# **581.** *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part XI.* The Mechanism of Interaction of Sulphur with Mono-olefins and* 1 : 5*-Dienes.*

By L. Bateman, C. G. Moore, and M. Porter.

A polar chain mechanism is advanced for reaction of olefins with sulphur at about 140°; the initiation step is heterolysis of a polysulphide into polar persulphenyl intermediates, at variance with the current view that thermal dissociation of S–S bonds under these conditions occurs homolytically. A review of the literature indicates that, while such homolysis can be induced photochemically or by reaction with other free radicals, it does not occur simply on heating sulphur or organic di- and poly-sulphides at about 140°.

The reaction mechanism, which is consistent with kinetic data (Part X), accounts for the formation of complex polysulphides, including cyclic structures, from oct-1-ene, di- and tri-alkylethylenes and 2 : 6-dimethylocta-2 : 6-diene. The products are complex because a bridged persulphonium intermediate can lose a proton to, or gain a hydride ion from, the olefin (thereby becoming a polysulphide), or combine with sulphur to produce a persulphenium ion which ultimately forms a multi-bridged polysulphide derived from two or more olefin units. These competitive reactions occur in different proportions with different olefins—proton loss is more important than hydride ion gain in an alk-1-ene, while the converse is true for trialkylethylenes.

Cyclic monosulphides formed from the 1 : 5-diene are essentially secondary products resulting from the first formed polysulphides which engage in proton-transfer processes to give sulphurated carbonium ion species: these effect intramolecular heterolysis of adjacent polysulphide linkages, the processes being similar to those postulated for the initial reaction.

Believing an alkenyl alkyl polysulphide to be the major product of sulphur–mono-olefin interaction at about 140° and the main constituent of the cyclic monosulphide fraction likewise obtained from 2 : 6-dimethylocta-2 : 6-diene to be the thia*cyclo*hex-3-ene (II),

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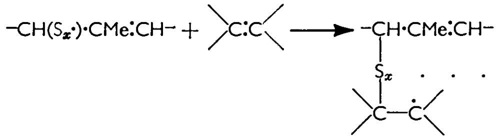
* Part X, preceding paper.

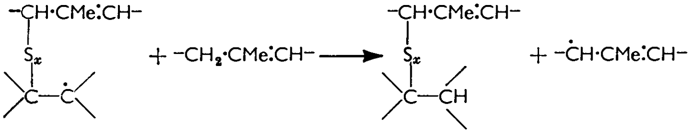
Farmer and his co-workers[1] advanced the following free-radical chain mechanism for olefinic sulphuration:

$$-CH_2\cdot CMe{:}CH- + \cdot S_x\cdot \longrightarrow -\dot{C}H\cdot CMe{:}CH- + HS_x\cdot \qquad (1)$$

$$-\dot{C}H\cdot CMe{:}CH- + S_x \longrightarrow -CH(S_x\cdot)\cdot CMe{:}CH- \qquad (2)$$

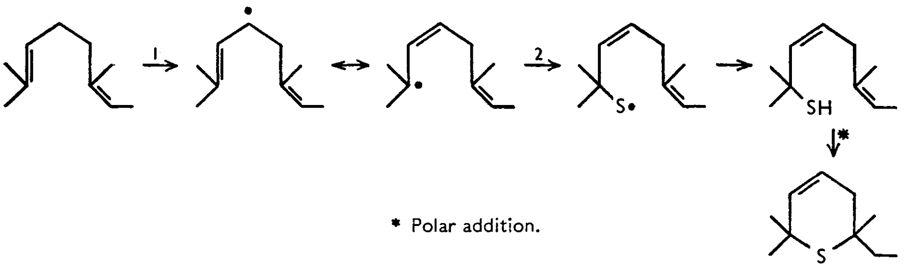


(3)



(4)

In the special case where the sulphurated radical formed in (2) contains one sulphur atom, alternative reactions to (3) and (4) were proposed, *viz.*, capture of a hydrogen atom, followed by polar or radical addition of the alkenethiol to a second double bond, and this was regarded as the main route to the cyclic monosulphides from 1 : 5-dienes:



(I)

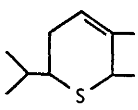
(II)

· · · · (5)

* Polar addition.

This mechanism has been widely quoted[2] despite little supporting evidence; it was based mainly on an assumed analogy with olefinic autoxidation whose radical-chain nature is well founded.[3]

The detailed structural and kinetic studies reported in the preceding three papers now show: (i) that alkenyl alkyl polysulphides are not the sole primary products of the reaction of mono-olefins with sulphur; (ii) that the alkenyl alkyl polysulphides formed have not the structures to be expected from reactions (1)—(4); (iii) that 2 : 6-dimethylocta-2 : 6-diene does not yield cyclic monosulphides having structures consistent with a wholly free-radical reaction (*e.g.*, III), or with a free-radical reaction yielding a dienethiol (*e.g.*, I) which then undergoes polar intramolecular addition to give (II) as detailed in (5); and (iv) that the kinetic characteristics indicate a polar and not a free-radical mechanism.



