THE SULFURIZATION OF UNSATURATED COMPOUNDS

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Received March 28, 1946

CONTENTS

I. INTRODUCTION

The high reactivity of unsaturated compounds, as manifest by their easy addition of certain simple molecules such as halogens, has long been one of the salient characteristics of organic chemistry. The nature and products of the common additions have become well known, and the principles governing them have been established. The reaction of sulfur with saturates was also discovered early; but because its chief importance lay in the use of a complicated polymeric olefin, rubber, its mechanism has remained obscure up to the present day. Charles Goodyear discovered the vulcanization of rubber in 1839, and no work on the theory of the process was reported until the turn of the century. Since that day much labor has been expended on the structure of vulcanized rubber and, more recently, on that of factice and of the sulfurization products of olefins. It is the purpose of this review to elicit from all this research a more harmonious view of the pertinent reactions. Sulfurization of the various classes of unsaturated substances will be considered in turn.

II. SIMPLE OLEFINIC HYDROCARBONS

The first interest in the direct sulfurization of the simple olefinic hydrocarbons came with Victor Meyer's discovery of thiophene in coal-tar benzene (48). In his researches on the structure and formation of thiophene, Meyer (49, 51) showed that ethylene or acetylene and molten sulfur reacted at 300°C., forming traces of thiophene together with carbon, carbon disulfide, and hydrogen sulfide. Steinkopf and Kirchhoff (75) improved the yield of thiophene greatly by mixing the sulfur with pyrite.

The reaction of acetylene with sulfur was studied in more detail by Peel and Robinson (60), who determined that, below the boiling point of sulfur, acetylene reacts with it to give about a 5 per cent yield of thiophene, together with large

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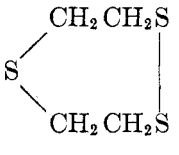
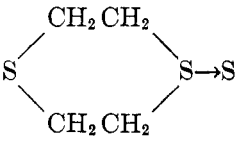
amounts of carbon disulfide and hydrogen sulfide and a substance with an "unidentified garlic-like odor." At 500°C., 75 per cent of the acetylene was transformed into a brown oily product of composition 77 per cent carbon disulfide, 12 per cent thiophene, and 6 per cent thiophten. Briscoe, Peel, and Robinson (7) demonstrated that the thiophene was formed by direct reaction with the sulfur and not by a secondary reaction with carbon disulfide, for mixtures of acetylene and carbon bisulfide gave only traces of thiophene up to 350°C. and only a 12 per cent yield at 700°C. More recently Bhatt, Nargund, Kanga, and Shak (4) identified the "garlic-like odor" of Peel and Robinson as being due to thiophenol. No one seems to have speculated on the possible connection between the mechanism of the reaction and these observations that acetylene, which is known to polymerize over a wide variety of catalysts at the temperatures used (34, 79), gave all sulfuriferous products. This fact could be a clue to the course of the reaction, if studied in that light.

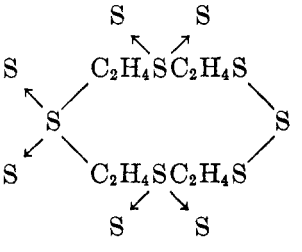
Meyer and Hohenemser (50) noted that ethylene failed to react with sulfur at 140°C. Jones and Reid (38) passed ethylene through sulfur at 325°C., to form much hydrogen sulfide and small amounts of ethyl mercaptan, ethyl sulfide, and carbon disulfide. The mercaptan and the sulfide apparently resulted from side reactions of the ethylene with the hydrogen sulfide already formed and of the mercaptan with more ethylene. The first isolation of true products from the reaction of ethylene with sulfur has been described by Westlake, Mayberry, Whitlock, West, and Haddad (88). From a reaction under pressure, using xylene as a solvent, they separated two main products, an insoluble elastomer and a xylene-soluble oil. Part of the latter was volatile. From experiments carried out to determine the structures of these products nothing could be conclusively proved, but, on the basis of the evidence obtained, they assigned either structure I or structure II to the volatile fraction and structure III to the non-volatile fraction, and expressed the belief that the polymeric insoluble sulfide was a chain of ethylene groups linked through monosulfide and random polysulfide groups, possibly cyclized, with all sulfide linkages saturated with labile



I



II

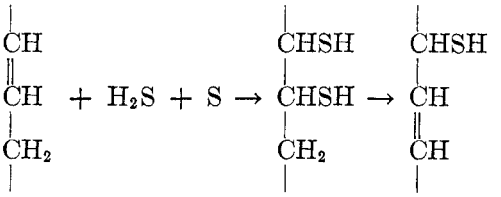


III

sulfur atoms. Brown (8) found in a study of this reaction that the products were strong catalysts for the reaction.

The sulfurization of the higher olefins has been given more attention. Friedman (26) heated hexene and sulfur under pressure and obtained a mixture of $C_6H_{12}S$, $C_{12}H_{24}S$, and $C_{18}H_{34}S$, together with an asphaltic non-volatile residue

of the composition $C_{24}H_{20}S_2$. He postulated that hydrogen sulfide formed during the reaction added to the double bond to form a thioglycol, which then split hydrogen sulfide with the α-methylene group to yield an unsaturated mercaptan.

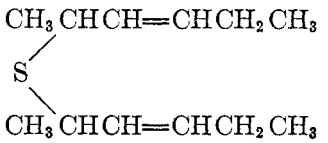


(1)

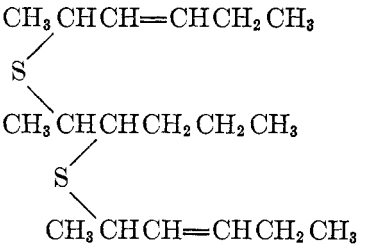
The compound $C_6H_{12}S$ he described as this mercaptan, using as a test its easy exothermic reaction with lead oxide. He then postulated an addition of this derivative to itself to form an unsaturated sulfide (equation 2). He assigned structure IV thereto

$$2C_6H_{12}S \rightarrow C_{12}H_{24}S \qquad (2)$$

and structure V to the compound $C_{18}H_{34}S_2$.



