

The Reaction of Sulfur and Sulfur Compounds with Olefinic Substances.

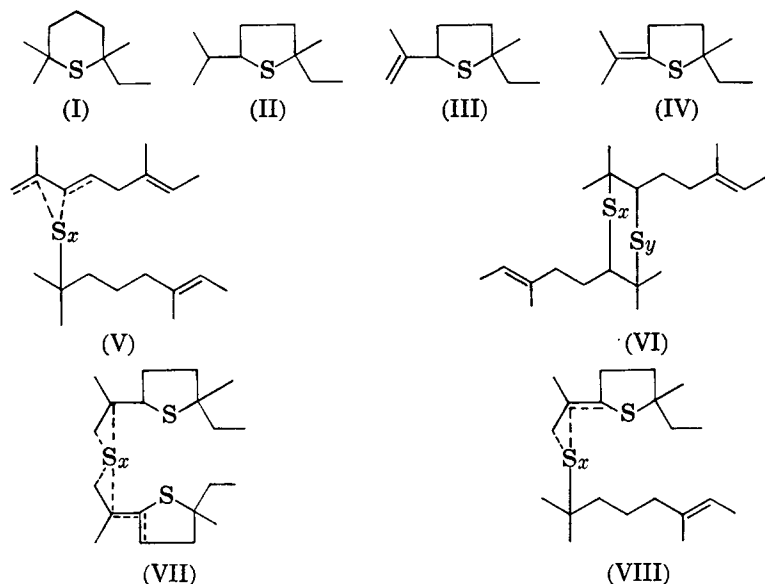
Part XII.* Effects of Vulcanizing Additives on the Reaction of Sulfur with 2,6-Dimethylocta-2,6-diene, and Their Bearing on the Mechanism of Sulfur Vulcanization of Natural Rubber

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I. INTRODUCTION

We have shown recently¹ that the interaction of sulfur and 2,6-dimethylocta-2,6-diene at 140°C. (a model system for the sulfur vulcanization of natural rubber) yields a complex mixture of products, viz., 2,6-dimethylocta-2,4,6-triene (*allo-ocimene*), the cyclic sulfides (I) to (IV), and cross linked polysulfides typified by (V)–(VIII), where



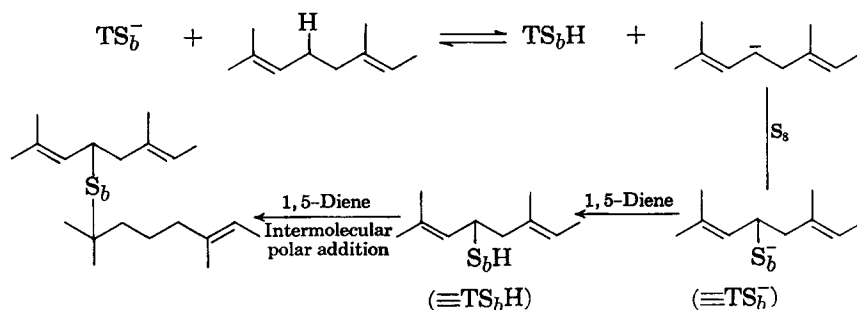
ings can be correlated by a general mechanism of olefinic sulfuration,² supported by kinetic data,³ which was developed from a study of monoolefinic systems⁴ and which requires that crosslinked polysulfides such as (V) and (VI) are the primary products and that the other products result from secondary reactions kinetically equivalent to those producing (V) and (VI). This view is contrary to

the dotted lines indicate different possibilities for isomerism and x and y vary from 1 to 6. For short reaction times (5 hours), the polysulfide mixture is composed largely of compounds typified by (V) and (VI), but at longer times (50 hours) structures such as (VII) and (VIII) (x mainly 1–2) predominate, and the cyclic sulfides (I) to (IV) are formed in increasing amounts. These find-

earlier postulates about the origin of the cyclic sulfides.⁵

Sulfuration is now considered^{2,3} to proceed by a polar chain-type reaction which is initiated by the polarization of a polysulfide $TS_a \cdot S_b T$ (T = alkyl or alkenyl unit) by interaction with olefinic double bonds to form a reactive species $TS_a^+ \dots -S_b T$. The persulfonium ion (TS_a^+) then attacks a double bond to give a cyclic persulfonium ion

* Part XI, ref. 2.



