Oxidative Aging of Natural Rubber Vulcanizates. Part III. Crosslink Scission in Monosulfidic Networks

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Synopsis

A natural rubber vulcanizate containing almost entirely monosulfidic crosslinks was oxidized in oxygen and with *tert*-butyl hydroperoxide. The changes in physical properties due to oxidation were followed by stress–strain measurements, and the changes in chemical structure were investigated with chemical probes, and by spectroscopic methods. The results show that when the oxidized vulcanizates are heated at 75°C., the monosulfidic crosslinks are broken, that crosslinks containing two sulfur atoms are formed, and that conjugated diene and triene structures are introduced into the main polyisoprene chains.

The loss in physical properties which occurs when vulcanized natural rubber degrades through oxidation is due to cleavage of the vulcanizates network structure. This can obviously occur in two ways: via main-chain scission or crosslink scission.

From previous studies by stress relaxation[1-3] or sol–gel[4] methods it has been suggested that only main-chain scission occurs, and more recently this was said to be confirmed by stress–strain[5] measurements on peroxide and sulfurated vulcanizates. Each of the above three methods, however, has theoretical and practical limitations.

The method of sol–gel analysis, although capable of discriminating between the extreme cases of crosslink and random main-chain scission, is unable to exclude the occurrence of some crosslink breakdown occurring concurrently with main-chain scission, and the mathematical treatment of Horikx[4] does not consider the consequences of crosslink formation during aging.

Measurement of continuous and intermittent stress relaxation during oxidative aging yield, respectively, information about the total and net extents of degradation. From these data the amount of crosslink formation can be calculated, but it is not possible to discriminate between main-chain and crosslink scission.

Mercurio and Tobolsky[6] compared the stress relaxation behavior of sulfurated vulcanizates from several rubbers with different backbone

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structures. They found that the relaxation of vulcanizates obtained from saturated rubbers such as polyisobutylene, polyester, and adduct rubber, was much slower than that of natural rubber cured in a similar way. It was assumed that the crosslink structures present in the various vulcanizates were similar, and it was concluded from the above results that main-chain scission was all-important and that crosslink scission did not occur in natural rubber vulcanizates.

This conclusion is valid only if it is assumed that crosslink scission results from a primary oxidative attack at the crosslink. It will be seen later that oxidation of the sulfur atoms in the crosslinks does not occur in this way; it occurs via a secondary oxidation by the hydroperoxide or peroxy radical groups attached to the main polyisoprene chains. Consequently, the chemical structure of the main chain will always be an important factor in determining the rate of degradation of the network, even if crosslink scission is occurring to a considerable extent.

DISCUSSION

The elastic constant C_1 can be obtained from stress–strain measurements[7] since

$$f = 2A_0 (C_1 + C_2 \lambda^{-1})(\lambda - \lambda^{-2}) \tag{1}$$

where f is the force, A_0 the original cross-sectional area, λ the extension ratio, and C_1 and C_2 are constants. Mullins[8] has shown that as λ is increased, a stage is reached at which the tension begins to rise quite sharply above that given by eq. (1). The critical value of the extension ratio λ^*, taken as the value at which the measured tension deviated by $2^1/_2\%$ from that given by eq. (1) was found to be solely dependent on the density of crosslinking. It has also been shown that the elastic constant C_1 is related to the molecular weight of the polymer chains ($\bar{M}_n$) and to the molecular weight between crosslinks M_c as follows:[9]

$$C_1 = (^1/_2\rho RT M_c^{-1} + 0.78 \times 10^6) (1 - 2.3\ \bar{M}_n^{-1}M_c)\ \text{dyne/cm.}^2 \tag{2}$$

where ρ is the density of the rubber network.

Determinations of C_1 and λ^* at intervals during aging were used by Dunn and Scanlan[5] to follow changes in $\bar{M}_n$ and M_c. For peroxide vulcanizates they found that during oxidation C_1 decreased and λ^* remained constant. The latter observation indicates that the crosslinking density has remained constant during aging. Furthermore, since intermittent and continuous stress relaxation measurements showed that very little crosslinking occurs during aging,[3,10] it was concluded that degradation was due to main-chain scission only. This conclusion is in agreement with our knowledge of the chemical structure of peroxide vulcanizates. There is no structural feature in the neighborhood of the crosslinks introduced into natural rubber by di-*tert*-alkyl or di-*tert*-aralkyl peroxides which would be expected to promote markedly preferential attack by oxygen at the crosslink.[11]

For accelerated sulfur vulcanizates, Dunn and Scanlan[5] found that C_1 and λ^* decreased during aging, and since the change in the latter indicates an increase in crosslink density, they again concluded that degradation was due to main-chain scission only.

