TEMPERATURE EFFECTS ON THE STABILITY OF INTERMEDIATES AND CROSSLINKS IN SULFUR VULCANIZATION*†

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INTRODUCTION

The rubber compounder, in designing a vulcanizate for a particular application, nearly always has to accept a compromise between cost, processability, the best combination of properties appropriate to the application, and the preservation of those properties for as long as possible under the conditions of use. Many factors influence these four features. Among the most important are the nature of the elastomer and the curing system, the nature and concentration of antidegradants, and the nature and concentration of fillers and extender oils. This paper will be concerned with the sulfur vulcanization of diene rubbers and the extent to which the curing system and the response of the elastomer to it determines the initial vulcanizate properties and the changes in those properties brought about by service conditions. In most applications, the causes of changes in properties during service are twofold: purely thermal reactions taking place in the network and oxidative changes brought about by a combination of heat and attack by oxygen (or ozone)—mainly on the elastomer backbone. Oxidative changes can be minimized by adequate protection of the vulcanizate with antidegradants and although interaction of these with various components of the network can have important consequences, the present discussion will be limited to the thermal behavior of the network itself since, if thermal changes are rapid, no amount of oxidative protection will prevent changes from occurring in physical properties.

The single most important factor in determining physical properties is, of course, the degree of crosslinking. All network properties depend to some extent on this variable although not always in a straightforward way (Table I). The primary objective of the compounder, then, must be to select a mix composition and vulcanizing conditions to achieve an appropriate degree of crosslinking but which will produce a network which will maintain its degree of crosslinking for as long as possible during storage and under service conditions. With vulcanizing systems which form stable crosslinks at moderate to high temperatures, *e.g.*, organic peroxides, this is not usually a problem, but sulfur vulcanizing systems normally form di- and polysulfidic species which are not only thermally fugitive but are highly susceptible to nucleophilic, electrophilic, and free-radical attack. They therefore tend to undergo further reactions under most conditions of use. Depending upon the elastomer, the temperature, and other factors, this may result in an increase or decrease in the degree of crosslinking.

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†Dedicated, with respect, to the memory of Merton L. Studebaker (1914-1982).

TABLE I

INFLUENCE OF DEGREE OF CROSSLINKING ON PHYSICAL PROPERTIES OF VULCANIZATES

Property	Change with increase in degree of crosslinking
Properties dependent only on degree of crosslinking	
stiffness (modulus)	increase
hardness	increase
Properties partly dependent on degree of crosslinking	
breaking elongation	decrease
resilience	increase
heat build-up	decrease
solvent swelling	decrease
creep, stress relaxation	decrease
set	decrease
abrasion resistance	increase
fatigue cracking	increase
low-temperature crystallization	decrease in rate
tensile strength, tear strength	increase, then decrease

In the case of sulfur vulcanization also, the position is further complicated because the nature of the crosslink and the presence of other rubber-bound side-products of vulcanization may influence physical properties. The evidence here has mainly been obtained with NR. In the general case (Figure 1), diene rubbers form not only mono-, di-, and polysulfidic crosslinks, but pendent sulfidic groups terminated by an accelerator residue, cyclic sulfides, conjugated diene and triene units, *cis, trans*-isomerized olefin units, and vicinal crosslinks. Di-, and especially polysulfide crosslinks not only display poor thermal aging resistance (for the reasons already given) but, as a consequence of their high chemical reactivity, affect other physical properties (Table II). Their enhancement of relaxation and swelling processes is almost certainly due to their ability to undergo rapid interchange reactions[1,2] which allow crosslink breakage and reformation to occur. The same mechanism has been put forward[3,4] for the improvement of strength properties by polysulfide crosslinks, but this has been contested[5-7], and the conflict of evidence[8] has remained unresolved. Nevertheless, there seems to be no doubt that networks formed with high proportions of polysulfide crosslinks display higher tensile strengths[4,8,9] and tear strengths[10] than networks prepared with monosulfide or carbon-carbon crosslinks. There is also some evidence that resilience[8] and resistance to fatigue failure[10] are enhanced.

The main-chain modifications formed by side reactions also appear to affect a selection of properties (Table III). Some of these are probably a consequence of an increase in polarity and/or an increase in the glass-transition temperature of the rubber. Others are a result of interruptions in the stereoregularity of the elas-

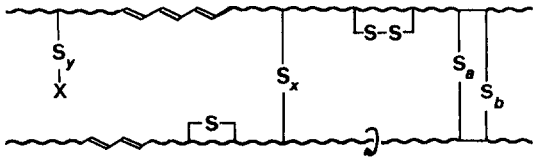


FIG. 1.—Generalized structure of a sulfur vulcanizate of a diene rubber. a,b,x,y = 1-6; X = accelerator residue: 2-benzothiazolyl, dialkylthiocarbamyl, etc ; curved arrow signifies *cis,trans*-isomerization.

TABLE II
INFLUENCE OF DI- AND POLYSULFIDE CROSSLINKS ON PROPERTIES

Property	Change with increase in proportion of di- and polysulfides
creep, stress relaxation	increase
set	increase
incremental swelling	increase
tensile strength, tear strength	increase
resilience	increase
fatigue failure	decrease
heat resistance	decrease
thermal aging resistance	decrease

tomeric backbone, as a consequence of which the tendency to crystallize is reduced. (It is interesting to note that, on the basis of limited evidence so far available[8,11], accelerator-terminated pendent groups do not appear to hinder the low-temperature crystallization of NR significantly.)

The extent to which the type of crosslink and type and degree of main-chain modification play a role in determining physical properties varies considerably with the nature of the elastomer and other factors such as the presence of fillers and oils. Tables I-III have largely been constructed on the basis of results obtained with NR because of the general dearth of information on the structure of synthetic rubber vulcanizates (*e.g.*, from BR, SBR, EPDM) prepared under various conditions. In any case, many of the properties of the vulcanized rubbers, *e.g.*, strength, low-temperature crystallization, are determined more by the microstructure of the polymer than by the structure of the network.

The aim of the present paper is to review the course of sulfur vulcanization in the light of recently obtained information on the reactivity of some of the intermediates in the process and on the stability of monosulfide crosslinks. All the recent results relate to NR, but reference to previous work with BR allows some major differences in behavior to be discerned. In the case of NR, the key role of zinc accelerator–thiolate complexes in promoting various reactions has been emphasized by the new findings. In addition, the importance of the position of sub-

TABLE III
INFLUENCE OF MAIN-CHAIN MODIFICATIONS ON PROPERTIES

Property	Change with increase in degree of modification		
	Olefinic[a]	Cyclic sulfide	Pendent group
resilience	decrease	decrease	little effect?
strength[b]	decrease	decrease	little effect?
fatigue failure	decrease?	decrease?	little effect?
swelling in hydrocarbon oils	decrease?	decrease	decrease?
oxidative aging resistance	decrease	decrease	decrease?
low-temperature crystallization	rate decrease	rate decrease	little effect

[a] Includes conjugated diene and triene groups and *cis, trans*-isomerized units.
[b] Especially high-temperature strength.