IV



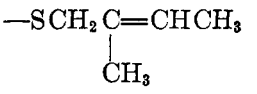
V

Friedman isolated analogous products from octene ($C_8H_{16}S$, $C_{16}H_{32}S$) and from hexadecene ($C_{16}H_{32}S$).

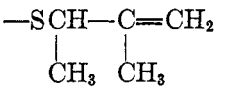
Quite recently an investigation has been reported by Armstrong, Little, and Doak (1), in which a number of higher olefins were sulfurized at temperatures ranging from 120°C. to 140°C. and both with and without the presence of catalysts such as rubber accelerators (2-mercaptobenzothiazole, zinc propionate, zinc oxide). Volatile and non-volatile products were obtained in varying amounts, depending on the olefin used and the conditions of the reaction (temperature, catalyst, etc.). The structure of the volatile products was investigated by ozonolysis, and it was found that they corresponded to the simplest cross-linked structures in which two olefin units were joined by one or two sulfur atoms connected to α-methylene groups. All products thus contained carbon-to-carbon cross-linking through sulfur. For example, 2-butene gave almost entirely dicrotyl sulfide (with traces of the disulfide):

$$2CH_3CH{=}CHCH_3 + 2S \rightarrow (CH_3CH{=}CHCH_2)_2S \qquad (3)$$

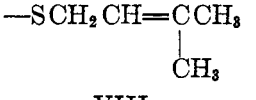
Other olefins afforded mixtures of the sulfides and disulfides of allylic radicals, both symmetrical and mixed.



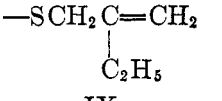
VI



VII

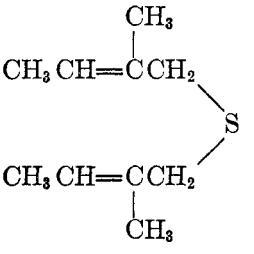


VIII

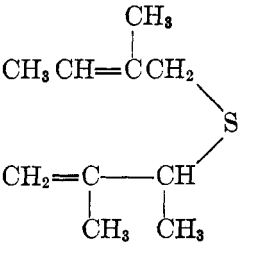


IX

2-Methyl-2-butene gave 70 per cent type VI radicals, 20–30 per cent type VIII, and 10 per cent type VII, and among the compounds proved to be present was bis(β-methylcrotyl) sulfide (X). 2-Methyl-1-butene formed a mixture of



X



XI

radicals VI and IX connected by mono-and di-sulfide linkages.

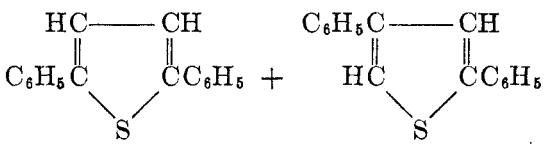
To balance equation 3 a hydrogen sulfide molecule must be eliminated for every sulfur added. Armstrong, Little, and Doak found practically none where 5-methyl-4-nonene was heated with sulfur in the presence of a stream of nitrogen, although a methyl nonenyl disulfide was formed. The hydrogen sulfide must have been at least partly responsible for the polymers which were isolated in every case. It could also be partly responsible for the inorganic sulfide which was formed when inorganic compounding ingredients were included in the reaction mixture.

Studies have also been reported on the cycloölefins. Markownikoff and Spady (46), in a study of the constitution of naphthenes by use of the Vesterburg reaction (dehydrogenation with sulfur), had noticed the formation of high-boiling sulfur compounds in addition to the identified benzene homologs. Friedman (27) showed that dehydrogenation of cylcohexane with sulfur gave thiophenol and diphenyl sulfide as well as benzene. As sulfur does not react appreciably with benzene even at 250°C., except to form biphenyl (68), a fact which has been used to purify benzene of olefinic impurities (35, 83), this reaction may have involved partial dehydrogenation to cycloölefins and sulfurization thereof. It is more likely that the sulfurization occurred first, however, for Borsche and Lange (6) obtained cylcohexyl mercaptan from sulfur and cyclohexane, and Meyer and Hohenemser (50) found that cyclohexene and sulfur gave cyclohexyl mercaptan and cyclohexyl sulfide. The latter reaction was explained as being due to a dehydrogenation, followed by addition of the resulting hydrogen sulfide to cyclohexene. Friedman (28) sulfurized dicyclopentadiene and reported a

product $C_{10}H_{12}S$, which from its formula could be an unsaturated mercaptan, but he stated that there were insufficient data to enable even a guess as to its constitution.

A number of substituted unsaturates have been subjected to sulfurization reactions, mostly quite drastic Thus Baumann and From (3) reacted cinnamic acid with sulfur at 210°C. for several hours, followed by 6 hr. of refluxing at 240°C., to get a mixture of diphenylthiophenes:

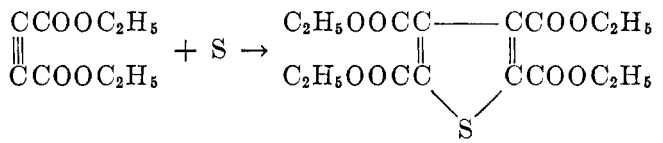
$$C_6H_5CH{=}CHCOOH + S \rightarrow$$



(4)

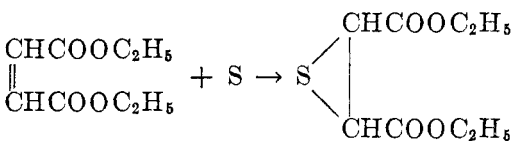
Similar treatment of styrene gave the same products. Michael (52) sulfurized styrene at 150–160°C. and reported the isolation of a compound having the composition C_8H_8S. Westlake (87) has sulfurized styrene in xylene solution and isolated as the sole product a mixture of the average composition $(C_8H_8S_3)_{2.5}$, which could be decomposed by pyrolysis to diphenylthiophene.