Although crosslink densities in unaged vulcanizates can be measured[8] by determination of λ^*, its application to oxidized vulcanizates in order to determine crosslink scission, and formation must be viewed with some caution.

Doubt about the ability of λ^* to detect crosslink scission in aged networks arises from the following result. Cleavage of the polysulfide crosslinks in an accelerated sulfur vulcanizate[12] by treatment with an n-heptane solution of piperidine and propane-2-thiol (a reaction well substantiated in model systems)[13] led to a fall in C_1 from 1.32×10^6 to 1.05×10^6 dyne/cm.[2], but λ^* changed only from 2.63 to 2.58. With the large decrease in crosslink density indicated by the fall in C_1, λ^* should have undergone a considerable increase.
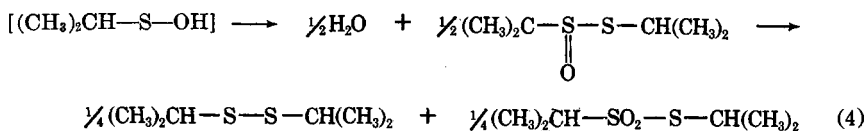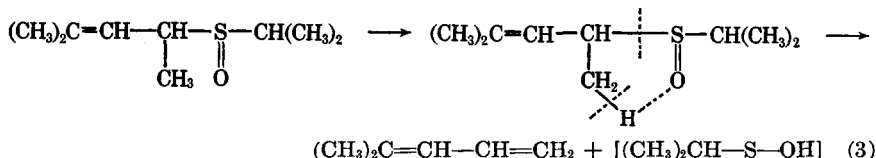
It therefore appears that all three of the above physical methods are unable to give unequivocal evidence for the occurrence of crosslink scission during the aging of sulfurated vulcanizates. In the present paper both physical and chemical methods are used to investigate the occurrence of crosslink scission during the oxidative aging of sulfurated vulcanizates.

Chemistry of the Oxidation of Organic Monosulfides and its Relation to Crosslink Scission

Previous investigations of the chemistry of the autoxidation of simple organic sulfides showed the existence of reactions which, if simulated in vulcanizates, would cause crosslink scission; i.e., apart from the well-known scission of polysulfide crosslinks via interchange reactions.[14,15] Briefly the results with the simple sulfur compounds were as follows. Small amounts (comparable to the amounts present in vulcanizates) of certain sulfur compounds inhibited the autoxidation of squalene after the absorption of a very small amount of oxygen.[16] It can therefore be concluded that these sulfur compounds are rapidly involved in the oxidative chain reaction of the olefin. The actual inhibitor is the sulfoxide produced from oxidation of the sulfide by the olefin hydroperoxide or peroxy radical.[16-18] Other studies on the autoxidation of alkenyl alkyl sulfides themselves showed that their oxidation was a chain reaction which proceeded through peroxy radicals, and that the corresponding sulfoxides and products from the scission of the weaker C—S bond were formed.[19-21] Later it was found that some of the sulfoxides readily decomposed into scission products,[22] and a mechanism has been suggested to account for the results obtained with two saturated sulfoxides.[23-25]

To extend the relevance of these observations to the dialkenyl crosslinks found in natural rubber vulcanizates obtained from tetramethylthiuram disulfide (TMTD), sulfurless, or accelerated sulfur recipes,[26-28] the thermal decomposition of an alkenylalkyl sulfoxide was investigated.

In carbon tetrachloride at 75°C. 1,3-dimethylbut-2-enyl isopropyl sulfoxide decomposed to give a high yield of 4-methylpenta-1,3-diene, water, and a thiolsulfinate, together with diisopropyl disulfide, a thiol-sulfonate, and minor amounts of propylene and 2-methylpenta-1,3-diene. These products indicate that the decomposition occurs via a five-membered transition state similar to that previously proposed for the saturated sulfoxides,[23-25] as shown in eqs. (3) and (4):

$$(CH_3)_2C\text{=}CH\text{---}\underset{\underset{CH_3}{|}}{CH}\text{---}\underset{\underset{O}{\|}}{S}\text{---}CH(CH_3)_2 \quad \longrightarrow \quad (CH_3)_2C\text{=}CH\text{---}CH\text{---}S\text{---}CH(CH_3)_2 \quad \longrightarrow$$

$$(CH_3)_2C\text{=}CH\text{---}CH\text{=}CH_2 + [(CH_3)_2CH\text{---}S\text{---}OH] \quad (3)$$

