcanized rubber with aqueous solutions of sodium sulfite reveals the presence of a very small proportion of polysulfide sulfur, but the actual amount present may well be considerably in excess of that indicated, since a low order of reactivity toward sodium sulfite is shown by some of the higher polysulfides (*e.g.*, Thiokols and the squalene polysulfide described above; even dicyclohexyl tetrasulfide is fairly stable toward this reagent).

Structure of the Polysulfides. No great differences have been observed in boiling point, refractive index, and reactivity of samples of dialkyl tetrasulfides prepared, respectively, from alkyl halides and sodium tetrasulfide and from mercaptans and sulfur monochloride. Since sodium sulfite readily removes two atomic proportions of sulfur from samples of diethyl tetrasulfide prepared by either method, it follows that this reagent can abstract sulfur atoms from a linear chain because—whatever the structure assigned to sulfur monochloride—three of the sulfur atoms of the corresponding tetrasulfide must be in a linear chain. But, since Palmer[6] has obtained evidence favoring the wholly linear structure, Cl·S·S·Cl, for sulfur monochloride, a wholly linear structure, R.S.S.S.S.R, for the tetrasulfides seems highly probable. Hence it cannot be assumed that ability to yield up sulfur to sodium sulfite or caustic alkali is evidence of the presence of co-ordinated sulfur atoms.

Thermal Stability of Polysulfides. The intermolecularly linked squalene polysulfide underwent appreciable loss of unsaturation, accompanied by a small increase in mercaptan content, on being heated to 160–180°, although the over-all composition was not appreciably changed. This behavior is not altogether surprising since tetrasulfides have been shown to react fairly readily with olefins[7] at temperatures exceeding 140°. Even disulfides undergo thermal dissociation into RS* radicals.[8]

In the determination of the unsaturation of vulcanized rubber a necessary prerequisite is bringing the sample into solution by heating it to 160–180° with a nonvolatile solvent, during which treatment there is a high probability of breakdown of polysulfide linkages with a corresponding reduction of unsaturation of the rubber. The ultimate finding, after dissolution, of an average loss of unsaturation amounting to one double bond per sulfur atom is not, therefore, inconsistent with the presence of polysulfide linkages which would normally require a loss of unsaturation of $\models_0$, $\models_1$, or $\models_2$ per x sulfur atoms in dialkenyl, alkyl alkenyl, or dialkyl polysulfides, respectively. It is noteworthy that the bimolecular squalene polysulfide exhibits a considerably smaller loss of unsaturation than that corresponding to $\models_1$ per sulfur atom unless it is given severe heat treatment comparable with that prescribed for a vulcanized rubber. The small decrease in unsaturation on overcure of some accelerated vulcanizates (notably when accelerated by zinc dimethyldithiocarbamate) reported by Brown and Hauser[9] appears to be a result of oxidation since an identical experiment conducted with rigid exclusion of air showed no change in unsaturation on overcure. There is good ground for believing that the necessity for heating the vulcanizates prior to determination of their unsatura-

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[6] K. J. Palmer, *J. Am. Chem. Soc.*, 60, 2360 (1938).

[7] S. O. Jones and E. E. Reid, *ibid.*, 60, 2452 (1938).

[8] A. Schönberg, *Ber.*, 66, 1932 (1933).

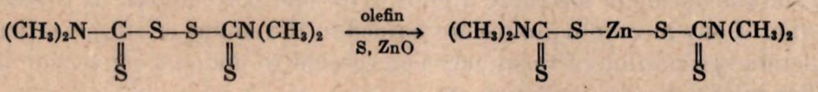
[9] J. R. Brown and E. A. Hauser, *Ind. Eng. Chem.*, 30, 1291 (1938).

tion is in itself sufficient to obscure any real change in unsaturation produced by sulfur redistribution.