Michael also sulfurized acetylenedicarboxylic acid ester to form thiophene-tetracarboxylic acid ester:



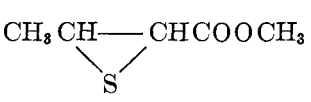
(5)

On the other hand, he reported that ethyl fumarate and sulfur gave an ethylene sulfide derivative:



(6)

This compound did not have any tendency to polymerize and could be saponified by potassium hydroxide without decomposing the sulfur ring. In view of the sensitivity to various reagents, including alkali, which Delépine (16) found ethylene sulfides of this structure to possess, and in view of the almost violent polymerization resulting therefrom, it is doubtful that the structure postulated by Michael was correct. Michael also found methyl crotonate to add one sulfur atom to give the compound $C_5H_8SO_2$, which he presumed to have the structure:

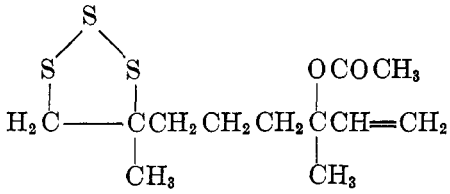


XII

The simple polyolefins have been sulfurized only at high temperatures. From butadiene and sulfur at 320–420°C. Shepard, Henne, and Midgely (70) obtained 6 per cent conversion to thiophene, while isoprene gave 47 per cent conversion to 3-methylthiophene under the same conditions. Apparently the methyl group in isoprene can affect the configuration of the molecule so as to make cyclization more probable. Westlake (87) has found no difficulty in reacting butadiene with sulfur under pressure in xylene solution. The products are red odorous oils resembling the ethylene sulfides described earlier. From the similarity in properties, a similarity in structure has been inferred but not investigated experimentally.

III. TERPENES

As one of the most plentiful sources of unsaturated compounds, the terpenes have been reacted with sulfur to form many useful products, such as resins, oil additives, bonding materials, and rubber substitutes. A review of such products and references to their original disclosure can be found in Ellis' *The Chemistry of Synthetic Resins* (17). The structure of the products has not received the attention it deserves. One of the first researches of relevance was that of Erdmann (18), who quite rightly pointed out that any theory regarding the sulfurization of unsaturates was dependent on the state of knowledge of the structure of sulfur. He began with the assumption that the reactive, labile, deep-red form of liquid sulfur was a short sulfur chain S_3 or thiozone, analogous to ozone, and postulated from his experimental evidence the addition of this thiozone to the unsaturate in a manner similar to ozonolysis. He reacted linaloöl and its acetate with sulfur. No reaction appeared at 150°C., but at 160°C. a lively, spontaneous exothermic reaction began with evolution of hydrogen sulfide. The product from linalyl acetate had the composition $C_{12}H_{20}O_2S_3$, which he described as the thiozonide (XIII).

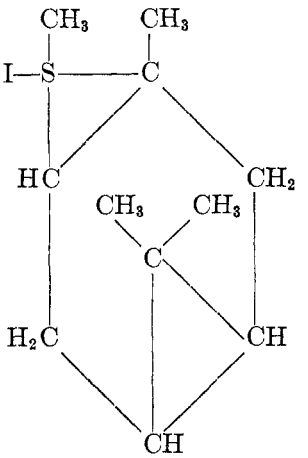


XIII

He found that, with a large excess of sulfur, the product after mechanical separation of the latter was the same $C_{12}H_{20}O_2S_3$. When he used an excess of the linalyl acetate he always obtained the same product, never a lower sulfurized compound. These products were always isolated as residues, with no attempts at further purification. Erdmann further claimed that the free alcohol absorbed twice as much sulfur to form a compound which he described as a dithiozonide and which lost hydrogen sulfide on standing.

Taken by itself, Erdmann's work seems quite conclusive, except for his failure to purify his products by distillation or treatment with solvents. But no other

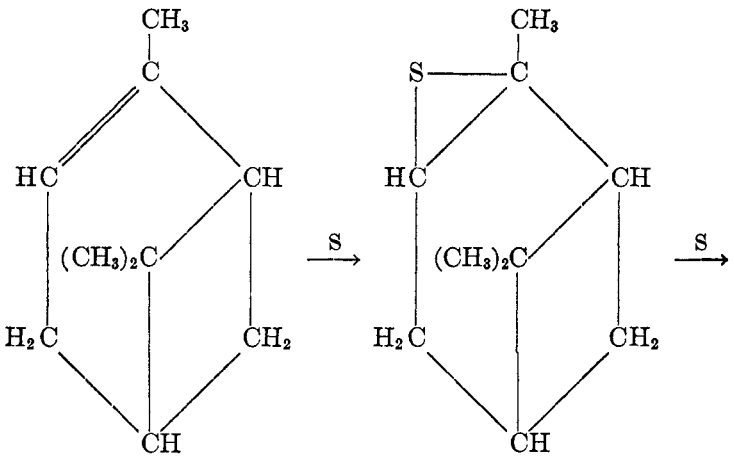
investigator in all the fields affected by the sulfurization of unsaturated compounds has ever duplicated Erdmann's thiozonides, and some of the later work on terpenes, as well as in other sectors, appears to be quite contradictory. Budnikoff and Schilow (10, 11, 62) settled on the purification question as the cause of the differences between Erdmann's and their results. They sulfurized pinene and also Russian turpentine, which is a mixture of limonene and silvestrene, and treated the reaction products with methyl iodide to purify them, isolating a methyl iodide addition compound, apparently a sulfonium salt convertible into a sulfonium base. Their products were all compounds containing one terpene to one sulfur. For example, the product from pinene was $C_{10}H_{16}S \cdot CH_3I$, to which they gave formula XIV, although without proof.