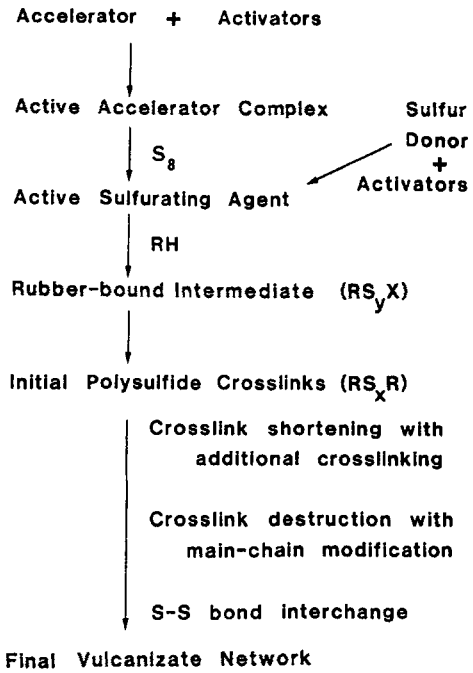


FIG. 2.—Outline reaction scheme for the sulfur vulcanization of diene rubbers. R represents the rubber chain and H is normally an allylic hydrogen atom; X = accelerator residue.

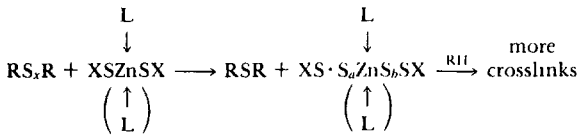
stitution of sulfur on the rubber backbone in determining the subsequent fate of the system has been further underlined. It turns out that neither of these features can play any significant part in the sulfur vulcanizations of BR.

GENERAL COURSE OF SULFUR VULCANIZATION

An outline reaction scheme for the course of sulfur vulcanization, originally proposed for NR[12], is now generally accepted (Figure 2). The critical features of this scheme were the identification of an accelerator-terminated polysulfidic pendent group as the rubber-bound precursor to crosslinks and the postulation that the initially formed crosslinks were polysulfides which subsequently underwent a number of competing reactions. Since the scheme was first proposed, further evidence for the existence and identity of the rubber-bound intermediate has been obtained[13-15], but there is as yet no general agreement on the chemical nature of the active sulfurating agent—in particular, as to whether it contains zinc or not[16-18].

In the transformation of the initial polysulfidic network into the more complex "final" network present in the vulcanizate as prepared, two principal reactions were identified.

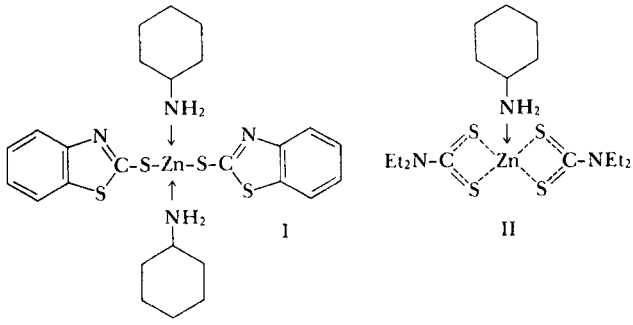
The first reaction is desulphuration [Reaction (1)], giving rise to crosslink shortening and leading eventually to monosulfide crosslinks. This reaction was shown to be effected by zinc complexes derived from the accelerator (or sulfur donor) and the zinc compounds present in the rubber mix.



(1)

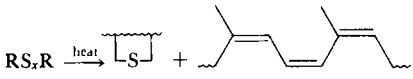
(L = ligand; X = accelerator residue)

Examples of such complexes are:



(I and II are formalized structures and represent the stoichiometry but not necessarily the actual structures of the complexes). The sulfur removed from the polysulfides is able to sulfurate more olefin to form additional crosslinks.

The second reaction is thermal decomposition [*e.g.*, Reaction (2)], forming cyclic mono- and disulfides and conjugated dienes and trienes in the rubber backbone, and zinc sulfide. Monosulfide crosslinks were found to be resistant to such decomposition up to about 170°C.

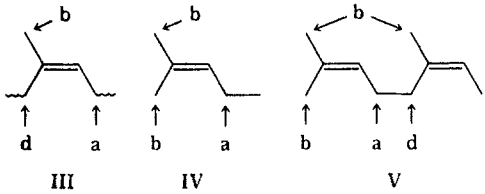


(2)

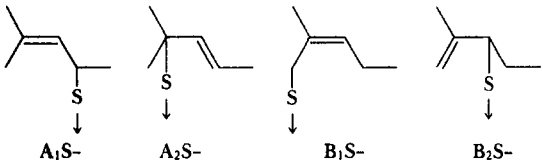
The balance between these two reactions was found to determine, in large measure, the type of vulcanizate network formed. If the concentration *in the rubber* of zinc accelerator-thiolate complexes such as I and II is high, the polysulfide crosslinks are desulfurated rapidly to stable monosulfides and a heat-resistant network with a high degree of crosslinking is formed—the so-called efficient vulcanization system. If the zinc complexes are present in low concentration or are insufficiently soluble, desulfuration is slow and, unless the vulcanization temperature is low, the polysulfide crosslinks suffer thermal decomposition with consequent modulus reversion and extensive modification of the main chains (conventional or inefficient vulcanization).

The concentration of zinc accelerator-thiolate complexes in the rubber is not the only factor determining the balance of the two reactions in NR. Both the rate of desulfuration of polysulfide crosslinks and the rate of their thermal decomposition depend upon the positions of attachment of the sulfur chains to the backbone rubber chains and the detailed structure of the hydrocarbon at the ends of the crosslinks. In the course of normal accelerated vulcanization, there are three different positions of attack on the polyisoprene backbone: two of these are methylene groups in the main chain (labelled d and a in III), the third is the side-chain methyl group (labelled b in III). Direct analysis of the distribution of

the sites of attack cannot yet be made on actual rubber vulcanizates, and information has had to be obtained solely by sulfuration of the model olefin, 2-methyl-2-pentene and, more recently, 2,6-dimethyl-2,6-octadiene. The former (IV) models the α-methylic site but only one of the two α-methylenic sites of polyisoprene; the latter (V) models all three sites but at the present time these are



not all supported by the synthesis of relevant sulfides. Because allylic rearrangements are common in subsequent reactions of the sulfurated rubber, sulfur substituents appear not only on allylic carbon atoms but on isoallylic carbon atoms. Thus, from 2-methyl-2-pentene, the following groups are formed:



In practice, because of their similar reactivities, A_1S- and A_2S- can be considered together, as can B_1S- and B_2S-groups. Using the same olefin, it was found that synthetic polysulfides of B-type structure, *e.g.*, B_1SSSB_1, were desulfurated by Reaction (1) much more rapidly than A-type sulfides, *e.g.*, A_1SSSA_1, under the same conditions[18,19]. However, B-type polysulfides also decomposed more rapidly than A-type polysulfides. For B-type polysulfides, the balance between these reactions was such that, when a high concentration of desulfurating agent, *e.g.*, I was present, monosulfides were formed rapidly. In the presence of the parent olefin, their yield was greater than 100 percent because of new sulfuration by sulfur removed from the polysulfide. Evidently, desulfuration was sufficiently rapid to minimize Reaction (2). With A-type polysulfides, Reactions (1) and (2) were much more in balance and, with lower concentrations of desulfurating agent, polysulfide decomposition predominated.