$$[(CH_3)_2CH\text{---}S\text{---}OH] \quad \longrightarrow \quad \tfrac{1}{2}H_2O + \tfrac{1}{2}(CH_3)_2C\text{---}\underset{\underset{O}{\|}}{S}\text{---}S\text{---}CH(CH_3)_2 \quad \longrightarrow$$

$$\tfrac{1}{4}(CH_3)_2CH\text{---}S\text{---}S\text{---}CH(CH_3)_2 + \tfrac{1}{4}(CH_3)_2CH\text{---}SO_2\text{---}S\text{---}CH(CH_3)_2 \quad (4)$$
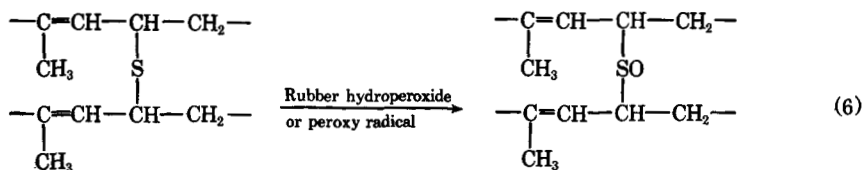
The isolation of diisopropyl disulfide and a thiolsulfonate indicates some disproportionation of the initially formed thiolsulfinate. Since only a minor amount of propylene is formed, the decomposition of the sulfoxide via the alternative transition state involving the β-hydrogen atoms of the isopropyl group can only occur to a very limited extent.

The presence of only trace amounts of the isomeric 2-methylpenta-1,-3-diene confirms that heterolytic or homolytic fission of the C—S bond does not occur, since this would lead to significant amounts of this diene from isomerization of the ion or radical intermediate according to eqs (5):
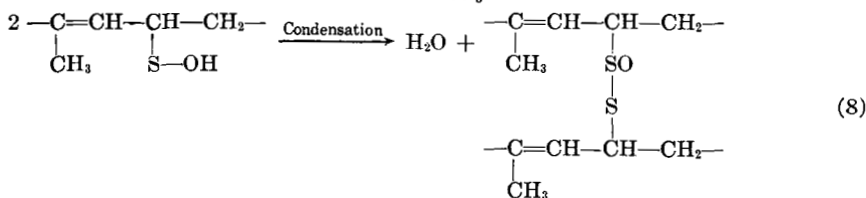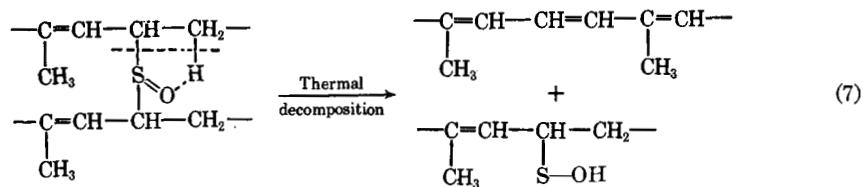

$$(5)$$
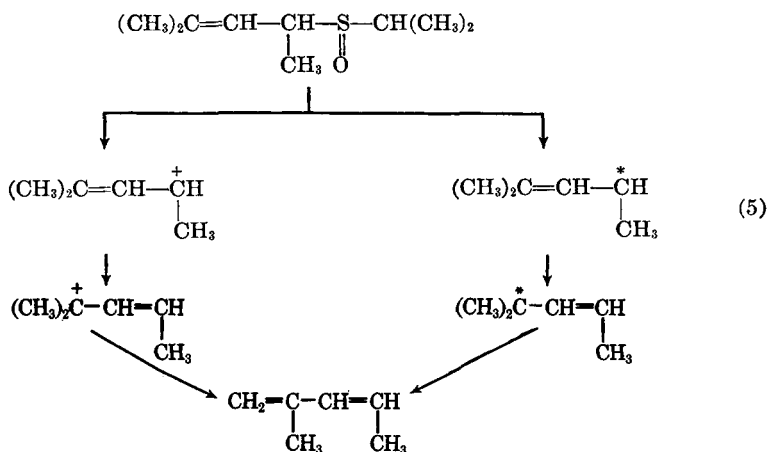
### Mechanism for Crosslink Scission in Monosulfidic Natural Rubber Vulcanizates

The above results suggest that the reactions (6)–(10) which lead to scission of monosulfidic crosslinks could occur during the oxidative aging of vulcanizates.