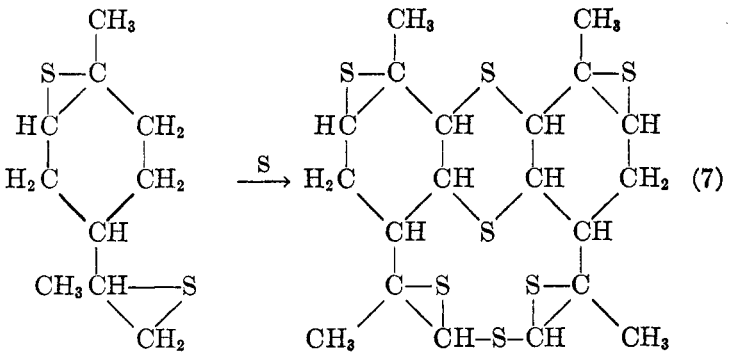


XIV

The sulfurization of American turpentine, which is principally α-pinene, has been described by Pratt (62, 63). The mixture first gave a dark liquid, which became a viscous mass and eventually a brittle substance resembling hard rubber, depending on the time and temperature of heating. By distillation and fractionation he isolated from the early liquid product without apparent decomposition a compound having the composition $C_{20}H_{24}S_5$; he postulated that it was formed by the process shown in equation 7. Analyses and molecular-weight determinations revealed that the double bonds had become saturated and that terpene residues were linked together, but no other experimental attempts to ascertain the structures were reported. The brittle product was found to have the molecular formula $C_{10}H_{12}S_4$, but no effort was made to write a structural formula for it.

A rather extensive series of researches by Nakatasuchi (55, 56, 57) on many different terpenes confirmed the results of Budnikoff that there occurred a one-to-one addition of sulfur to terpene. Thus, *d*-limonene reacted with sulfur to give a product $C_{10}H_{16}S$, to which he ascribed the structure XV, and some *p*-cymene (XVI). Many other terpenes also yielded a monosulfide.





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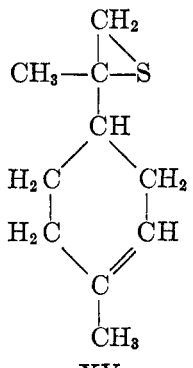
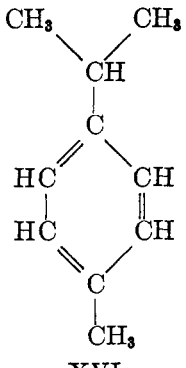
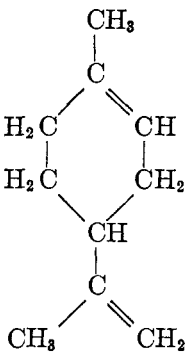


XV

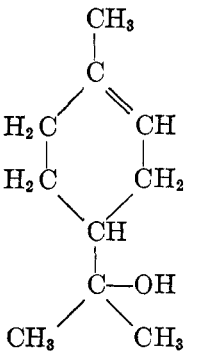


XVI

Dipentene (XVII) and α-terpineol (XVIII) gave the same $C_{10}H_{18}S$, which added one molecule of methyl iodide to furnish $C_{10}H_{18}S \cdot CH_3I$ and one bromine molecule to afford $C_{10}H_{18}SBr_2$, and was oxidized by potassium permanganate to $C_{10}H_{18}SO_2$,

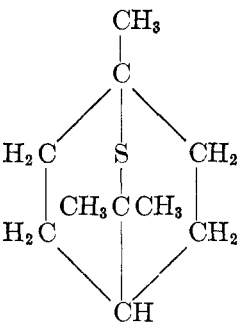


XVII



XVIII

$C_{10}H_{18}SO_3$, and $C_{10}H_{18}SO_4$. Nakatasuchi considered this compound to be a thiocineole (XIX), which is a much more likely structure than the three-mem-



XIX

bered rings favored by Pratt, Budnikoff, and even Nakatasuchi in his first paper. Probably the limonene sulfide (XV) was also a similar bicyclic compound. A structure involving substitution on each of two methylene groups alpha to a double bond would be more consistent with the observations made by other investigators on the sulfurization of the simple olefins. Certainly the possibility of such substitution will have to be investigated thoroughly before positive structures can be assigned to terpene sulfides.

Nakatasuchi also refuted Erdmann's work by the observation that both linalyl acetate and linaloöl reacted with sulfur to give *p*-cymene, dipentene, and an unknown terpene, $C_{10}H_{16}$ or $C_{10}H_{14}$, but no sulfur compound. Unconfirmed by any other investigator, and, in fact, directly contradicted by one, Erdmann's thiozonides appear to have places on the roll of products of chemical speculation.

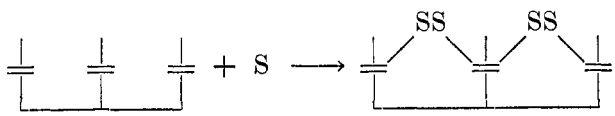
IV. DRYING OILS—FACTICE

Another plentiful source of unsaturated compounds is the group of glycerides of unsaturated fatty acids, usually known as the drying oils. The vulcanization of these natural products to form rubber substitutes and extenders, coatings,

plasticizers, and other useful articles of commerce has been important commercially for many years. A review of their technologic aspects can be found in Ellis' *The Chemistry of Synthetic Resins* (17).

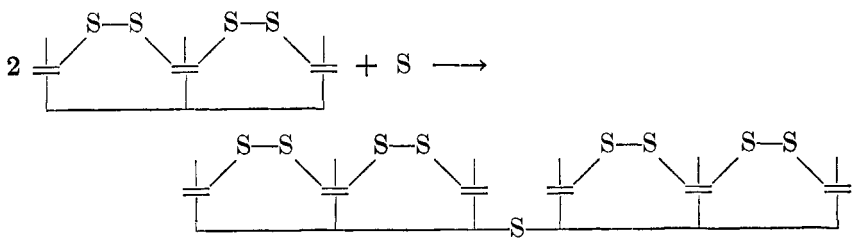
Whereas much has been published and patented concerning commercial utilization of the sulfurized drying oils, the complicated composition of the products has been relatively neglected. If sulfur is heated at vulcanizing temperatures with linseed oil, a three-stage process takes place (89). First of all, a chemical combination of the sulfur and the oil causes formation of a homogeneous mass. An acetone-insoluble polymer richer in sulfur than the remaining liquid then forms and causes gelation. Further heating transforms the gel into a solid polymer. Long, Knauss, and Small (44) showed that the second step involved a marked increase in molecular weight, indicating that the glycerides were coupling together.