REACTIONS OF POLYSULFIDIC PENDENT GROUPS

It has now become possible to enlarge on the outline scheme in Figure 2 and the reactions represented in Reactions (1) and (2). The similarity in structure of the rubber-bound intermediate, RS_yX, and the polysulfide crosslink, RS_xR, suggests that the intermediate, like the crosslinks, should be susceptible to desulfuration and to thermal decomposition. Some evidence for the first of these processes was originally obtained by D. S. Campbell[13] and both reactions were later invoked by Newell, Porter, and Tidd[20] to explain the reduction in crosslinking efficiency displayed by efficient vulcanization systems at high temperatures (see also Reference 21). The recent synthesis of model pendent groups containing benzothiazolyl functions[22] has enabled their thermal behavior to be studied directly.

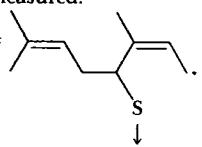
Table IV shows that simple thermal decomposition of the model pendent

TABLE IV

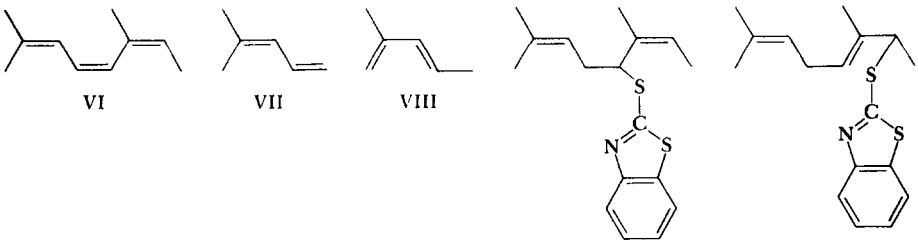
PRODUCTS OF DECOMPOSITION OF MODEL DISULFIDIC PENDENT GROUPS[a]

Reactants	Time, min	Temperature, °C	Unreacted RSSX, %	Products, mole %					
				V	VI	(VII + VIII)	RSX[b]	(IX + X)	crosslinked sulfides
A_1SSX, IV	30	140	70–85	—	—	27	<2	—	<1[c]
A_1SSX, IV, I	15	140	8–12	—	—	4	~30	—	33
D_1SSX[e], IV	15	180	<1	[d]	30	[d]	5	14	[d]
D_1SSX[e], IV, I	15	180	<1	27	26	[d]	19	22	[d]

[a] Reference 23.
[b] R = A_1, B_1, B_2.
[c] 16 mole % MBT also formed.
[d] Not measured.
[e] D_1S =



group, A_1SSX (X = 2-benzothiazolyl), proceeds slowly at 140°C, giving methylpentadienes and 2-mercaptobenzothiazole (MBT) as the only significant products identified. The addition of the zinc complex, I, greatly increases the overall rate of reaction and produces substantial yields of both crosslinked sulfides and the monosulfidic pendent groups A_1SX, B_1SX, and B_2SX. A_1SX, formed to the extent of 15 mole percent, can be regarded as a desulfuration product of A_1SSX, but the formation of B_1SX and B_2SX indicates that other routes are available for the formation of monosulfidic pendent groups. One of these presumably involves the reaction of some XS-containing species with olefin since A_1SX, B_1SX, and B_2SX were also formed when D_1SSX was heated in 2-methyl-2-pentene in the absence or presence of the complex, I. In these cases, there was also unequivocal evidence for direct desulfuration in the formation of substantial quantities of D_1SX(IX) and D_2SX(X).



These experiments therefore confirm that, in the temperature range 140–180°C, polysulfidic rubber-bound intermediates can suffer decomposition and desulfuration in addition to their normal transformation to crosslinked sulfides. They also suggest that the conversion to crosslinks does not occur to a significant extent in the absence of a zinc compound (in this case, I). Elimination to triene groups occurs, as expected by analogy with Reaction (2), but a path also exists for re-formation of the parent olefin, as shown by the extensive formation of V from D_1SSX (Table IV). Cyclic sulfides have not yet been detected in decompositions of pendent groups. There is evidently at least one other route to monosulfidic pendent groups besides desulfuration. The stability of such groups at 140–170°C has not yet been specifically tested, but they cannot give rise to crosslinks[24] and the evidence available points to their remaining inert in the rubber network, once formed.

REACTIONS OF MONOSULFIDE CROSSLINKS

The heat-resistant nature of NR vulcanizates containing very high proportions of monosulfide crosslinks (as obtained from an adequately cured efficient vulcanization system) is now well known. However, the thermal stability of these monosulfide-crosslinked networks is still about an order of magnitude lower than the stability of carbon-carbon crosslinked NR, which shows only very slow modulus reversion even at 200°C (Figure 3)[20]. An extensive investigation of the chemical reactivity of allylically unsaturated monosulfides in the temperature range 140–205°C has now thrown light on modes of breakdown of monosulfide crosslinks[25]. Three different types of decomposition have been observed, depend-

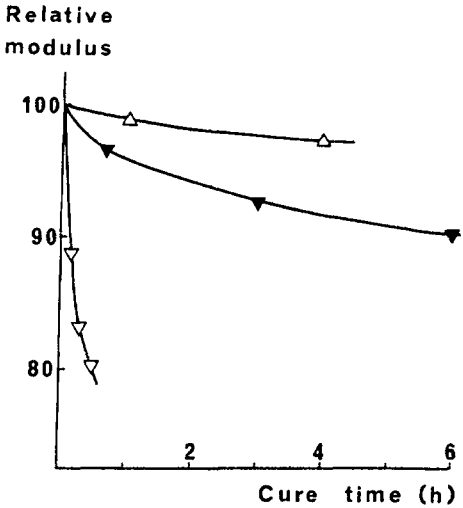
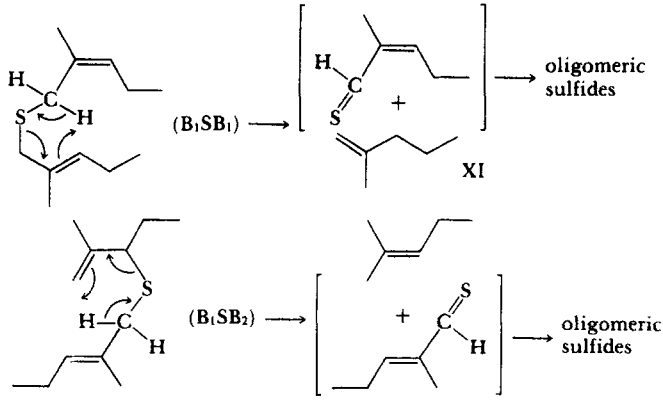


FIG. 3.—Modulus reversion in carbon-carbon and monosulfide crosslinked NR. △, monosulfide at 140°C; ▽, monosulfide at 200°C; ▼, carbon-carbon at 200°C.

ing on the structure of the monosulfide, the temperature, and what catalysts are present.