$$-\underset{\underset{\text{CH}_3}{|}}{\text{C}}=\text{CH}-\underset{\underset{\text{S}}{|}}{\text{CH}}-\text{CH}_2-$$
$$-\underset{\underset{\text{CH}_3}{|}}{\text{C}}=\text{CH}-\text{CH}-\text{CH}_2-$$

Dialkenyl crosslink

$\xrightarrow[\text{or peroxy radical}]{\text{Rubber hydroperoxide}}$

$$-\underset{\underset{\text{CH}_3}{|}}{\text{C}}=\text{CH}-\underset{\underset{\text{SO}}{|}}{\text{CH}}-\text{CH}_2-$$
$$-\underset{\underset{\text{CH}_3}{|}}{\text{C}}=\text{CH}-\text{CH}-\text{CH}_2-$$

(6)

$\xrightarrow[\text{decomposition}]{\text{Thermal}}$ (7)

$$2\ -\underset{\underset{\text{CH}_3}{|}}{\text{C}}=\text{CH}-\underset{\underset{\text{S—OH}}{|}}{\text{CH}}-\text{CH}_2- \xrightarrow{\text{Condensation}} \text{H}_2\text{O} +$$

(8)

The rubber hydroperoxide or peroxy radical formed via the usual autoxidation cycle, oxidizes the sulfur atom in the dialkenyl crosslink (illustrated

(9)

Hemithioacetal

$\longrightarrow$ +

½

Oxy radical

$\longrightarrow$ + (10)
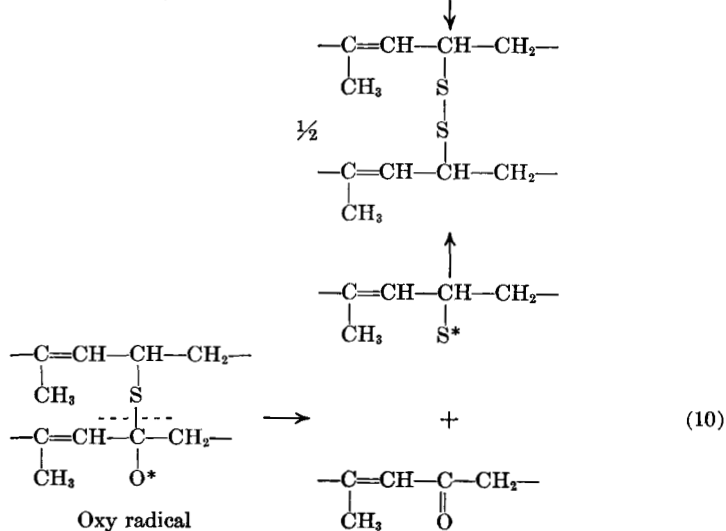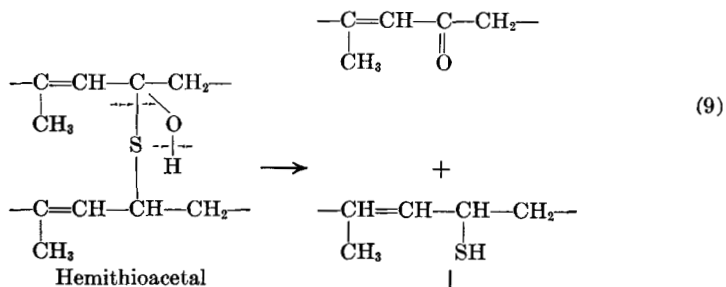
here with one of the possible types of crosslink[11]) to the sulfoxide which
then decomposes with cleavage at the C—S bond, forming a sulfenic acid
and a conjugated triene.   It will be seen later that the sulfoxides derived
from other types of dialkenyl crosslink give conjugated dienes.   The
intermediate sulfenic acid[29] undergoes condensation, giving water and a
thiolsulfinate which may disproportionate to disulfide and thiolsulfonate.
If the rubber hydroperoxide or peroxy radical taking part in eq. (6) results
from oxidation at the carbon atom adjacent to a crosslink, then a further
method of crosslink scission via the derived hemithioacetal or oxy radical
is possible as shown in eqs. (9) and (10).[21]

The above series of reactions has three consequences: (*1*) monosulfide
crosslinks are replaced by crosslinks containing two sulfur atoms; (*2*) one
new crosslink is formed for every two broken; and (*3*) conjugated structures
(dienes, trienes, and ketones) are introduced into the main polyisoprene
chain.