Stamberger (73, 74) studied the reaction with triolein in considerable detail. He fractionated the rubbery, sulfurized triolein into three parts: acetone-soluble, acetone-insoluble but benzene-soluble, and benzene-insoluble fractions. He was able to demonstrate by molecular-weight studies and by analysis that the second fraction was about twice the molecular weight of the first and had more than twice as much sulfur. By allowing the glycerides to stand for 24 hr. in 0.5 *N* potassium hydroxide, he succeeded in saponifying them. All three fractions yielded the same tribasic acid, which analysis and molecular-weight determinations showed was a combination of three oleic acid molecules and three or four sulfur atoms. Some of the sulfur was not accounted for by this oleic acid sulfide, especially with the second and third fractions. From these data it was concluded that the first step in the reaction consisted of sulfurization and mutual linking of the three oleic acid chains, illustrated schematically by equation 8.



(8)

The formation of the second fraction was then postulated as



(9)

and the final step was pictured as involving continued polymerization through the glycerol residues.

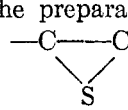
Although the work of Stamberger was conducted on a single pure glyceride, it seems highly probable that the conclusions drawn therefrom are scopeful and that natural oils combine with sulfur to form polymers whose general structures

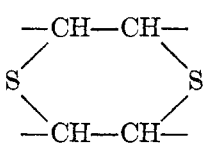
resemble those assumed for sulfurized triolein. However, the details of how the sulfur is linked in the molecule remain to be learned.

Hauser and Sze (33) recently studied the effect of sulfurization on the unsaturation and on the diene number of tung oil, which contains the triply conjugated unsaturated acid, eleostearic acid. They found that the unsaturation decreased with increasing combined sulfur but that the diene number remained constant until nearly all the sulfur which would combine had reacted. At this point one double bond had disappeared. Although the determination of diene number requires but two of the three conjugated double bonds, it is difficult to see how 1,2-addition could inhibit the further reactivity of the 5,6-position toward sulfur. They therefore concluded that the sulfur added 1,6 to the conjugated system and that steric affects rendered the remaining unsaturated system less reactive, explaining the failure of any more sulfur to combine. Hydrogen sulfide was not liberated in the early part of the reaction. The primary reaction, before secondary reactions set in, consequently appeared to be a 1,6-addition of sulfur to the conjugated system, saturating one double bond.

Hauser and Sze also investigated the rate of sulfurization of linseed oil. Here, too, the sulfur began combining at a rate of nearly two atoms for each double bond lost, but this reaction fell off rapidly. The rate of combination was greatly accelerated by the presence of zinc oxide or mercaptobenzothiazole.

It is to be noted that both the work of Nakatasuchi on terpenes (56) and that of Hauser and Sze on drying oils indicate a saturation of the double bond, while the researches of Armstrong, Little, and Doak (1) and of Friedman (26) on olefins point to a substitution on the α-carbon atom. This controversy will be met again in the following section, wherein the vulcanization of rubber is discussed.

Of interest to the general conception of the structure of factices is the work of Kaufmann, Gindsberg, Röttig, and Salchow (39) and that of Salchow (65, 66) on the preparation of ethylene sulfide derivatives of natural oils of the structure  by a procedure analogous to the thiocyanate method of Delépine (16) and the polymerization of these compounds to factices. By using what they called a free fat acid instead of a drying oil, they were able to get crystalline products which they considered to be dithiane derivatives:



They obtained the same compounds upon reacting sulfur chloride with the fat acid but could secure no such product from direct sulfurization. Rankoff (64), however, had reported a crystalline derivative from the action of sulfur on elaidic acid and Kaufmann believed this compound to be a dithiane-elaidic acid.

V. THE VULCANIZATION OF RUBBER

Commercially, the vulcanization of rubber forms the most important single example of the sulfurization of unsaturated compounds. From the theoretical standpoint this situation is unfortunate, for the sulfurization of a highly complex hydrocarbon such as rubber could at best be an involved process. Much more research has been carried out on the theory and mechanism of the reaction with rubber than on all the rest of the types of unsaturated compounds previously considered put together and only very recently has the importance of studying the reaction with simple molecules been recognized. Because of the complexity of the reaction and the size of the hydrocarbon, much of the earlier work was indeterminate and gave rise to many conflicting theories.

The leading controversy in the past was whether or not the change in physical properties was due to a chemical reaction and, if so, what reaction. This dispute began with the earliest researches on the theory of vulcanization and continues to the present day. Hohn (36) proposed that vulcanization consisted of adsorption of sulfur on the rubber hydrocarbon. Weber (90, 91), however, found that a part of the sulfur was not acetone-extractable and asserted that it was chemically combined. He thought he had evidence of definite compounds, but Stern (77) and Hubener (37) demonstrated that the amount of combined sulfur was proportional to the time of heating and to the initial concentration of sulfur. Ostwald (59) supported Hohn's theory mainly on the basis that Weber's data showed too low a temperature coefficient for a chemical reaction. But Spence and Young (72) determined the temperature coefficient of vulcanization to be about 2.65 per 10°C. and very recently Gerke (30) repeated the determination, confirming that it was above 2. Furthermore, Spence and Ward (71) showed that the rate of vulcanization was not dependent on the mechanical dispersion of the sulfur, a factor which would have controlled surface area in an absorption theory. It was therefore conceded that chemical combination of sulfur occurred during vulcanization. The type, degree, and method of such chemical combination remained and still are to be determined.