The first type, which predominates in sulfides containing B groups at around 180°C, produces an olefin of allylically rearranged structure and oligomeric sulfides. There is good evidence that these are formed *via* an intramolecular rearrangement in the allylic sulfide, *e.g.*:

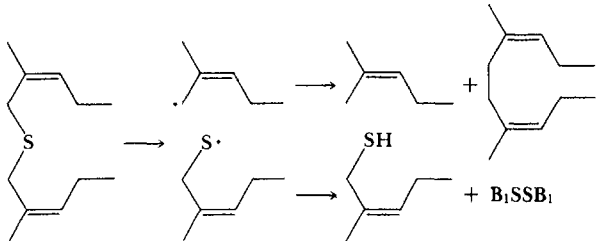


(3)

(4)

Monosulfides of A type also undergo this mode of reaction but at higher temperatures (around 205°C). The second type of decomposition, which intrudes in the case of B-type sulfides at long times or above 190°C, produces mainly olefin, thi-

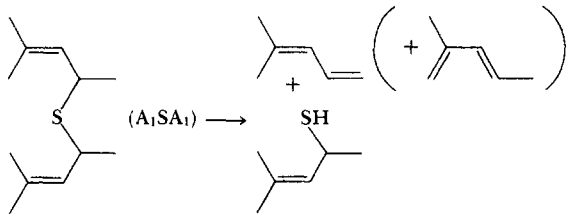
ols, and disulfides. It is promoted by sulfur, oxygen, dicumyl peroxide, and the complex I and is possibly a free-radical decomposition, *e.g.*:



(5)

(B_1SB_1)

The third mode of decomposition is only important in A-type monosulfides (and D-type from the diene model V) and then only in the presence of catalysts. This is a simple elimination reaction, but its course is often obscured by secondary reactions of the primary products[25]:



(6)

Many accelerators and accelerator transformation products are catalysts for this decomposition. They include zinc benzothiazole-2-thiolate (ZMBT) and zinc dithiocarbamates and their amine complexes, as well as CBS, MBT, and MBTS (which would normally not be present in quantity when monosulfide crosslinks are formed during the course of vulcanization).

Reactions (3)-(6) readily explain the shortfall in thermal stability of monosulfide crosslinks compared to carbon-carbon crosslinks. The origin of the lower stability is seen to lie in reaction paths which are not available to the latter [Reactions (3), (4)] or in paths for which the energy gain in the formation of analogous products would be less [Reactions (5), (6)]. All the reactions clearly depend upon the presence of olefinic unsaturation allylic to the sulfur atom. The corresponding saturated sulfides should be much more stable and a technically feasible way of introducing such crosslinks into polyisoprene is highly desirable.

PATHWAYS OF SULFUR VULCANIZATION IN POLYISOPRENES

The conclusions reached in the two previous sections allow the second part of the reaction sequence for sulfur vulcanization outlined in Figure 2 to be expanded into that shown in Figure 4 (at least as far as NR and IR are concerned). We now see that the rubber-bound polysulfidic pendent group has not one fate, but three. The two which do not immediately lead to crosslinks both give rise to a loss of crosslinking efficiency: (i) the decomposition route by main-chain modification and diversion of sulfur, and (ii) the desulfuration route by the removal of accelerator as inactive monosulfidic pendent groups which appear to be rea-

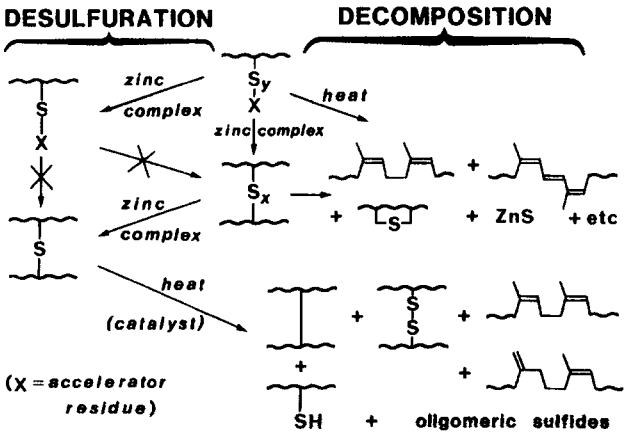


FIG. 4.—Desulfuration and decomposition of pendent groups and crosslinks in polyisoprenes.

sonably stable except at high temperatures[26], but which, in any case, are not converted into crosslinks. The existence of at least one other route to such pendent groups has been deduced.

Whereas the decomposition of polysulfidic pendent groups and crosslinks always leads to the loss of potential or actual crosslinks, the thermal breakdown of monosulfide crosslinks may give rise to crosslinks of a different type: disulfides or carbon-carbon crosslinks [*cf.*, Reaction (5)]. A proven route for the formation of carbon-carbon crosslinks during sulfur vulcanization has not previously been identified for NR, in contrast to the butadiene-based rubbers, in which the presence of vinyl side groups leads to carbon-carbon crosslinking at high temperatures.

The complexity of the competition between desulfuration and decomposition of polysulfidic species (in determining the structure of NR vulcanizate networks) can be readily appreciated from Figure 4. This complexity is even more evident since there are probably different responses of the various reactions to temperature changes. The central role played by zinc accelerator-thiolate complexes is clear from their direct involvement in at least three of the six reaction routes. The activity, concentration, rubber solubility, and thermal stability of these compounds must obviously all be important in determining the overall course of reaction. What is not clear from Figure 4 is: (i) that the structure of the rubber chain at the points of attachment of the various sulfidic groups has an effect on reaction rate, and (ii) the extent to which the Arrhenius activation energies of the various reactions influence the result.

ROLE OF ZINC ACCELERATOR-THIOLATE COMPLEXES

In the conversion of polysulfidic pendent groups to crosslinks.—The formation of crosslinks from pendent groups has been shown to take place by two routes[24]: combination of two pendent groups on different chains [Reaction (7)] and reaction of a pendent group on one chain with an olefin unit on another [Reaction (8)]. Reactions (7) & (8).

$$2RS_yX \longrightarrow RS_xR\ (+XS_zX) \tag{7}$$

$$RS_yX + RH \longrightarrow RS_xR \tag{8}$$

TABLE V

INFLUENCE OF ZINC COMPOUNDS ON YIELD OF CROSSLINKS FROM MODEL PENDENT GROUP B_1SSX IN 2-METHYL-2-PENTENE AT 140°C[a]

Additive	Reaction time, h	Unreacted B_1SSX, %	Yield of RSX[b], mole %	Yield of crosslinked sulfides, mole %
none	4	50–65	4	2
zinc oxide	0.5	75–84	1	9
zinc stearate	0.5	60–71	2	17
complex I	0.5	<2	26	54

[a] Reference 23.
[b] R = A_1, B_1, B_2.