Scheme II

portions vary rationally in different olefinic systems.^{1,2,4}

Emphasis was directed^{2,3} to the persulfenium ion (TS_a^+) as the prime reactant with the olefin (just as, for example, in the polar interaction of halogens (X_2) with an olefinic double bond the halonium ion (X^+) is regarded likewise⁶) because (a) substantial addition of sulfur groups to the double bonds occurs, even to form $\alpha\beta$ derivatives, e.g., (VI), and this is consistent with the electrophilic additive reactivity of TS_a^+ but not with the anticipated reactivity of a persulfenyl anion (TS_b^-), which would be expected to add only to double bonds activated by an electron withdrawing substituent²; and (b) the formation of the cyclic sulfides (I) to (IV) from 2,6-dimethylocta-2,6-diene is explicable on this basis,^{2,3} but not *via* reactions initiated by TS_b^- . The main function of the latter has therefore been regarded as chain termination with carbonium and persulfenium ions to form cross-linked polysulfides, but a more positive function (as in Scheme II) may be displayed under suitable conditions.

In oct-1-ene, these reactions can only be of minor importance^{2,4}; in 2-methylpent-2-ene, while also not of major importance, they may account for the formation of a polysulfide having a *tert*-alkyl-S-linkage and the same unsaturation pattern as the olefin, i.e., mainly (IX) and/or (X) (see, however, ref. 2). It will be shown later that TS_b^- ions may assume a more dominant role under other conditions which are of great technological interest.

A notable feature of the *polar* mechanism of sulfuration is that it provides an intelligible basis

for explaining the action of the important and characteristically polar auxiliary vulcanizing agents such as metal oxides, fatty acids, and accelerators of the amine and complex thiol or disulfide types, in a way which a previously advanced free radical chain mechanism^{6,7} never has done. [In view of the marked influence which certain carbon blacks exert on vulcanization, it is pertinent to note recent emphasis of their ionic surface properties.⁹]

We now report the effects of the typical auxiliary vulcanizing agents, zinc oxide, stearic acid, and 2-mercaptobenzothiazole on the sulfuration of 2,6-dimethylocta-2,6-diene, and attempt to correlate chemical changes in the model systems with technological consequences in the vulcanization of natural rubber. This work extends earlier investigations of the effect of these additives on the proportion of cyclic sulfide to crosslinked polysulfide from the diene-sulfuration,⁵ and of their effect on monoolefin-sulfur interaction¹⁰ where correlation with vulcanization data is necessarily limited owing to the importance of cyclization reactions in polyisoprenes.

II. EXPERIMENTAL METHODS

The methods used for the preparation, isolation, and characterization of the sulfuration products in the various systems have been described previously.¹

III. EXPERIMENTAL RESULTS

Details of the reactions studied are given in Table I. Addition of zinc oxide increases the rate of sulfur combination and causes changes in prod-

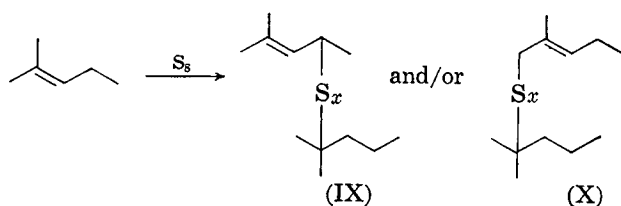


TABLE I
Reaction of 2,6-Dimethylocta-2,6-diene with Sulfur and Auxiliary Vulcanizing Agents at 140°C. *in vacuo*