Oxidative Scission of Monosulfidic Crosslinks

Two methods were used to demonstrate that the mechanism of crosslink
scission given above occurs during the aging of sulfurated vulcanizates.
Firstly it was shown that on oxidation monosulfidic crosslinks were con-
verted into a thermally unstable intermediate, which when decomposed
reduced the total number of crosslinks and formed some crosslinks which
contained two sulfur atoms.   Initially, in order to eliminate any effects
arising from main-chain oxidation and scission, the oxidation was carried
out *in vacuo* with *tert*-butyl hydroperoxide, but subsequently autoxidation
at 35°C. was shown to produce similar results.

Secondly, it was demonstrated that conjugated structures were produced
during the thermal decomposition of the oxidized crosslinks.   In this case
the use of *tert*-butyl hydroperoxide instead of oxygen was essential, in
order that the conjugated structures produced were not oxidized aero-
bically.   The overall degradation of the networks was followed by measur-
ing changes in the elastic constant C_1, which is a function of the main-chain
molecular weight ($\bar{M}_n$) and the molecular weight between crosslinks (M_c)
[eq. (2)].

Oxidation with *tert*-Butyl Hydroperoxide

Treatment of a peroxide vulcanizate with *tert*-butyl hydroperoxide at
25°C. caused only a very small decrease in C_1, and no further change
occurred on heating *in vacuo* at 75°C. (Table I).   This treatment therefore
does not cause main-chain scission.   With a TMTD sulfurless vulcanizate
some degradation occurred on treatment with the hydroperoxide, and a
substantial decrease in C_1 was observed on heating *in vacuo* (Table I).
Treatment of this heated network with piperidine–*n*-hexanethiol[30] resulted
in a further drop in C_1, and thus established the presence of a significant
number of crosslinks containing two sulfur atoms.   The amount of this
type of crosslink present in the original TMTD network was much less,

TABLE I
Scission of the Crosslinks in TMTD Sulfurless Networks by
Oxidation with *tert*-Butyl Hydroperoxide

|	Monosulfidic network		Peroxide network	
Treatment of network	C_1, dyne/ cm.^{2} $\times$ 10^{-6}	C_2, dyne/ cm.^{2} $\times$ 10^{-6}	C_1, dyne/ cm.^{2} $\times$ 10^{-6}	C_2, dyne/ cm.^{2} $\times$ 10^{-6}
Unoxidized	1.99	0.58	2.03	0.69
n-Hexanethiol in piperidine	1.91	0.62	1.97	0.66
Oxidized with *t*-BuO$_2$H	1.74	0.67	1.96	0.73
Oxidized with *t*-BuO$_2$H and heated *in vacuo* at 75°C.	1.18	0.51	1.95	0.72
Oxidized, heated *in vacuo*, and treated with thiol–amine	0.84	0.54	—	—

since when it was treated with the thiol–amine reagent only a small change in C_1 occurred (Table I).

The ultraviolet absorption spectra of the TMTD network (maintained *in vacuo*) was recorded before and after treatment with the hydroperoxide and after heating at 75°C. The latter treatment resulted in the appearance of absorption bands at ~240 and ~284 mμ, the former being identified with a 1,3,6 partially conjugated triene as observed in the ocimenes (I) (λ_{max}, 237 mμ),[31]

I   II

and the latter with a fully conjugated triene containing the same chromophore as alloocimene (II) (λ_{max} ~280 mμ dependent on geometrical isomer).[32,33] The multiple absorption maxima characteristic of the alloocimenes[32] were indicated in the vulcanizate spectra by inflections at ~270 and 290 mμ.

The partially and fully conjugated triene structures arise from decomposition of the sulfoxides [in the manner shown in reaction (7)] derived from the various types of dialkenyl monosulfide crosslinks (III–VII) known to be present in TMTD sulfurless networks.[11] One other type of crosslink (VIII) is

III   IV   V

VI   VII
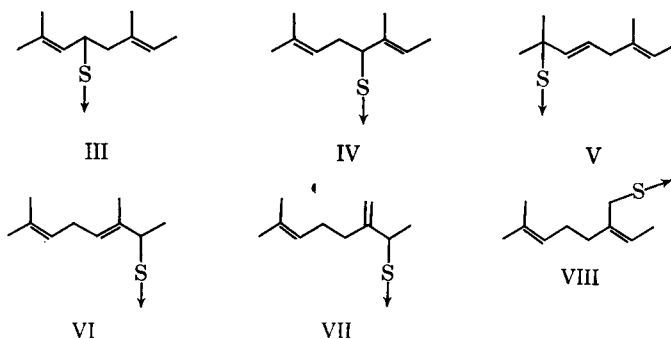
also present, but since its sulfoxide has no β-hydrogen atom available for bonding with the S—O, it will not be thermally unstable.