Both reactions evidently only take place very slowly, if at all, without catalysis, but the presence of zinc compounds, especially the accelerator-thiolate complexes, greatly speeds up and improves the efficiency of the conversion. This is demonstrated in model compounds by the data of Tables IV and V. Reference to the latter shows that both zinc oxide and zinc stearate increase the yield of crosslinks in a given time, but they are both easily surpassed in effectiveness by the complex I. That similar effects operate during actual vulcanization was shown by Parks, Parker, Chapman, and Cox[14,15], who found that the presence of zinc oxide and stearic acid (or a zinc carboxylate) caused rapid conversion of accelerator pendent groups into crosslinks. In this case, the exact nature of the zinc-containing catalyst is uncertain since zinc accelerator-thiolate complexes would have been formed *in situ*.

In desulfuration of polysulfidic pendent groups and crosslinks.—Evidence has already been presented that desulfuration of model pendent groups is accelerated by the zinc complex I and evidence for the desulfuration of dialkenyl polysulfides by both I and amine complexes of zinc dimethyldithiocarbamate has been given elsewhere[18,19]. In the second case, it is clear that the sulfur abstracted from the polysulfides may be utilized to sulfurate olefin. In the case of pendent groups, unequivocal evidence is more difficult to obtain because crosslinks are formed anyway. Furthermore, the experiments carried out so far have been limited to disulfidic pendent groups.

The irreversible binding of accelerator moieties by desulfuration or by some other reaction limits the formation of zinc accelerator complexes and subsequently hinders desulfuration of both pendent groups and crosslinks. Although direct evidence for this pathway being responsible is lacking, it does appear that with NR at high temperatures, or with butadiene-based rubbers at all temperatures, removal of the accelerator by combination with the polymer gives the system many of the characteristics of an unaccelerated sulfur vulcanization[20] (see also below).

In decomposition of monosulfide crosslinks.—As indicated in an earlier section, the zinc complexes catalyze two of the three modes of decomposition of dialkenyl monosulfides, one of which proceeds rapidly with B-type sulfides [Reaction (5)], the other with A-type sulfides [Reaction (6)]. In each case, the effect was very substantial (Table VI), but in each the effect could be completely nullified by the addition of zinc stearate[25]. The mechanism of this protective effect is not known, but it is consistent with observations made in efficiently vulcanized NR at high temperatures[27].

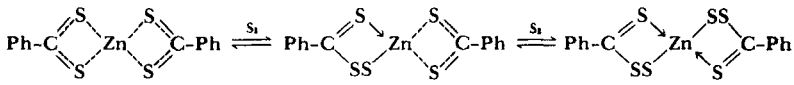
TABLE VI

EFFECT OF COMPLEX I (50 MOLE %) ON THERMAL DECOMPOSITION OF DIALKENYL MONOSULFIDES IN PENTANE[a]

Sulfide	Time, h	Temperature, °C	Unreacted Sulfide, %	Products, mole %						
				IV	XI	(VII + VIII)	V	VI	B_1SH	B_1SSB_1
B_1SB_1	4	180	2(84)[b]	139	36	—	—	—	15	1
A_1SA_1	4	150	74(100)[b]	11	—	22	—	—	0	—
D_1SA_1	4	180	0(~100)[b]	55	—	16	36	16	2	—

[a] Reference 25.
[b] Result in parentheses obtained in absence of I.

In initial sulfuration of the rubber.—The question of the involvement of zinc in the actual reaction in which carbon-sulfur bonds are formed in the rubber chains remains the major unresolved problem in sulfur vulcanization. Polysulfidic pendent groups are formed in the absence of zinc[14,15], probably *via* accelerator polysulfides[16,17]. The evidence that zinc accelerator-thiolate complexes are involved in the primary sulfuration step when an accelerator and zinc are present has been summarized elsewhere[18]. The most compelling in the present context is that, since the zinc complexes are able to remove sulfur from polysulfide chains in crosslinks and use it to sulfurate olefin, it seems probable that they would be able to effect the same process utilizing molecular sulfur or some ring-opened form such as a polysulfide anion or radical-ion. The putative sulfur-rich complexes which would be intermediates in all these reactions have never been detected. However, analogous compounds such as XIII and XIV have been prepared and have been shown to possess rapidly exchangeable sulfur atoms[28]:



XII XIII XIV

There is no evidence that polysulfidic versions of XIII or XIV can exist[17] but it has been shown[29] that XIV is itself a vulcanizing agent for EPDM rubber in addition to being, like XII, an effective accelerator.

In exchange reactions of di- and polysulfides and in sulfur insertion reactions.—Milligan showed that I and similar amine complexes are catalysts for disulfide interchange reactions [Reaction (9)] and for the insertion of sulfur into organic disulfides [Reaction (10)]. Both these catalytic effects are likely to be

$$RSSR + R'SSR' \rightleftharpoons 2RSSR' \quad (9)$$

$$RSSR + S_8 \rightleftharpoons RS_xR \quad (10)$$

operating during vulcanization but they will not usually be detectable and, in the case of Reaction (9), many other nucleophiles and free radicals are also catalysts. Two points which are relevant to the present discussion are: (i) catalysis of Reaction (9) helps to rationalize the fact that I and like complexes are very effective catalysts for the conversion of polysulfidic pendent groups to crosslinks. Of the two routes by which this conversion takes place, Reaction (7) is simply a special case of Reaction (9), and Reaction (8) is similarly a special case of the postulated initial sulfuration which is thought to proceed through a sulfur-rich version of I or its analogs[12]. (ii) Reaction (10) implies that the desulfuration of polysulfides to disulfides is reversible under vulcanizing conditions. The recognition[30] that at least some allylic monosulfides can undergo sulfur insertion suggests that monosulfide crosslinks too may be capable of re-sulfuration to di- and polysulfides under some conditions.

INFLUENCE OF THE STRUCTURE OF THE ALKENYL GROUPS

At present, the influence of the structure of the crosslink or pendent group terminus on its reactivity can be described only in terms of the derivatives of 2-methyl-2-pentene. The relevance of the information to behavior in polyisoprenes will be discussed subsequently.

On the reactivity of polysulfidic pendent groups.—The only direct information available involving conversion to crosslinks is shown in Table VII. The B-

TABLE VII

PRODUCT YIELDS ON HEATING MODEL DISULFIDIC PENDENT GROUPS WITH COMPLEX I (1:1 WT. RATIO) FOR 15 MINUTES AT 140°C IN 2-METHYL-2-PENTENE[a]

Reactant	Unreacted RSSX, %	Yield of dienes,[b] mole %	Yield of RSX,[c] mole %	Yield of crosslinked sulfides, mole %
A_1SSX	8-12	4	~30	33
B_1SSX	<4	<1	33	54

[a] Reference 23.
[b] VII + VIII.
[c] R = A_1, B_1, B_2.

type pendent group is clearly more reactive than the A-type in the presence of a substantial quantity of the complex I. Under these conditions, conversion of the former to crosslinks is over one and a half times as efficient as conversion of the latter, while yields of desulfuration products are about the same. Other experiments[23] suggest that A_1SSX is slightly less resistant to heat than B_1SSX.