| | Expt. 1 ^a | Expt. 2 ^a | Expt. 3 | Expt. 4 | Expt. 5 |
|---|----------------------|----------------------|---------|---------|---------|
| Reactants | | | | | |
| Diene, g. | 200 | 200 | 200 | 200 | 200 |
| Sulfur, g. | 20 | 20 | 20 | 20 | 20 |
| Zinc oxide, g. | — | — | 20 | 20 | 20 |
| Stearic acid, g. | — | — | — | 20 | 20 |
| 2-Mercaptobenzothiazole, g. | — | — | — | — | 4 |
| Reaction time, hr. | 5 | 50 | 5 | 5 | 1.5 |
| Reaction Products | | | | | |
| Cyclic sulfide (C.S.) (I-IV), g. | 10 | 41 | 26 | 9.5 | 4.5 |
| Polysulfide (P.S.), g. | 24 | 49 | 37 | 20 | 22 |
| S in P.S., % | 40 | 25 | 36 | 34 | 30 |
| Polysulfidic sulfur in P.S., mole fraction ^b | 0.52 | 0.08 | 0.42 | 0.33 | 0.53 |
| <i>Allo</i> -ocimene, g. | 1.0 | 3.2 | 2.3 | 2.3 | — |
| Ratio, C.S./P.S., by weight | 0.42 | 0.84 | 0.70 | 0.48 | 0.20 |
| Ratio of diene in C.S./diene in P.S., by weight | 0.56 | 0.92 | 0.87 | 0.58 | 0.24 |
| Initial sulfur combined in cyclic sulfide, % | 9.4 | 38 | 24 | 8.9 | 4.2 |
| polysulfide, % | 48 | 61 | 67 | 34 | 33 |

^a Data of Bateman, Glazebrook, and Moore.¹

^b Mole fraction of sulfur in polysulfide which is liberated as hydrogen sulfide on hydrogenolysis.

TABLE II
Composition of Cyclic Sulfide Products, Wt.-%

| Expt. no. | (III) | (IV) | (I) + (II) |
|----------------|-------|------|------------|
| 1 | 41 | 11 | 48 |
| 2 ^a | 26 | 30 | 43 |
| 3 | 46 | 17 | 37 |
| 4 | 47 | 25 | 28 |

^a Also contains ~1% of 2-isopropyl-5-ethyl-5-methylthiacyclopent-2-ene, probably formed by sulfur-catalyzed isomerization of (IV).

uct composition broadly paralleling those found on increasing the time of the diene-sulfur reaction (cf. expts. 1, 2, and 3); relatively more cyclic

sulfide is formed, in conformity with its postulated mode of formation (Scheme I), and the amount of sulfur in crosslinks greater than —S₂— diminishes. When stearic acid is also present (expt. 4), the rate of sulfur combination is reduced below that of the straight diene-sulfur reaction (expt. 1), but both sulfur and olefin are combined in similar proportions in the two types of products. The further addition of 2-mercaptobenzothiazole (expt. 5) has a more profound effect; the rate of reaction is increased and the proportion of cyclic sulfide considerably reduced.

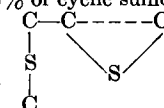
The compositions of the cyclic sulfide fractions show a marked trend towards the formation of the

TABLE III
Hydrogenolysis Products of the Polysulfides (Expressed as Wt.-% of Polysulfide)

| Expt. no. | C/H ratio of polysulfide | Polysulfidic sulfur ^a | Monothiol C ₁₀ H _{17,18} SH | Dithiol C ₁₀ H ₁₈₋₂₂ S ₂ (2SH) | Mercapto-cyclic sulfide C ₁₀ H _{18,20} S ₂ (1SH) | Products of higher M.W. | Loss |
|----------------|--------------------------|----------------------------------|---|---|---|-------------------------|------|
| 1 | 10/18.0 | 21 | 30 | 18 | 16 | 12 ^c | 3 |
| 2 ^b | 10/17.6 | 2 | 8 | 1 | 17 | 67 ^c | — |
| 3 | 10/17.8 | 15 | 22 | 16 | 28 | 19 | — |
| 4 | 10/16.8 | 10 | 47 | 16 | 7 | 14 | 6 |
| 5 | 10/16.9 | 16 | 53 | 18 | 1 | 12 ^d | — |

^a Sulfur liberated as hydrogen sulfide on hydrogenolysis.

^b Polysulfide contained ca. 5% of cyclic sulfide and *allo*-ocimene as impurity.

^c Sulfur combined mainly in  groupings, e.g. (VII), *x* = 1.

^d Sulfur combined mainly in dialkanyl sulfide structures.

unsaturated constituents (III) and (IV) at the expense of (I) and (II) in passing from the reaction without additive to those with zinc oxide and then zinc oxide plus stearic acid (Table II). The significance of this trend, which is of wider generality, will be discussed later.