Autoxidation

When the peroxide vulcanizate was oxidized in oxygen at 35°C., C_1 decreased, but no further degradation took place when it was heated *in vacuo* at 75°C. or when this product was treated with the thiol–amine reagent (Table II). When the TMTD sulfurless vulcanizate was similarly oxidized, degradation occurred, and a further fall in C_1 took place on heating *in vacuo* at 75°C. Furthermore, treatment of this product with the thiol–amine reagent, showed that the number of crosslinks containing the cleavable — S — S — structure had considerably increased from that originally present (Table II).

TABLE II
Scission of the Crosslinks in TMTD Sulfurless
Networks during Autoxidation

	Monosulfidic network		Peroxide network	
Treatment of network	C_1, dyne/ cm.^{2} × 10^{-6}	C_2, dyne/ cm.^{2} × 10^{-6}	C_1, dyne/ cm.^{2} × 10^{-6}	C_2, dyne/ cm.^{2} × 10^{-6}
Unoxidized	2.09	0.71	2.03	0.69
~1% oxygen absorbed at 35°C.	1.82	0.63	1.71	0.62
Oxidized and heated *in vacuo* at 75°C.	1.60	0.43	1.71	0.58
Oxidized, heated *in vacuo*, and treated with thiol–amine	1.40	0.43	1.68	0.49

It is concluded that the above results clearly establish the occurrence of crosslink scission in sulfurated vulcanizates under the aging conditions employed.

Relative Extent of Main-Chain Scission, Crosslink Oxidation, and Crosslink Scission

The data for the TMTD vulcanizate in Table II can be used to compare the following: (1) the amount of main-chain scission occurring on oxidation at 35°C., (2) the number of crosslinks oxidized; and (3) the number of crosslinks cleaved on heating *in vacuo* at 75°C.

It is not unreasonable to assume that no crosslink scission or formation occurs during the autoxidation of the TMTD vulcanizate at 35°C., since the fall in C_1 obtained on heating *in vacuo* at 75°C. indicates that crosslink scission requires temperatures higher than 35°C., and studies with peroxide vulcanizates show that crosslinking via a direct reaction between the main chains and oxygen is unlikely.[5] Then 7×10^{-6} mole/g. of main-chain scission events [calculated from eq. (2), M_c remaining constant] are occurring, and 43 molecules of oxygen are absorbed per main-chain scission.

For the peroxide vulcanizate (Table II), a value of 40 molecules of oxygen per scission event is obtained, and a value of 37 can be obtained by extrapolation of the data of Bell and Tiller.[34] The chemistry given above shows that the crosslinks broken on heating at 75°C. and by treatment with the thiol–amine reagent must have been oxidized, and hence the fall in C_1 from 1.82×10^6 to 1.40×10^6 dyne/cm.^{2} is derived from 1.7×10^{-5} mole/g. of oxidized crosslinks [calculated from eq. (2), $\bar{M}_n$ remaining constant]. Furthermore, this is likely to be an underestimate, because the sulfoxide derived from VIII is thermally stable. Since the initial concentration of crosslinks was 6.7×10^{-5} mole/g., about 25% of the crosslinks have been oxidized, and approximately two crosslinks are oxidized and subsequently broken on heating *in vacuo* at 75°C. for every main-chain scission event.

EXPERIMENTAL

Preparation of 1,3-Dimethylbut-2-enyl Isopropyl Sulfoxide

1,3-Dimethylbut-2-enyl isopropyl sulfide prepared as described previously[35] was treated with hydrogen peroxide (30 vol.-%) in acetone at 0°C. After suitable working up, a mixture of the diastereoisomers of the sulfoxide was obtained. Low-temperature crystallization of this liquid product, followed by recrystallization three times from light petroleum (Analar, b.p. 30–40°C.) at −15°C. resulted in the isolation of one of the diastereoisomers, m.p. 56°C.

ANAL. Calcd. for $C_9H_{18}OS$: C, 62.1%; H, 10.3%; S, 18.4%. Found: C, 61.7%; H, 10.7%; S, 18.4%.

It was characterized by infrared spectroscopy, including strong absorption (assigned to the sulfinyl group) at 1050 cm.$^{-1}$ in carbon tetrachloride.