On the reactivity of polysulfidic crosslinks.—The decomposition of polysulfide crosslinks was known to give rise to cyclic mono- and disulfides, conjugated trienes (dienes in the case of the 2-methyl-2-pentene model) and zinc sulfide [see Reaction (2)]. More recent experiments have shown that isolated olefin units are also formed but are usually undetected because the main type of double bond present is the same as that in the parent olefin. In polyisoprene vulcanization, this might give rise to *cis, trans-* isomerized isoprene units. With disulfides derived from 2-methyl-2-pentene, *viz.*, A_1SSA_1 and B_1SSB_1 (Table VIII),[31] the former decomposes to produce rather more mono-olefin than diolefin, whereas with the latter the ratio is nearly 3:1. A similar product distribution is observed with the corresponding trisulfides. This predisposition of A_1 sulfides to undergo elimination to dienes while B_1 sulfides are more prone to what is presumed to be a free-radical decomposition forming olefin is as observed for the monosulfides [Reactions (5) and (6)] but the preferences are less clear cut than for the latter (*cf.*, Table VI). The data of Table VIII do not allow any deductions to be made regarding relative reaction rates, but an indication that B-type polysulfides are less stable than A-type is available from experiments with polysulfides obtained from the diene V[11]. Sulfuration was under two sets of conditions which, when applied to the mono-ene IV, give a very high, and a very low, B:A ratio, respectively. When the isolated polysulfides were freed from other products and heated at

TABLE VIII

HYDROCARBON PRODUCTS OF THERMAL DECOMPOSITION OF METHYLPENTENYL DI- AND TRISULFIDES IN PENTANE (6 H AT 140°C)[a]

Polysulfide	Products[b] Mono-enes IV	Mono-enes others	Dienes (VII + VIII)
A_1SSA_1	51	0	41
B_1SSB_1	60	3	25
A_1SSSA_1	59	4	40
B_1SSSB_1	58	2	22

[a] Reference 31.
[b] Moles per 100 moles sulfidic reactant.

TABLE IX

PRINCIPAL VOLATILE PRODUCTS FORMED ON HEATING POLYSULFIDES DERIVED FROM DIENE V IN DECANE AT 140°C FOR 7.5 H[a]

Polysulfide fraction[b]	Formula	Volatile products			
		Total[c]	Dienes[d,e]	Trienes[d,f]	Cyclic monosulfides
1	$C_{20}H_{34.0}S_{4.30}$	38	14	20	37
2	$C_{20}H_{35.0}S_{4.01}$	88	31	15	43

[a] Reference 11.
[b] 1. Fraction from: diene V, 44; sulfur, 2.0; zinc oxide, 2.0; zinc dimethyldithiocarbamate, 2.0 parts by wt, heated 3 h at 100°C. B:A ratio in IV = 0.54.
2. Fraction from: diene V, 25; sulfur, 1.5; zinc oxide, 5.0; propionic acid, 0.51; cyclohexylammonium benzothiazole-2-thiolate, 2.39 parts by wt, treated 4 months at room temperature. B:A ratio in IV = 3.4.
[c] Weight percent of polysulfide reactant.
[d] Moles per 100 moles polysulfidic reactant.
[e] Mainly *cis*- and *trans*-V.
[f] Mainly VI.

140°C in decane, those characterized by a low B:A ratio decomposed to a lesser extent than those with a higher B:A ratio (Table IX). In addition, the former produced less parent olefin but more trienes than the latter, thus reflecting the behavior of the A_1 and B_1 sulfides described by Table VIII. The polysulfides with high B:A ratio formed more cyclic monosulfides than those with low B:A ratio.

On decomposition of monosulfide crosslinks.—The dependence of the course of decomposition of dialkenyl monosulfides derived from 2-methyl-2-pentene on the structure of the alkenyl groups has already been described, and mechanisms have been put forward. The effects on actual thermal stability are shown in Table X. It is quite clear that, in the absence of additives, the A-type sulfides are stable at 195°C and are only very slowly decomposed at 205°C. The B-type sulfide is found to be intrinsically much less stable, undergoing decomposition at an appreciable rate even at 180°C, presumably because of the availability of the internal rearrangement route [Reaction (3)]. For the design of polyisoprene vulcanizates with good heat resistance, this order of stabilities is not helpful, since networks containing monosulfide crosslinks of A-type structure have so far proved to be technologically inaccessible. This is because A-type polysulfides are much more resistant to desulfuration than those of B-type. Furthermore, as will be seen in the next section, vulcanizing systems forming high concentrations of a desulfurating agent tend to cause sulfuration preponderantly at the side-chain methyl groups to give B-type sulfides.

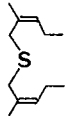
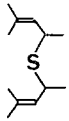
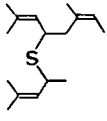
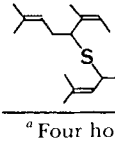
Distribution of alkenyl groups during initial sulfuration of the rubber.—Upwards of one hundred sulfurations of 2-methyl-2-pentene have been carried out under a variety of conditions in which variations have been made *inter alia* in the source of sulfur, the type and amount of accelerator used, the types and amounts of activators used, and the temperature and time of reaction. Full details of the structural analyses of the products cannot be given here, but the following generalizations can be made among others:

1. In the bulk of normal accelerated systems, the products contain only the four allylically unsaturated groupings: A_1S–, A_2S–, B_1S–, B_2S–.

2. Although the proportions of total B groups ($B_1 + B_2$) to total A groups

TABLE X

THERMAL STABILITY OF MODEL MONOSULFIDES[a]

Sulphide	Heating temperature	Decomposition (%)
 B_1SB_1	180°	15
	195°	67
 A_1SA_1	195°	0
	205°	5
 E_1SA_1	195°	0
	205°	13
 D_1SA_1	195°	0
	205°	20

[a] Four hour heating period.

($A_1 + A_2$) cover a wide range, the absolute concentrations of B_2 and A_2 groups rarely exceed 5% each.

3. Recognized mechanisms exist for the interconversion during heating of a given system: (i) of the isoallylic groups, $A_1 \rightleftharpoons A_2$ and $B_1 \rightleftharpoons B_2$; (ii) of the diastereoisomers of A_1 and of B_2; (iii) of the *cis* and *trans* isomers of B_1 and of A_2. There is also evidence in a small number of cases for: (iv) the interconversion of A and B groups, but the mechanism for this is unknown. With this possible exception, the overall ratio of B:A groups in the total crosslinked sulfides may be taken as characteristic of a given set of vulcanizing conditions.

4. As reaction time is increased with a given system, the B:A ratio usually decreases.

5. In the small number of cases investigated, an increase in reaction temperature gives rise to a reduced B:A ratio.

6. Overall B:A ratios have been found to lie generally in the range 6 to 0.33.

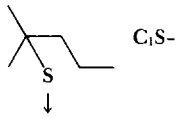
7. While individual accelerators may give rise to different B:A ratios at comparable concentrations, more striking differences are produced by variations in the accelerator:sulfur ratio and by changes in the type and concentration of activators.