Considerable differences occur in the polysulfide fractions as revealed spectroscopically and by the nature of the hydrogenolysis products obtained by lithium aluminum hydride reduction (Table III).

is approximately 31% of the total combined sulfur for experiment 1 and 47% for experiment 5. The amount of polysulfidic sulfur ($-\text{S}_{x-2}$, column 3), indicative of sulfur in crosslinks in excess of two atoms per link, is seen to be the same in both cases, but this does not imply that the polysulfidic crosslinks have the same average lengths, since the number of crosslinks is greater in the accelerated system. Comparison of the proportion of polysulfidic sulfur ($-\text{S}_{x-2}$) with that of sulfur com-

TABLE IV
Distribution of Combined Sulfur in Sulfuration Products (% of Total Combined Sulfur)

| | 1 | 2 | 3 | 4 | 5' | 5'' | 6 | |
|------------------------|--------|----------|----------|-------------------------|----------|------------|----------------------------------|----------------------------------|
| Grouping | | | | Free cyclic sulfide | | | Noncleavable by LiAlH_4 | |
| Expt. no. ^a | 1 5 | 12 27 | 11 16 | 43 43 | 10 10 | 5.5 0.2 | 5.5 0.2 | 7 ^b 4 ^c |

^a Figures refer to % of total sulfur which is combined in the circled sulfated groups (S).

^b Mainly thio-cyclic monosulfide groups, e.g. (VII), $x = 1$.

^c Mainly dialkenyl monosulfide.

The effect of zinc oxide is to reduce the amount of "polysulfidic" sulfur (i.e., $x > 2$) in the polysulfide and also the proportion of simple crosslinked structures, e.g., (V), which yield monothiol on hydrogenolysis, but to increase the more complex structures containing cyclic sulfide units, e.g., (VII). When stearic acid is also present, there is a greater retention of unsaturation (mainly trialkylethylenic) as shown spectroscopically and by the C/H ratio, there are more simple polysulfidic crosslinks which yield monothiol on hydrogenolysis, and there is a marked reduction in the cyclic sulfide-polysulfide units as in (VII) and (VIII) ($x \geq 2$) which yield mercapto-cyclic sulfides on hydrogenolysis. The addition of 2-mercaptobenzothiazole (expt. 5) further favors all these changes.

From the data in Tables I and III, the distribution of the total combined sulfur in various sulfur linkages can be determined in detail. Experiments 1 and 5 are so compared in Table IV, and show clearly the superior efficiency of the "accelerated" system (expt. 5) for utilizing the sulfur for crosslinking. The sulfur combined in mono- or disulfidic crosslinks (given by columns 1, 2, 5', and about one third the amount of column 6 for expt. 1 and the whole amount for expt. 5)

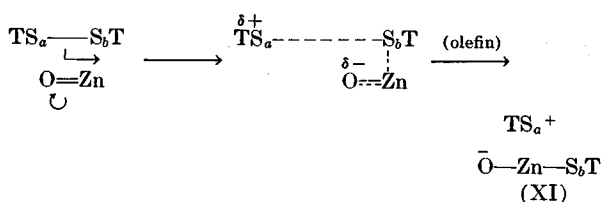
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IV. DISCUSSION

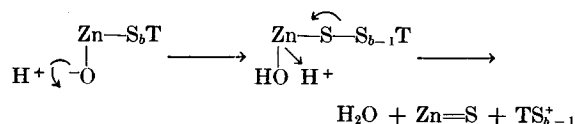
Comparison of Chemical and Physical Effects of Auxiliary Vulcanizing Agents

1. Zinc Oxide. In the absence of fatty acid, zinc oxide has little effect on the rate of combination of sulfur with natural rubber (acetone-extracted) or on the properties of the resulting vulcanizate.¹¹ The latter feature is in keeping with the overall similarity in product composition of the diene-sulfur reactions in the absence and presence of zinc oxide, but the former is at variance with the increase in rate found in the model system (Table I), which has also been reported by Bloomfield.⁵

This difference is attributed to surface-promoted polarization of the polysulfide (or sulfur):



The zinc complex (XI) then either dissociates to reform the oxide and liberate a persulfenyl anion (TS_b^-), or absorbs protons to form water, zinc sulfide, and another persulfenium ion:



The absence of such catalysis in rubber-sulfur interaction probably reflects much less facile adsorption and desorption processes due to the highly viscous medium and to poisoning of the oxide surface by nonhydrocarbon constituents of the rubber. The same effects undoubtedly account for the difficulty of catalytically hydrogenating rubber (in solution) as compared with simple olefins.¹²