On heating together a polysulfide and an olefin, three types of reactivity of the polysulfide have been observed: (*1*) Some disulfides gave small proportions of the corresponding mercaptans, probably by a radical mechanism:

$$\mathrm{R_2S_2} \longrightarrow 2\,\mathrm{R\underset{\cdot}{S}^{*}} \xrightarrow{R'H} \mathrm{RSH} + \mathrm{\dot{R}'}$$

(*2*) Tetrasulfides and some disulfides gave evidence of the occurrence of partial addition to the olefin of radicals resulting from fission of —S—S— linkages, but part of the sulfur liberated from the tetrasulfide also reacted with other olefinic linkages. Throdahl and Beaver[10] observed that alkyl tetrasulfides do not vulcanize rubber in a physical sense, but they did not report any tendency for nonvulcanizing combination of either liberated sulfur or liberated sulfurated fragments to occur with the rubber. On the other hand, the known rubber-vulcanizing properties of some long-chain polysulfides[11] of the type —R—S_x—R—S_x— may be due to attachment of polyfunctional long-chain dissociation fragments to unsaturated centers in the rubber. (*3*) Tetramethylthiuram disulfide gives evidence of both mercaptan formation:[12]



$$\mathrm{(CH_3)_2N{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}N(CH_3)_2} \xrightarrow[\text{S, ZnO}]{\text{olefin}} \mathrm{(CH_3)_2N\underset{\underset{S}{\|}}{C}{-}S{-}Zn{-}S{-}\underset{\underset{S}{\|}}{C}N(CH_3)_2}$$

and radical dissociation, the latter process yielding sulfur, thiourea, and carbon disulfide. It is noteworthy that the yield of carbon disulfide amounts to 40% of the theoretical in the presence, and 70% in the absence, of zinc oxide.

Role of Zinc Oxide in Vulcanization

The addition of zinc oxide to rubber and sulfur does not increase the rate of combination of sulfur with the rubber, but does substantially increase the rate of physical cure. Various workers have suggested that additional cross linking is brought about by mercaptide formation or by the subsequent action of sulfur on a mercaptide.[3] The sulfur–zinc oxide combination, however, reacts readily with mercaptans in a manner quite different from the action of sulfur on mercaptides as expressed by the equation:

$$\mathrm{R{\cdot}S{-}Zn{-}S{\cdot}R} \xrightarrow{S} \mathrm{R{\cdot}S{\cdot}S{\cdot}R} + \mathrm{ZnS}$$

Indeed, at temperatures above 70° a reaction occurs which involves liberation of hydrogen sulfide but not any significant degree of formation of zinc sulfide:

$$2\,\mathrm{RSH} + \mathrm{S} \xrightarrow{ZnO} \mathrm{RS_{\mathit{x}}R} + \mathrm{H_2S}$$

The zinc oxide functions mainly as a catalyst and only a small proportion is required; zinc stearate is almost equally effective. Polysulfides are readily formed in the presence of an excess of sulfur, but with smaller amounts of sulfur a disulfide is the major product. The corresponding reaction of mercaptans with sulfur alone is extremely slow, even at 140°.

Many accelerators of rubber vulcanization show the same type of reaction-promoting activity toward mercaptan and sulfur as does zinc oxide, but they are considerably more

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[10] M. C. Throdahl and D. J. Beaver, *Rubber Chem. Tech.*, **18**, 110 (1945).

[11] J. C. Patrick, U. S. Pat. 2,235,621 (March 18, 1941).

[12] A. Jarrijon, *Rev. gén. caoutchouc*, **20**, 155, 177 (1943).

effective than the latter, and polysulfides are readily formed even at room temperature. The nitrogenous basic accelerators, piperidine, piperidine pentamethylene dithiocarbamate, diphenylguanidine, and butyraldehyde-aniline are the most reactive and tetramethylthiuram disulfide is somewhat less reactive; zinc dimethyldithiocarbamate shows considerable activity at 70°, doubtless due to its relationship with tetramethylthiuram disulfide, but in general the disulfide accelerators and the corresponding mercaptan accelerators are relatively ineffective.

When rubber, sulfur, and either cyclohexyl or ethyl mercaptan were heated together at 140° at least 50% of the mercaptan was converted to isolable disulfides and polysulfides in the course of an hour; the reaction of the mercaptan with the sulfur did not in this instance necessarily require the presence of either zinc oxide or an organic accelerator, although in their absence the conversion to di- and polysulfides did not proceed quite so readily. In none of these experiments was more than a trace of hydrogen sulfide liberated; consequently the hydrogen sulfide resulting from the mercaptan oxidation must have entered into immediate reaction with the vulcanizing rubber, possibly by a radical mechanism. The formation of no more than trace quantities of hydrogen sulfide during ordinary vulcanization processes is no proof of the absence of reactions involving the conversion of mercapto groups to di- and polysulfides; it therefore appears certain that if any mercapto groups are formed in the course of vulcanization reactions, a considerable proportion of them may be expected to undergo conversion into di- and polysulfide intermolecular linkages.