8. Increase in accelerator:sulfur ratio causes an increase in B:A ratio provided that the additional zinc accelerator-thiolate is soluble.

9. Use of a sulfur donor instead of molecular sulfur does not fundamentally change the pattern of sulfuration.

10. Addition of either a basic nitrogen compound or a zinc carboxylate (or zinc oxide plus a carboxylic acid) causes a significant increase in B:A ratio.

11. Systems which are starved of accelerator and/or zinc give rise to B:A ratios approaching 0.33, the ratio given by sulfur alone, but alkyl-S-groups, specifically the C_1S-group:



and -S-alkylene-S- groups intrude in the products.

It will be noted that generalizations 8 and 10 both refer to increases in B:A ratio by changes which will increase the concentration of soluble zinc accelerator-thiolate complex in the rubber. Since these are catalysts for desulfuration of pendent groups and crosslinks and since B-type junctions favor rapid desulfuration of pendent groups and crosslinks, these factors all work in the same direction; that is, increasing the concentration of the desulfurating agent also increases the proportion of those polysulfides which are most susceptible to desulfuration. It is this fact in particular which gives confidence that B:A ratios observed in 2-methyl-2-pentene sulfurations have relevance to the vulcanization of polyisoprenes. The generalizations cannot be applied directly to polyisoprenes because the numbers of replaceable (allylic) hydrogen atoms are not the same in the two olefins and polyisoprenes possess an additional type of allylic hydrogen not modelled in 2-methyl-2-pentene (*cf.*, III, IV). However, it is found that vulcanizing systems which give high B:A ratios in the model olefin produce networks in NR which rapidly become monosulfidic on further heating, in which efficient use is made of the added sulfur or sulfur donor and which, from their properties, have not suffered extensive main-chain modification. By contrast, systems which give low B:A ratios form polysulfidic networks which tend to revert rapidly, which undergo extensive main-chain modification on further heating, and which make inefficient use of sulfur.

EFFECTS OF TEMPERATURE

Difficulties in separating the sequence of consecutive and competing reactions summarized in Figures 2 and 4 have prevented the measurement of their Arrhenius activation energies. However, some ranking of the response to temperature can be made. By using complexes such as I and II as accelerators or by arranging for them to be formed in the rubber at low temperature, it is possible to effect crosslinking slowly at room temperature. From the balance between polysulfidic pendent group formation and their reaction to form crosslinks at more normal vulcanizing temperatures, it may be deduced that sulfuration of the rubber and the subsequent initial crosslinking are reactions of rather low and comparable activation energy. The other reactions depicted in Figure 4 do not intrude below about 50°C; but at 100°C, the desulfuration of polysulfides becomes fast enough for typical mixtures of mono-, di-, and polysulfide crosslinks to be produced (Figure 5). Presumably, desulfuration of pendent groups also takes place at this temperature, since its activation energy should be similar to that for crosslinks. Decomposition reactions leading to net crosslink loss are not normally apparent at 100°C but begin to show up above this temperature, and it must be presumed that pendent groups decompose likewise. Desulfuration and

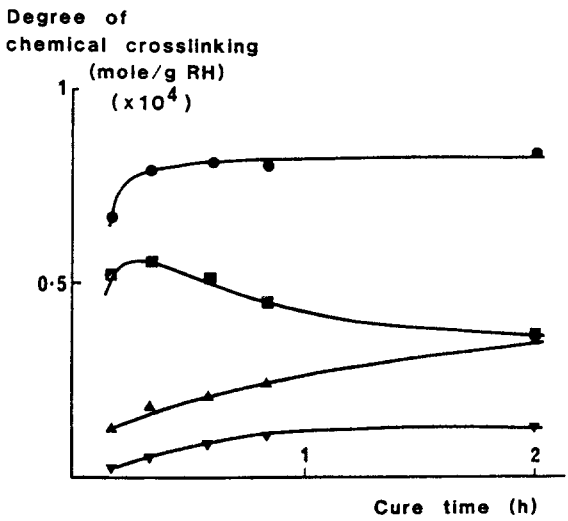


FIG. 5.—Distribution of mono-, di- and polysulfide crosslinks as a function of reaction time for whole-latex NR vulcanized at 100°C. Cure system in parts by weight per hundred of rubber: Sulfur, 2.5; zinc oxide, 3.0; zinc diethyldithiocarbamate, 1.0; zinc benzothiazole-2-thiolate, 1.0 ●, total crosslinks; ■, polysulfide; ▲, disulfide; ▼, monosulfide crosslinks.

decomposition continue to gain in rate relative to sulfuration and crosslink formation up to 150–160°C when the least stable types of monosulfide crosslink begin to decompose and the desulfuration of pendent groups begins to affect vulcanization efficiency[20]. These reactions gain in rate up to 200°C by which temperature the half-life of polysulfides is extremely short and that of monosulfides is measured in minutes. At about 210°C, the weakest carbon–carbon bond in the polyisoprene backbone (that between isoprene units) begins to undergo slow decomposition.

At vulcanization or service temperatures up to about 100°C, it is feasible to prepare a vulcanizate containing a high proportion of polysulfide crosslinks and to maintain the degree of crosslinking and the network structure (and hence physical properties) over moderate periods of time. At temperatures above this, it is progressively necessary to sacrifice something in strength and fatigue resistance in order to preserve the degree of crosslinking at the desired level by reducing the polysulfide content of the crosslinks. At 180°C, the network must be highly monosulfidic if the degree of crosslinking is to be sustained for a substantial period of time.

VULCANIZATION PATHWAYS IN POLYBUTADIENE RUBBERS

Although relatively little is known about the course of sulfur vulcanization of polybutadienes (BRs), it is instructive to compare their response to vulcanizing systems and what is known of the structure of their vulcanizates with the information given above for polyisoprene rubbers. One immediately obvious difference is in the behavior at high temperatures, where BR and SBR undergo 'thermal' vulcanization, especially in the presence of substances capable of acting as free-radical initiators[32–34]. This thermal vulcanization, which must occur by car-

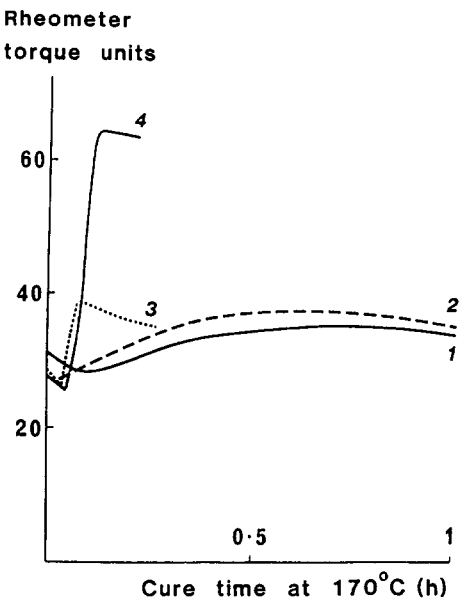


FIG. 6.—Effect of accelerator and activators on crosslink formation in NR at 170°C. Curve 1: sulfur, 1.8. Curve 2: sulfur, 1.8; zinc oxide, 3.0; lauric acid, 1.4. Curve 3: sulfur, 1.8; lauric acid, 1.4; CBS, 1.0. Curve 4: sulfur, 1.8, zinc oxide, 3.0, lauric acid, 1.4; CBS, 1.0 phr (after Skinner[36]).

bon-carbon crosslink formation, may be superimposed on sulfur crosslinking during vulcanization at high temperature. A second, less apparent, difference is that BR is much more susceptible than IR or NR to *cis, trans*-isomerization in the presence of sulfur[34]. It is not clear to what extent this has an effect, for example, on the strength properties of high *cis*-polybutadiene in practical systems, but the time scale is such that the *cis* content is reduced from 94% to 70% when BR is heated with sulfur for 140 min at 160°C[35].