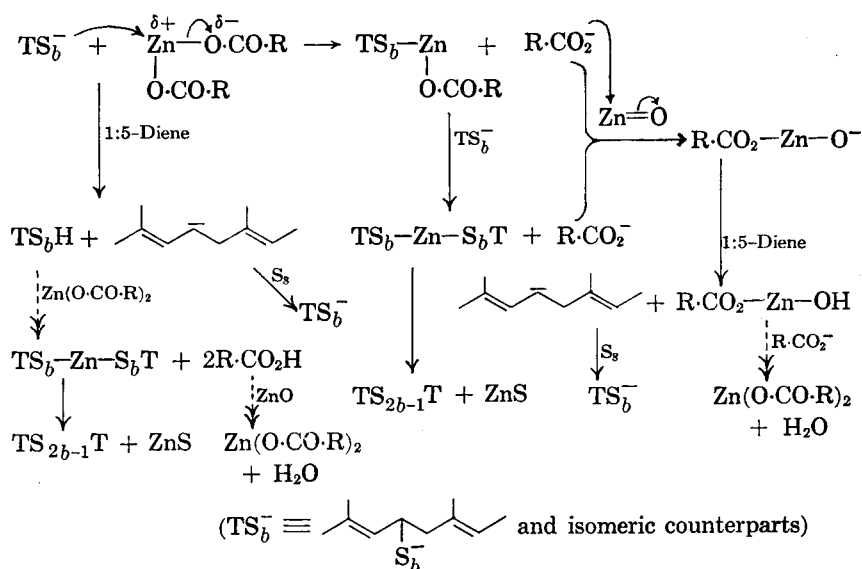
2. Zinc Oxide plus Stearic Acid. When zinc oxide is solubilized in rubber by conversion to a fatty acid salt, it then modifies the vulcanization process significantly.¹¹ The rate of sulfur combination is slightly reduced, as in the model experiments (Table I), but the number of crosslinks introduced (as measured by the elastic modulus at moderate extensions) is increased, in conformity with the higher proportion of combined sulfur in crosslinking groups in the model system, as shown by the higher yield of monothiol and lower yields of mercapto-cyclic sulfide and polysulfidic sulfur on hydrogenolysis (Table III). The control on sulfur combination thus imposed, such that crosslinking is favored at the partial expense of the introduction of pendant cyclic sulfide groups along the hydrocarbon chain leads to polymer chains of greater structural regularity and therefore more prone to crystallize on stretching and cooling. Comparative measurements show this to be so,¹¹ although, since admixed stearic acid and zinc stearate act as nucleation sites and catalyze crystallization,¹³ the evidence is not critical.

Detailed information on the function of the zinc salt is lacking, but an important fact is that associated with the enhancement of crosslinking at the expense of cyclization is the retention of more

olefinic unsaturation in the polysulfide (Table III and experimental section III), as is also found in vulcanizates.¹⁴ This implies that the action of the zinc salt is not confined to stripping sulfur atoms from prior-formed polysulfides such as (V) and (VI) ($x > 2$), but that it interferes with the proton transfer processes shown in Scheme I, so that protons which would otherwise add to the double bonds (and in doing so would in part promote cyclic sulfide formation) are removed from the site of reaction. Further pertinent observations are: (1) that the action of a zinc salt is much enhanced by the presence of zinc oxide¹⁵; (2) that the formation of zinc sulfide, which proceeds concurrently with crosslinking in a vulcanizing system, does not occur in the absence of interaction of sulfur with the olefin, as, for example when polyisobutylene is heated with a vulcanizing mixture¹⁶; and (3) that magnesium oxide, which can replace zinc oxide in these reactions (in the presence of fatty acid) but does not undergo conversion to the sulfide,¹⁷ is far less effective in promoting crosslinking¹⁷ and, indeed, actually inhibits the action of zinc compounds in this respect.¹⁶

The mechanistic conditions to be met, therefore, are (1) that zinc sulfide formation accompanies the introduction of crosslinks,^{10,15,16} although not necessarily with any definite stoichiometric relationship with the amount of combined sulfur (contrast, however, Adams and Johnson¹⁸); (2) that the soluble zinc compound promotes crosslinking and absorbs protons in the course of its conversion to zinc sulfide, and (3) that the overall rate of sulfur combination is not substantially affected. These appear to necessitate that either the persulfenyl anion, TS_b^- , or the derived perthiol, TS_bH (see Scheme II), reacts with the zinc compound as in Scheme III. These two possibilities are similar in involving a sequence of reactions in which a TS_b^- ion is regenerated while sulfur is absorbed, and in requiring zinc oxide to capture the anion RCO_2^- or acid RCO_2H so as to replenish the zinc salt undergoing conversion to zinc sulfide.