Thermal Decomposition of 1,3-Dimethylbut-2-enyl Isopropyl Sulfoxide

The sulfoxide (41.7 mg./ml.) in carbon tetrachloride was heated for 16.5 hr. at 75°C. Infrared spectroscopy and gas–liquid chromatography on a 20% poly(ethylene glycol) on brickdust column at 20°C. indicated the following. (1) From the decrease in intensity at 1050 cm.$^{-1}$, 65% of the sulfoxide had decomposed. (2) 4-Methylpenta-1,3-diene was the only significant olefin formed, only very small amounts of propylene and 2-methylpenta-1,3-diene could be identified. From absorption at 895 cm.$^{-1}$ the concentration of diene was 10.3 mg./ml. (i.e., 80% of theoretical yield based on sulfoxide decomposed). (3) A band of medium intensity was found at 1085 cm.$^{-1}$ and assigned to thiolsulfinate equivalent to about 4.9 mg./ml. of isopropyl propane-2 thiolsulfinate (∼40% yield based on sulfoxide decomposed). (4) Absorption bonds were found at 1275, 1315, and 1125 cm.$^{-1}$ consistent with the presence of diisopropyl disulfide and isopropyl propane-2-thiolsulfonate, respectively. (5) Some hydroxylic material was present. In a parallel experiment, water was estimated on

the total decomposition mixture by the Karl Fischer method as applied by Bateman and Shipley[20] and represented 96% of the theoretical amount based on the infrared spectroscopic estimate of sulfoxide decomposed.

Preparation of Vulcanizates

Highly purified natural rubber (U. S. Rubber Co.) was extracted with hot acetone in a Soxhlet apparatus under nitrogen for 24 hr. and dried and stored *in vacuo*. Sheets of the vulcanizates (10 × 10 × 0.03 cm.) were made in a suitable mold according to the following recipes. Peroxide vulcanizate: purified rubber 100 parts, dicumyl peroxide 2.0 phr, cured 10 min. at 100°C. followed by 50 min. at 150°C.; TMTD sulfurless vulcanizate: purified rubber 100 parts, tetramethylthiuram disulfide 8.0 phr, zinc oxide 6.0 phr, lauric acid 3.0 phr, cured 7 hr. at 140°C.; sulfenamide-accelerated sulfur vulcanizate: RSS1 100 parts *N*-cyclohexyl-2-benzo-thiazyl sulfenamide (CBS) 6.0 phr, sulfur 0.4 phr, zinc oxide 5.0 phr, lauric acid 1.0 phr, cured 30 min. at 140°C.

All the vulcanizates were extracted after cure for 64 hr. with hot chloroform–methanol–acetone azeotrope under reflux in nitrogen, dried, and stored *in vacuo*. Strips (10 × 0.5 × 0.03 cm.) were used for the aging experiments and for the stress–strain measurements.

Stress–Strain Measurements

Equilibirum stress–strain properties in simple extension were determined on the strips of the vulcanizates with an apparatus developed in these laboratories by Greensmith.[36] The parameters C_1, C_2, and λ^* were derived from the stress–strain data by the methods previously described.[5,7,8]

Cleavage of the Polysulfide Crosslinks in the Sulfenamide-Accelerated Sulfur Vulcanizate

A strip of the vulcanizate was placed horizontally in the reaction tube (Fig. 1) and, after blowing through with nitrogen, 6 ml. of a solution in *n*-heptane of piperidine (0.4M) and propane-2-thiol (0.4M) was added.
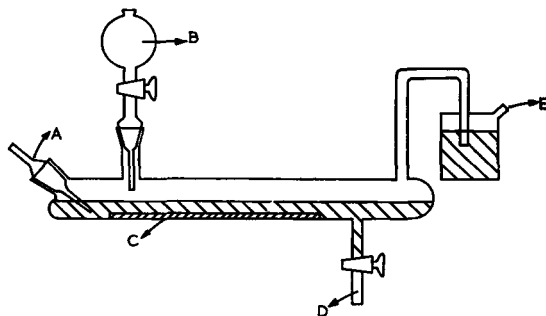

Fig. 1. Apparatus for treating vulcanizates with the thiol–amine reagent: (A) nitrogen inlet; (B) thiol–amine reagent and light petroleum added from this vessel; (C) strip of vulcanizate; (D) exit for excess reagents; (E) nitrogen outlet.

After standing for 2 hr. at room temperature the excess of the reagent was run off, and during 7 hr. 500 ml. of light petroleum (Analar, b.p. 30–40°C.) was run through the reaction vessel, the strip remaining completely immersed in the solvent. A slow stream of nitrogen was passed through the apparatus throughout the reaction and extraction periods. The vulcanizate was thoroughly dried *in vacuo* before determination of its stress–strain properties.