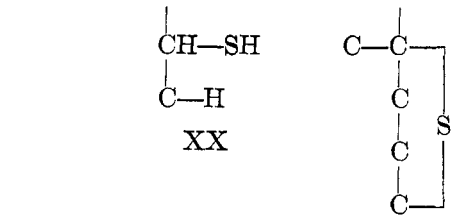
The early observations indicated that vulcanization was always associated with a disappearance of unsaturation. This inference led naturally to a theory that sulfur saturated the double bonds, setting up cross-linkages between hydrocarbon chains. Moreover, the vulcanization to soft rubber could be accomplished with only a small percentage of sulfur. Hard rubber, or ebonite, was formed with much more sulfur. Spence and Young (72) reported that just enough sulfur to saturate the double bonds would combine and that further heating caused no further combination. This conclusion has been somewhat disproved by Steven and Stevens (79) and by Hauser and Sze (33), who have brought out that more than the theoretical 32 per cent of sulfur will combine, owing to a substitution reaction with evolution of hydrogen sulfide. Fisher and Schubert (25) have adduced from analyses of hard rubber that, where the amount of sulfur used is theoretical (32 per cent), it adds to the unsaturation until saturation is complete, but that larger quantities of sulfur give substitution reactions. A carefully prepared ebonite had the same carbon–hydrogen ratio as rubber. This

fact was confirmed by Armstrong, Little, and Doak (1), who demonstrated that no hydrogen sulfide was evolved. Wrück (94), Hauser and Sze (33), and Brown and Hauser (9, 31) have shown that the bromine or iodine number of the rubber hydrocarbon decreases in proportion to combined sulfur, a further confirmation that the vulcanization reaction involves a saturation of the double bonds. But Brown and Hauser found that, until optimum cure for soft rubber was reached, more than one sulfur per double bond was reacting.

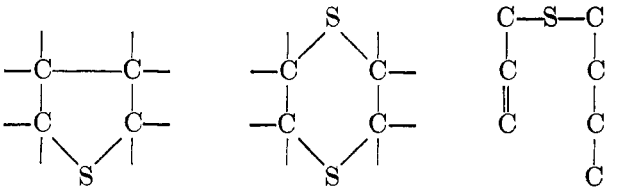
The mode of combination of sulfur in rubber has revealed itself to be just as baffling as every other phase of the complex problem. There is, for example, the belief of Kirchoff (42) that the end group on the rubber hydrocarbon is a ring which opens to give an active methylene group and that the first step of vulcanization occurs there by cross-linking of the chains. Boggs and Blake (5) concluded from a study of the heat of combustion of vulcanized rubber that Kirchoff was right, and Hauser and Sze (33) also accepted bridging at the terminal carbons as the explanation of soft rubber. The latter investigators also considered saturation of the double bonds in the middle of the chains the process which forms ebonite. Hauser and Smith (32) claimed to have obtained experimental evidence for cross-linking from x-ray examination of stretched vulcanized rubber.

Although modern investigators agree that chemical reaction between sulfur and rubber occurs, many still do not think that the phenomenon of vulcanization involves cross-linking of the hydrocarbon chain. Stevens (80) believed that vulcanization was caused by a colloidal dispersion of a rubber sulfide in the rubber. Midgley, Henne, Shepard, and Renoll (54) fractionated vulcanized rubber between benzene and alcohol and isolated a series of sulfides of the general structure RS, RS_2, RS_3, etc. They pointed out that cross-linked chains would give a series RS, R_2S, R_3S_2, etc., and regarded this observation to be evidence of no cross-linking. Williams (93) also claimed to have fractionated vulcanized rubber into portions of different sulfur content, but Kemp, Malm, Winspear, and Stirabelli (41) disproved such fractionation by a study of the diffusion of sulfur in rubber. Garvey and Forman (29) visualized vulcanication as a mechanical process involving the kinking of chains around one another, producing the effect of cross-linking with the sulfur reacting intramolecularly. Midgley, Henne, and Shepard (53) concluded from the destructive distillation of ebonite that such intramolecular addition was the case and that the thiophane rings thus formed prevented free movement of the chains, causing mechanical cross-linking.

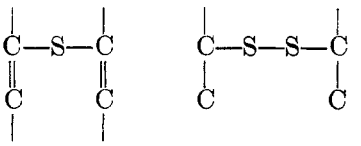
Of course the mechanism of vulcanization is not important to the subject of this paper, except as it affects knowledge of the chemical combination of the sulfur. That sulfur combines chemically is now generally conceded. The nature of the sulfide linkages in vulcanized rubber has not received the experimental attention it ought to have had. Speculation seems to have replaced research, at least in the past. Brown and Hauser (9) listed the types of linkages then believed possible, and Van Amerongen and Houvink (84) considered each of them from the standpoint of steric stability and bond strains, with the conclusion that seven were theoretically possible,—two intramolecular and five intermolecular.



XX XXI



XXII XXIII XXIV



XXV XXVI

XX would be formed by addition of hydrogen sulfide to a double bond, as advocated by Fisher (23), who thought that all vulcanization was caused by hydrogen sulfide generated by sulfurization of rubber or non-rubber hydrocarbon. This idea was discredited by Busse (13), who learned that hydrogen sulfide retarded the rate of vulcanization and especially interfered with accelerators, and also by Armstrong, Little, and Doak (1), who found no hydrogen sulfide evolved in the vulcanization not only of rubber but of simple olefins. Structure XXI is based on the thiophane rings favored by Midgley, Henne, and Shepard (53) from the types of thiophenes isolated by the pyrolysis of hard rubber. Because their evidence appears to be good, the occurrence of this linkage, at least in ebonite, is highly probable. XXII would be formed by simultaneous saturation of double bonds on two different chains by one sulfurization and consequent cyclization. The dithiane rings (XXIII) would result from saturation by sulfur of both ends of the two double bonds. Perhaps the ratio of between one and two sulfur atoms per double bond found by Brown and Hauser can be explained by formation of a mixture of XXII and XXIII. The type of structure represented by these two is the most probable result of any sulfurization mechanism involving direct saturation of the double bonds. Structure XXIV is the unsaturated sulfide to be expected from α-methylene attack, as postulated recently by Farmer and coworkers (19, 20, 21), which will be discussed later. It is strongly possible, as it appears to answer a number of facts. Structure XXV is far less likely, for it is difficult to see how it could be produced without substitution on double-bonded carbon itself, a reaction not

backed by practical experience as is α-methylene attack. There is no evidence in favor of structure XXVI, for the only conceivable way in which it could be formed is by oxidation of a mercaptan and the saturated mercaptan would be structure XX, arguments against which have already been presented. Furthermore, there is no evidence for the presence of disulfide groups. The most probable sulfur linkages thus seem to be XXI for intramolecular and XXII, XXIII, and XXIV for intermolecular reaction.