The reactivity of a persulfenyl anion towards an olefin and a zinc salt has not been investigated. It is known, however, that a sulfenyl anion RS^- is a much stronger nucleophilic reagent than the corresponding alkoxyl ion RO^- for substitutions at a carbon atom,¹⁹ and this may parallel a greater power of proton abstraction, although in solvating solvents a correspondence between nucleophilic activity towards carbon and towards hydrogen is by no means general.²⁰ Pending experimental



Scheme III

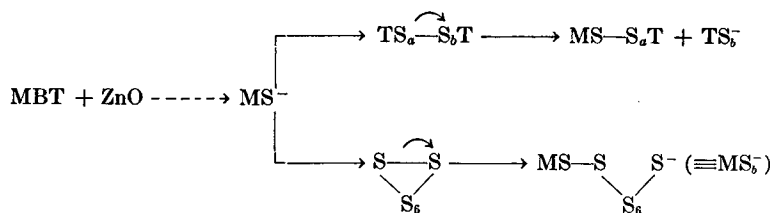
evidence, proton abstraction by the persulfenyl anion TS_b^- (Schemes II and III) is therefore advanced with reserve, but there can be no doubt that this ion will act as a strong nucleophile towards the intensely electrophilic center which a charged or partially charged zinc atom provides.²¹ Equivalent interaction is apparent in the oxidation of thiols to disulfides by lead tetraacetate.²² By thus reacting, the zinc salt will divert TS_b^- ions away from chain termination reactions with the cationic intermediates shown in Scheme I (leading to polysulfides capable of forming cyclic sulfide units) to the crosslinking reaction; evidence that this occurs is (a) the marked decrease in mercapto-cyclic sulfide groups in the polysulfidic product in experiment 4 (Table III), (b) the increase in simple crosslinking units (indicated by the proportion of sulfur combined in monothiol, Table III), and (c) the increased unsaturation of the polysulfide and cyclic sulfide products. The basic zinc salt anion, RCO_2ZnO^- , will have a strong affinity for protons, and this interaction offers the most direct route for transferring hydrogen from the olefin to the zinc oxide with formation of water.

The importance of maintaining the concentration of soluble zinc during reaction is demonstrated in experiments in which sulfur and zinc benzothiazolylmercaptide as a vulcanizing system is compared with sulfur-zinc benzothiazolylmercaptide-zinc oxide and with sulfur-2-mercaptobenzothiazole-zinc oxide.²³ The rate of sulfur combination is considerably greater in the first case, but the cross-

linking efficiency is far less, and this is now interpreted as due to a loss of "useful" zinc to zinc sulfide in a nonreplenishing system.

The greater unsaturation of the isolated polysulfide is accordingly ascribed to persulfenyl anions (TS_b^-) being coupled either directly or indirectly into dialkenyl polysulfides (Scheme III) instead of the addition of persulfenium ions (Scheme I) or possibly perthiols (Scheme II) to double bonds to give alkenyl alkyl polysulfides. Further, the dialkenyl polysulfides so produced will, on stereochemical grounds, be less prone to form cyclic sulfides by scission of an S—S bond *via* intramolecular interaction with a neighboring activated double bond (Scheme I), whereas alkenyl alkyl polysulfides can do so readily. Hence an increase in dialkenyl polysulfide groups is expected to parallel a decrease in cyclic sulfide units and to lead to a vulcanizate in which the linearity of the base-poly chain is less disturbed by attached side groups and complex crosslinks.