The butadiene-based rubbers show a much reduced response to zinc compounds in vulcanization, being able, unlike polyisoprene, to achieve substantial degrees of crosslinking in the absence of zinc (compare Figures 6 and 7)[36]. Furthermore, even when zinc is present, very little zinc sulfide is formed[36-38]; this suggests that utilization of zinc is minimal. There is also good evidence, obtained mainly by using model olefins such as 3-hexene[39], cyclohexene[39], and 1,5-cyclo-octadiene[38], for various differences in vulcanizate structure: (i) formation of monosulfide crosslinks is largely suppressed[39], di- and polysulfide remaining the only types present up to long reaction times (4 h at 140°C)[37]; (ii) the formation of crosslinks on both carbon atoms of an original double bond (vicinal crosslinking) is prominent, as is the formation of alkyl-S-linkages[38,39]; (iii) conjugated triene formation is suppressed[36]; (iv) there is direct and indirect evidence for enhanced formation of pendent groups, but these appear to be monosulfidic rather than poly- and disulfidic in type[38,39]. The first two of these features are characteristics of vulcanization by sulfur alone or by sulfur and an accelerator in the absence of zinc. Feature (iv) may hold the key to the situation[39] in that extensive

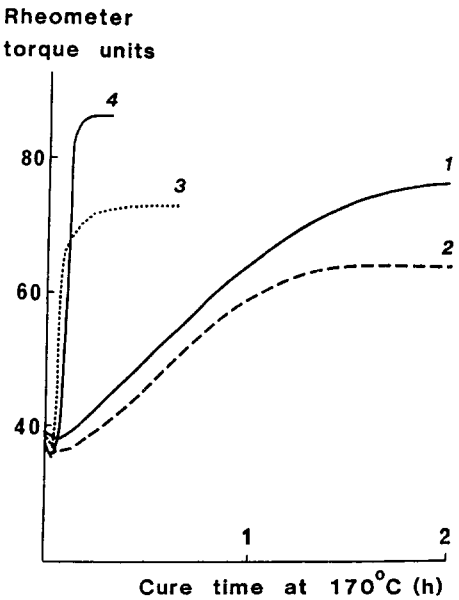


FIG. 7.—Effect of accelerator and activators on crosslink formation in BR at 170°C. Curve numbers as for Figure 6 (after Skinner[36]).

formation of monosulfidic pendent groups would irreversibly combine much of the accelerator with the rubber and therefore remove it from the vulcanizing system. (Skinner[36] concluded that 80–90% of the thiazole groups present in added CBS became rubber-bound in 1 h at 140°C). This would deprive the zinc carboxylate of its normal function (*cf.*, curves 2 and 4 of Figure 7) and zinc accelerator-thiolate complexes would not be formed. The absence of this desulfurating agent would lead, in turn, to very slow sulfur chain length shortening in polysulfides and the nonformation of zinc sulfide, as observed. The denuding of the system of accelerator would slow down the rate of sulfuration of the rubber by removing the normal active sulfurating agent—whether accelerator polysulfide[16,17] or zinc accelerator-perthiolate complex[12,18]—and favor the pathway of unaccelerated vulcanization. With polyisoprenes, this situation would also lead to extensive formation of conjugated triene and cyclic sulfide groups, but in the case of the disubstituted ethylenic units present in BR, elimination and intramolecular sulfuration appear to be very slow [*cf.*, (iii) above and refs.[36,39]].

Sulfur vulcanization of BR, therefore, appears to deviate in nearly every detail from the scheme constructed for the polyisoprenes in Figure 4. Polysulfidic pendent groups seem to be formed only in the early stages; thereafter, monosulfidic pendent groups predominate, but it is not clear whether this is because desulfuration is a rapid and efficient process until the accelerator becomes largely combined with the rubber or because the accelerator becomes combined from the outset by some quite distinct route. In the case of the polybutadienes, the structural features on the right of the figure are replaced by vicinal crosslinks and by *cis*, *trans*-isomerized double bonds.

SUMMARY

The dependence of the physical properties of sulfur vulcanizates of diene rubbers on network structure is reviewed and the influence of degree of crosslinking, crosslink structure, and main-chain modification are discussed. In polyisoprenes, these are determined, in practice, by the balance between three competing types of reaction: the conversion of polysulfidic pendent groups into polysulfidic crosslinks; the desulfuration of polysulfidic pendent groups and crosslinks, eventually to the corresponding monosulfides, with recirculation of the removed sulfur into the crosslinking pathway; thermal decomposition of di- and polysulfidic pendent groups and crosslinks with the formation of cyclic sulfide, conjugated diene and triene, and *cis, trans*-isomerized groups in the rubber chains. At temperatures above about 160°C, the thermal breakdown of monosulfide crosslinks and pendent groups has to be considered.

Zinc accelerator-thiolate complexes play a central role in controlling the balance between the various reactions because they promote the primary sulfuration of the rubber to form polysulfidic pendent groups and the conversion of these to crosslinks; they are the agents which desulfurate both pendent groups and crosslinks; they catalyze polysulfide exchange reactions; and in some cases they promote the decomposition of crosslinks. Other factors which affect the balance between these reactions are the temperature and the structure of the main rubber chain in the immediate vicinity of the crosslink. The latter is, in turn, at least partly controlled by the structure and concentration of zinc accelerator-thiolate complexes.

The vulcanization of polybutadiene rubbers deviates substantially from this reaction pattern, evidently because the bulk of the accelerator becomes irreversibly bound to the rubber at an early stage. This denudes the vulcanizing system of zinc accelerator-thiolate complexes and, therefore, prevents desulfuration from occurring. The crosslinks thus remain di- and polysulfidic and are apparently less prone to decomposition than in the case of the polyisoprene rubbers, since cyclic sulfides and conjugated hydrocarbon groupings seem not to be prominent products. The removal of accelerator leaves the system unresponsive to zinc and gives it the characteristics of unaccelerated vulcanization with the result that vicinal crosslinking and crosslinks with saturated chain junctions become important products.

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