Research on the chemical nature of the sulfur linkages in vulcanized rubber is of recent date. Meyer and Hohenemser (50) first suggested the use of methyl iodide to determine monosulfide sulfur. They reported that 80 to 90 per cent of the sulfur present was as thioether linkages. Their method was further studied by Brown and Hauser (9), who accounted for 20 to 60 per cent of the combined sulfur as thioether linkages but could not correlate this conclusion with physical properties and, as a result, belittled this method of attacking the problem. Williams (93) also doubted its value. However, Selker and Kemp (69) investigated the reaction of methyl iodide with pure organic sulfur compounds and found that each type of compound gave characteristic products in characteristic periods of time, as illustrated by equations 10 through 12:

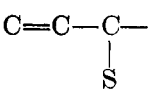
$$2RSH + 4CH_3I \xrightarrow{HgI_2} 2R_2CH_3I + 2HI \quad (10)$$

$$RSR + CH_3I \xrightarrow{HgI_2} R_2CH_3SI \quad (11)$$

$$\text{(unsaturated R)}\ RSR + 3CH_3I \xrightarrow{HgI_2} RR + (CH_3)_3SI + I_2 \quad (11a)$$

$$RSSR + CH_3I \xrightarrow{HgI_2} R(CH_3)_2SI + I_2 \quad (12)$$

They reported that reactions 10 and 12 were slow, even with the mercuric iodide catalyst, while reaction 11 was quite fast. Thus they were able to determine mercaptan by titrating the hydrogen iodide. Sulfide was determined in the presence of disulfide by the weight gain of the reaction vessel in 24 hr. of contact with excess methyl iodide. Three days of contact permitted determination of disulfide. These findings were used to study the chemical binding of sulfur in vulcanized rubber. The behavior of all vulcanizates was found to resemble closely that of allyl sulfide, indicating that the group



XXVII

which is the important feature of structure XXIV, was present in large quantity. The sulfur reactable with methyl iodide appeared to be involved in linkages of this type. But in no case was all the combined sulfur in the vulcanizate removable with methyl iodide. Thiophene does not react with methyl iodide, and Selker and Kemp thought some such ring system to be the possible way of accounting for the remaining sulfur. This conclusion is interesting in view of the results of Midgley, Henne, and Shepard (53), who obtained from the

pyrolysis of ebonite a distillate composed of a mixture of methyl- and ethylthiophenes. From these results they said that the thiophane rings were the principal sulfur structures formed. Probably Selker and Kemp are closer to the true picture, but it is still not entirely clear. Williams (92) has suggested that spectroscopic data might produce important evidence. The experimental difficulties involved in spectra work on a complex polymer would be in addition to the lack of spectroscopic data on sulfur linkages. Determination of such data and application to the structure of vulcanizates are certainly well-indicated lines of research. Other chemical methods of attacking the chemical linkages should also be sought.

VI. ASPHALTS AND PITCHES

The natural pitches and asphalts are sulfuriferous. Treatment of bituminous materials of various sorts with sulfur has been suggested many times as a method of preparing artificial pitches, and numerous such preparations have been patented or reported in the literature (17). The complexity of most bituminous materials, however, makes any identification of the reaction products an even more difficult problem than that encountered in vulcanized rubber. Since Lorand (45) has shown that the reaction of cracked petroleum distillates with sulfur chloride involves primarily the olefinic constituents, the same is probably true for the direct sulfurization of complex unsaturated materials.

Some of the few such products for which even the empirical composition is known were isolated by Friedmann (26, 27, 28) in his work on the sulfurization of olefins. He reported the empirical compositions of the asphaltic materials obtained as residues from the distillation of sulfur–olefin reaction mixtures. Thus, hexene and sulfur produced an asphalt $C_{24}H_{48}S_5$, octene gave $C_{24}H_{42}S$, and hexadecene yielded $C_{64}H_{48}S_5$; but their structures were not defined.

Nellensteyn and Thoenes (58) attempted to determine the part played by sulfur in the formation of natural asphalts by heating the sulfur dioxide extract of lubricating oil with sulfur at 135–300°C. They recovered most of the sulfur as hydrogen sulfide in proportion to the asphalt formed. McKinney, Mayberry, and Westlake (47) obtained products with large but undetermined percentages of combined sulfur by sulfurizing other petroleum extracts. The empirical nature of this type of sulfurization and the lack of other chemical data precluded any further discussion.

VII. MECHANISM OF THE SULFURIZATION REACTIONS

One of the complicating factors in the study of sulfurization reactions is the complex nature of sulfur itself. A halogen, for example, has a simple diatomic structure and its addition to a double bond presents no structural problem. Sulfur, on the other hand, exists in at least two allotropic solid forms and a number of reported liquid forms. It is therefore little wonder that the sulfurization of unsaturates has remained an unexplained reaction.

The possible effects of the allotropic forms of sulfur on the vulcanization of rubber have not escaped various investigators. Erdmann (18) based his theory

of thiozonides on the view that the sudden change in the properties of liquid sulfur at 160°C. was attributable to the formation of thiozone, S_3. This conjecture is but part of Erdmann's speculations which were to be disproved by later investigation. Van Iterson (85) believed that the transformation of of S_λ to S_μ might govern the velocity of vulcanization. Dannenberg (15) also thought that S_μ is the allotropic form of sulfur responsible. However, Twiss (82) demonstrated that theories involving S_μ and S_π were inadequate, since S_π was found to be no better in vulcanization than S_λ. Scholz (67) deduced from the effect of accelerators in depressing the freezing point of sulfur that an equilibrium occurred in liquid sulfur according to equation 13.

$$S_8 \rightleftarrows S_4 \rightarrow S_\mu \tag{13}$$

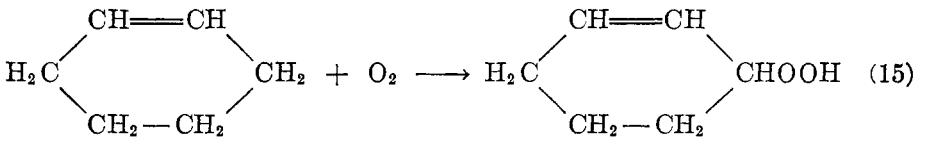
Hauser and Sze (33) also believed that an equilibrium occurred, with the formation of active forms of sulfur:

$$S_8 \rightleftarrows S_4 \rightleftarrows S_2 \rightleftarrows S_1 \tag{14}$$

However, calculations on the molecular species present in sulfur *vapor* (86), based on spectroscopic and other data (40), indicate that until well over 500°C. sulfur is principally S_8 and S_6.