3. Zinc Oxide plus Stearic Acid plus 2-Mercaptobenzothiazole. Technological effects of adding the thiazole to the zinc oxide-stearic acid mixture are further to increase elastic modulus and proneness to crystallization in vulcanizates having the same amount of combined sulfur,^{15,24} and to increase the rate of reaction so that these properties develop in a shorter time.²⁴ Again, these effects are reflected in the present chemical data (Tables I and III). In passing from the straight diene-sulfur system, the sulfur combined in cyclic sulfide

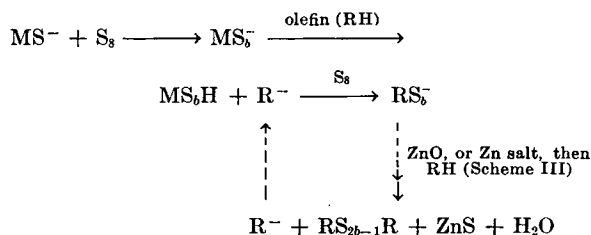


Scheme IV

groups falls from about 25% (Table IV) to about 12%, more crosslinks are associated with smaller polysulfidic chains, and the overall rate of sulfur combination is increased (Table I).

Acceleration by 2-mercaptobenzothiazole (MBT) is known to depend on, or to be strongly influenced by, zinc oxide (or salt),^{15,18} fatty acid,^{15,18} and traces of a nitrogenous base.²⁵ It is evident, therefore, that the zinc or amine salts of the thiazole, or related complexes, are the actual accelerators,^{15,18,26} which, in the presence of zinc oxide and stearic acid, enhance the effects induced by these last additives acting alone. This they appear to do in a manner consistent with their probable mode of increasing the rate of reaction.

In view of the known sensitivity of polysulfides and sulfur to attack by anions,² the benzothiazole-sulfenyl anion (MS^-) would be expected to facilitate S—S bond heterolysis as shown in Scheme IV. This reactivity imposed on the sulfuration mechanism hitherto considered has two important consequences. First, the autocatalysis observed in sulfur-olefin reactions³ (which suggests superficially a zero-order reaction with respect to sulfur for rubber-sulfur interaction²⁷) will tend to be overshadowed and a greater dependence on the concentration of unreacted sulfur will be evident during the course of the reaction. If ready anionic activation of sulfur is combined with efficient coupling and regeneration of persulfenyl anions, then the mechanism of sulfur-olefin interaction in the absence of additives (see Scheme I) will be superseded by one of different form:



in which attack by MS^- or R^- ions on sulfur is rate-determining (depending on the actual accelerator-

activator system), leading to first-order kinetics for sulfur combination, as found experimentally.^{23,28} The second consequence is that as the above series of reactions come into prominence at the expense of those initiated by persulfenium ions (Scheme I), there should be a greater degree of unsaturation in the polysulfidic product due to alkenyl-S-units with trialkylethylene-type unsaturation, and an accompanying decrease in the proportion of cyclic sulfide structures, as found experimentally (Table IV and ref. 14). An equivalent trend towards simpler crosslinked products and the formation of dialkenyl polysulfides has been found in the MBT-accelerated sulfuration of simple monoolefins.¹⁰

Concluding Remarks

To summarize, we conclude that the course of the interaction of sulfur with an olefin alone is determined principally by the electrophilic reactivity of labile polysulfides and by the reactions of cationic-type intermediates, and that the essential function of zinc salts is to stimulate the reactivity of complementary nucleophilic species. Accelerators of the thiazole-type specifically promote the latter reactivity, as almost certainly do other common vulcanization accelerators, e.g., certain amines,²⁹ metal dithiocarbamates and xanthates, and thiuram sulfides. It may be noted, for example, that reaction of 2,6-dimethylocta-2,6-diene with sulfur, zinc dibutyldithiocarbamate, and zinc oxide at room temperature, i.e., under conditions where direct sulfur-olefin reaction does not occur, yields a dialkenyl polysulfide and negligible cyclic sulfide³⁰ (a result also found with tetramethylthiuram disulfide and zinc oxide plus zinc propionate at 140°C.⁵), indicative of sulfuration by the nucleophilic mechanism becoming almost fully dominant under especially favorable reaction conditions.