Cleavage of the Disulfide Crosslinks in the TMTD Sulfurless Vulcanizates

Cleavage of the disulfide crosslinks in these vulcanizates (before and after oxidation), was carried out in a similar manner to that described for cleavage of the polysulfide crosslinks in the sulfenamide-accelerated sulfur vulcanizate. The only differences were that 10 ml. of a solution of *n*-hexanethiol (1.0*M*) in redistilled piperidine was used instead of the *n*-heptane solution of piperidine and propane-2-thiol, and the reaction period was extended from 2 to 16 hr. at room temperature.

Treatment with *tert*-Butyl Hydroperoxide

Several strips of the extracted vulcanizates were placed in one limb of an H tube, and about 40 ml. of a 3% solution of *tert*-butyl hydroperoxide (purified via the sodium salt, purity by gas–liquid chromatography and titration >98%) in light petroleum (Analar, b.p. 30–40°C.) was added to the other limb. After thoroughly degassing three times, the tube was sealed under vacuum (10^{-4} mm. pressure) and the hydroperoxide solution transferred onto the strips. The tube was maintained at 25°C. for 7 days, the excess of the solution was tipped into the empty limb which was then frozen in liquid nitrogen overnight in order to remove the majority of the solution from the swollen strips. Final extraction of the strips was accomplished by immersing them in 200 ml. of light petroleum (Analar, b.p. 30–40°C.) at 25°C. for 24 hr., followed by drying *in vacuo*. The strips were then used for stress–strain measurements either directly or after heating for 1 day *in vacuo* at 75°C. In control experiments the above procedure was followed, except that the *tert*-butyl hydroperoxide was omitted.

Autoxidation

Oxygen absorption measurements were carried out in an automatic apparatus[37] developed from that previously reported.[38] Approximately half of a cured sheet (i.e., 10 × 5 × 0.03 cm.) was oxidized at 35°C. and 760 mm. oxygen pressure, stress–strain measurements were then carried out on strips cut from the oxidized sheet and on a portion of the sheet which was subsequently heated *in vacuo* for 1 day at 75°C. The actual oxygen absorption of the vulcanizates shown in Table II was for TMTD sulfurless vulcanizate, 0.95% (w/w); for peroxide vulcanizate, 1.04%

(w/w). The oxidation took 35 hr. in the case of the TMTD vulcanizate and 275 hr. for the peroxide compound.

Detection of Conjugated Structures in Oxidized Vulcanizates

For these experiments the vulcanizates had to be specially prepared as follows.

Highly purified rubber was allowed to stand in contact with cyclohexane (purified by shaking with ferrous sulfate solution, washing with water, drying over anhydrous Na_2SO_4, and distilling) for several days, when the gel was removed by filtration through lens tissue. After gravimetrically determining the concentration of rubber in solution, tetramethylthiuram disulfide, lauric acid, and colloidal zinc oxide were added, the proportions of the reactants being: rubber 100; TMTD 4; lauric acid 1.5; zinc oxide 5.

The TMTD was added as a 0.1% solution in chloroform and the zinc oxide–zinc laurate was finely dispersed by high-speed stirring. Sufficient solution to deposit a film $\sim 2.5 \times 10^{-4}$ cm. thick on evaporation was rapidly introduced onto the inner plane face of a cylindrical quartz reaction cell (3 cm. $\times$ 3 cm. diameter), and the solvent removed in a slow stream of nitrogen followed by pumping *in vacuo*. The reaction cell was filled with nitrogen at 550 mm. pressure and heated at 136°C. for 7 hr. After curing, the vulcanizate film was pumped for 1 hr. *in vacuo* at 75°C. to remove volatile products and subsequently allowed to stand in contact with chloroform–methanol–acetone azeotrope (ca. 20 ml.) for 1 hr. The solvent was carefully poured from the cell and the last traces of solvent removed *in vacuo*. The approximate thickness of the resulting vulcanizate film was calculated from its area and weight, and its density (0.94 g./cm.³) which was obtained from a similar TMTD compound.

Ultraviolet absorption spectra were determined by using a Hilger Uvispek spectrophotometer, the cell being sealed under vacuum throughout.

tert-Butyl hydroperoxide (ca. 20 mg.) was distilled into the cell by high-vacuum distillation, and after sealing *in vacuo* the cell was maintained at 25°C. for 20 hr. The cell was then rigorously pumped to remove all volatile products and resealed under vacuum. The ultraviolet absorption spectrum was then recorded and also again after the cell had been heated for 20 hr. at 75°C., care being taken to maintain the film horizontal to minimize any tendency to flow.

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