The most recent publications on the structure of sulfur between 100° and 200°C. are the experimental reports of Bacon and Fanelli (2) on the viscosity of liquid sulfur and the companion theoretical studies of Powell and Eyring (61), based on Bacon and Fanelli's work. These investigators have concluded that the S_8 ring, proved by the electron-diffraction experiments of Chia-Si-Lu and Donahue (14), opens up in liquid sulfur to form S_8 chains and that the increasing concentration of those chains, as the temperature is raised, causes polymerization to long chains, forming the viscous S_μ. It is clear from this work that the conceptions of previous researchers as to the effect of the structure of sulfur on the reaction must be modified. One thing is certain, however: The structure of sulfur is intimately involved in the mechanism of sulfurization and any step in the solution of one problem is an advance in the solution of the other. The continual formation of monosulfide linkages in sulfurized products is not explained by the present accepted picture of the sulfur molecule.

Farmer and coworkers (19, 20, 21) evolved a theory of the mechanism of sulfurization which is worth much consideration. They based it on their own and other researches on oxidation. Thus, Stephens (76) and also Farmer and Sundralingam (22) had shown that cyclohexene was oxidized to a cyclohexenyl hydroperoxide (equation 15) by oxygen. Fisher and Gray (24) found that the

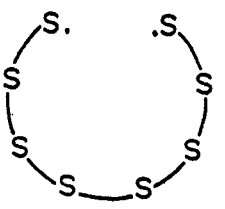


(15)

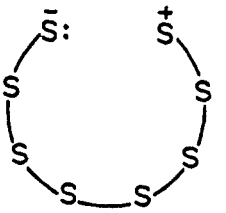
vulcanization of rubber with dibenzoyl peroxide occurred with the loss of unsaturation. Farmer believed that here was an instance of the reactivity of the

methylene groups, alpha to a double bond, for which he had gathered overwhelming evidence. Thornhill and Smith (81) reported that there was little change in the unsaturation of rubber with the first few percentages of combined sulfur, and Hauser and Brown (31) pointed out that the desirable physical properties of soft rubber were had where the combined sulfur was at the maximum obtainable without a sharp decrease in unsaturation. Farmer therefore postulated attack at the α-methylene group to form either unsaturated mercaptans or unsaturated sulfides. He felt that the later loss of unsaturation ensued from a secondary reaction, such as addition of mercaptans or hydrogen sulfide.

The normal mechanism of the addition of halogens to a double bond is ionic, but their substitution on the α-methylene group is believed to be through free radicals (21). Farmer ascribed a free-radical mechanism to the peroxidation reaction. The vulcanization of rubber has been described as a process analogous to peroxidation, involving attack on the methylene groups alpha to the double bonds. Whether the reaction is due to ions or free radicals, the opening of an S_8 ring would furnish either type of species, depending on whether the symmetrical (XXVIII) or the unsymmetrical (XXIX) splitting of the electrons occurred.



XXVIII

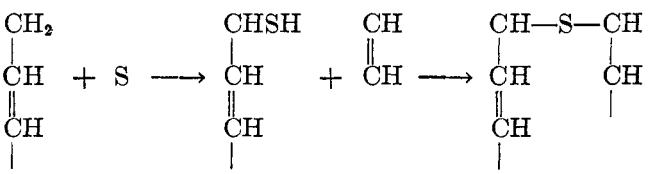


XXIX

In view of the evidence for a non-ionic mechanism quoted by Farmer, the former is the more likely.

In support of Farmer's conception of the mechanism are some of the researches previously described. Armstrong, Little, and Doak (1) isolated β,γ-unsaturated sulfides from the sulfurization of olefins. Selker and Kemp (69) showed that vulcanized rubber appeared to react like allyl sulfide toward methyl iodide. Friedmann (26) also reported obtaining unsaturated sulfides from olefins.

Opposed to the theory is much of the work on drying oils and terpenes. The investigators in these fields have almost unanimously described saturation of the double bonds rather than initial substitution. Of course the saturation could be explained by α-methylene attack followed by immediate secondary reaction of the mercaptan produced (equation 16), which is the way in which structure



(16)

XXIV for vulcanized rubber could be formed. But Nakatasuchi in his work on the terpenes (55, 56, 57) continually reported the formation of ethylene sulfide rings. In view of the known instability of these rings, their formation appears doubtful and Nakatasuchi's last-reported structure, a thiocineole, appears more likely. It would be well if his work could be checked carefully. The instability of terpene structures and their ease of rearrangement would probably interfere with the obtaining of definite data, but it might be possible to reconcile a thiocineole type of structure with α-methylene attack.

Three lines of investigation appear most promising for workers interested in how sulfur reacts with the double bond. Any or all of them should give results of vital interest. First of all, the structure of liquid sulfur itself might reveal something of the manner of attack. Secondly, research on the sulfurization of olefins and of simple unsaturated compounds, such as that of Armstrong, Little, and Doak, should in the end provide the most important single collection of basic experimental data on the problem and might even be the means of studying the reaction kinetics from a theoretical or chemicophysical viewpoint. Thirdly, other methods, like that of Meyer and Hohenemser as applied by Selker and Kemp, should be developed to attack the problem of the nature and location of the sulfur linkages in the sulfurization products of the naturally occurring unsaturates. Possibly studies with infrared spectra would be one such method. Too much of the speculation in the literature is based on empirical observation or on the physical properties of the vulcanized product, which have been shown repeatedly to have no correlation with total combined sulfur. Too many secondary reactions can take place and, until they are separated from the primary reaction, no correlation can be expected.

I am deeply indebted to Dr. W. A. Hamor of Mellon Institute for his encouragement and advice and to the Texas Gulf Sulphur Company for support in the preparation of this paper.

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