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Synopsis

The effects of zinc oxide, of zinc oxide and stearic acid, and of zinc oxide, stearic acid, and 2-mercaptobenzothiazole on the products of interaction of sulfur with the diisoprene, 2,6-dimethylocta-2,6-diene at 140°C. have been investigated in detail. Zinc oxide alone produces little change in the composition of the complex product mixture, but in the

presence of stearic acid, and more so when the thiazole is also present, significant changes are produced in the distribution of combined sulfur which reflect more efficient use of the sulfur in crosslinking reactions, and which can be related rationally to important effects exerted by these additives on the sulfur-vulcanization of natural rubber. It has recently been advanced that sulfur-olefin interaction proceeds by a polar mechanism in which the dominant feature is the additive reactivity of persulfenium ionic species (TS_a^+) towards double bonds. Evidence is now presented that the chemical and technological effects of soluble zinc salts and of thiazole accelerators stem from their action in enhancing the role of reactions promoted by the complementary persulfenyl anionic species (TS_b^-) which involve the displacement of hydrogen from, and the addition of sulfur to, carbon atoms adjacent to double bonds. Essentially similar mechanistic considerations appear to apply to systems accelerated by amines and by metal dithiocarbamates and xanthates.

Résumé

On a étudié en détails l'effet de l'oxyde de zinc, de l'oxyde de zinc et l'acide stéarique et de l'oxyde de zinc, l'acide stéarique et le 2-mercaptobenzothiazol en mélange, sur les produits d'interaction du soufre avec le di-isoprène, 2,6-diméthyl-octa-2,6-diene à 140°C. L'oxyde de zinc seul produit peu de changements dans la composition du mélange complexe, mais en présence de l'acide stéarique et plus encore quand le thiazole est présent, des changements significatifs sont produits dans la distribution du soufre combiné, ce qui montre d'autant mieux l'usage efficace du soufre dans les réactions de pontage et qui peut être relié raisonnablement aux effets importants produits par ces additifs dans la vulcanisation de la gomme naturelle. On a récemment avancé que l'interaction soufre-oléfine résulterait d'un mécanisme polaire. Le fait dominant est la réactivité additive des ions persulfénium (TS_a^+) à l'égard des doubles liaisons. Il semble que les effets chimiques et technologiques des sels de zinc solubles et du thiazol seraient dus au fait qu'ils facilitent le rôle des réactions favorisées par leurs anions persulfényles complémentaires (TS_b^-) qui comprennent le déplacement d'un atome d'hydrogène de l'atome de carbone adjacent à la double liaison et l'addition à celui-ci d'un atome de soufre. Des considérations mécanistiques essentiellement semblables peuvent s'appliquer à des systèmes accélérés par des amines et par des dithiocarbamates et xanthates métalliques.

Zusammenfassung

Die Einwirkung von Zinkoxyd, von Zinkoxyd und Stearinsäure und von Zinkoxyd, Stearinsäure und 2-Merkaptobenzthiazol auf die bei 140°C aus Schwefel und dem Diisopren, 2,6-Dimethylocta-2,6-dien, gebildeten Reaktionsprodukte wurde eingehend untersucht. Zinkoxyd allein ruft nur geringe Veränderungen in der Zusammensetzung des komplexen Reaktionsgemisches hervor, in der Gegenwart von Stearinsäure, und noch mehr ausgeprägt, bei gleichzeitigem Zusatz des Thiazoles, entstehen aber charakteristische Änderungen der Verteilung des gebundenen Schwefels, die eine wirksamere Ausnützung des Schwefels für Vernetzungsreaktionen erkennen lassen und die in einleuchtender Weise zu den wichtigen Funktionen in

Beziehung gebracht werden können, die diese Stoffe bei der Schwefelvulkanisation von Naturkautschuk ausüben. Kürzlich wurde die Meinung geäußert, dass die Reaktion zwischen Schwefel und Olefinen über einen polaren Mechanismus verläuft, bei welchem die Additionsfähigkeit eines Ions vom Persulfeniumtyp (TS_a^+) an die Doppelbindungen die massgebende Grösse ist. Es werden nun Beweise dafür beigebracht, dass die chemische und technologische Wirksamkeit von löslichen Zinksalzen und Thiazolbeschleunigern auf ihrer Fähigkeit beruht, die Bedeutung der Reaktionen

zu steigern in denen die komplementären Anionen vom Persulfenyltyp (TS_b^-) eine Rolle spielen und bei welchen an den den Doppelbindungen benachbarten Kohlenstoffatomen Wasserstoff abgespalten und Schwefel addiert wird. Im wesentlichen ähnliche Überlegungen über den Reaktionsmechanismus können offenbar auf Systeme angewendet werden, die mit Aminen und Metaldithiocarbamaten und -xanthaten beschleunigt werden.

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