(III)

The above mechanism is therefore rejected and a polar mechanism is proposed, which is represented in its simplest form by reactions (6)—(14):

$$\text{Initiation: Polysulphide} \longrightarrow TS_a^+ + TS_b^- \qquad (6)$$

$$\text{Propagation: } TS_a^+ + RH(C{:}C) \longrightarrow TS_aRH^+ \text{ (sat.)} \qquad (7)$$

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[1] Farmer and Shipley, *J. Polymer Sci.*, 1946, **1**, 293; Farmer and Shipley, *J.*, 1947, 1519; Farmer, *J. Soc. Chem. Ind.*, 1947, **66**, 86; Bloomfield and Naylor, XIth Internat. Congr. Pure Appl. Chem., London, 1947, Vol. II, p. 7.

[2] Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, 1953, p. 454; Burnett, "Mechanism of Polymer Reactions," Interscience Publ. Inc., New York, 1954, p. 89; Grassie, "Chemistry of High Polymer Degradation Processes," Butterworths, London, 1956, p. 246.

[3] Bateman, *Quart. Rev.*, 1954, **8**, 147.

$$\mathrm{TS_aRH^+\ (sat.) + RH(C{:}C)} \begin{cases} \nearrow \mathrm{TS_aRH_2\ (sat.) + R^+} & (8) \\ \searrow \mathrm{TS_aR(C{:}C) + RH_2{}^+} & (9) \end{cases}$$

$$\left.\begin{matrix} \mathrm{R^+} \\ \mathrm{RH_2{}^+} \end{matrix}\right\} + \mathrm{S_8} \begin{cases} \nearrow \mathrm{RS_a{}^+} & (10) \\ \searrow \mathrm{RH_2S_a{}^+} & (11) \end{cases}$$

$$\text{Termination: } \left.\begin{matrix} \mathrm{R^+} & (12) \\ \mathrm{RH_2{}^+} & (13) \\ \mathrm{TS_aRH^+} & (14) \end{matrix}\right\} + \mathrm{TS_b{}^-} \longrightarrow \text{Non-chain carriers}$$

where RH(C:C) is a mono-olefin; (sat.) denotes absence of C:C; H is an $\alpha$-methylenic hydrogen atom; T is R or $RH_2$; and $a$ and $b \geqslant 1$. The validity of this mechanism kinetically has been demonstrated by Ross;[4] it will be shown here that reactions (6)—(14) and rational extensions thereof logically account for the major products from mono-olefins or 1 : 5-dienes and sulphur.

The fundamental feature of the proposed mechanism is heterolysis of S–S bonds. Since the reactivity of organic di- and poly-sulphides has often been considered to reflect a susceptibility to homolysis, it is necessary to examine the justification for these suppositions.

*Homolysis of* S–S *Bonds*.—Convincing evidence exists for the homolysis of S–S bonds in certain thermal and photochemical reactions. Thus, disulphides are efficient radical-acceptors for hydrocarbon radicals formed in vinyl polymerisations initiated by free radicals[5] and during mechanical degradation of elastomers by cold mastication.[6] These reactions may be generalised as:

$$\mathrm{R\cdot + R'S{-}SR' \longrightarrow RSR' + R'S\cdot} \tag{15}$$

Disulphides have been shown[7] to be initiators of free-radical vinyl polymerisations, although it is significant that alkyl, aryl, and aralkyl disulphides are effective only under photolytic conditions; photolytic conditions are also essential for disulphides to undergo homolytic thiyl-exchange reactions and for them to initiate the free-radical addition of thiols to olefins.[8] These observations suggest that homolysis of S–S bonds cannot be effected by purely thermal means at temperatures commonly used in reactions of olefins with sulphur (about 140°), but requires either an external free-radical source [*e.g.*, reaction (15) or photochemical activation[9] reaction (16)]:

$$\mathrm{R'S{-}SR' \xrightarrow{h\nu} 2R'S\cdot} \tag{16}$$

Kharasch *et al.*[7] and Lecher[10] regard as inconclusive or incorrect earlier evidence cited in favour of thermal homolysis of S–S bonds, such as, *e.g.*, the thermochromic behaviour of disulphides and their non-obeyance of Beer's law,[11] and the reaction of disulphides with

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[4] Ross, preceding paper.

[5] Pierson, Costanza, and Weinstein, *J. Polymer Sci.*, 1955, **17**, 221; Costanza, Coleman, Pierson, Marvel, and King, *ibid.*, p. 319, and references therein; Dinaburg and Vansheĭdt, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 839 (U.S. transl.).

[6] Ayrey, Moore, and Watson, *J. Polymer Sci.*, 1956, **19**, 1.

[7] Kharasch, Nudenberg, and Meltzer, *J. Org. Chem.*, 1953, **18**, 1233; Birch, Cullum, and Dean, *J. Inst. Petroleum*, 1953, **39**, 206; Ferington and Tobolsky, *J. Amer. Chem. Soc.*, 1955, **77**, 4510; Kern, *ibid.*, p. 1382; Otsu, *J. Polymer Sci.*, 1956, **21**, 559.

[8] Rueggeberg, Cook, and Reid, *J. Org. Chem.*, 1948, **13**, 110; Rueggeberg, Chernack, Rose, and Reid, *J. Amer. Chem. Soc.*, 1948, **70**, 2292; cf. Kharasch *et al.*, ref. 7.

[9] Lyons, *Nature*, 1948, **162**, 1004.

[10] Lecher, *Science*, 1954, **120**, 220.

[11] Schönberg, Rupp, and Gumlich, *Ber.*, 1933, **66**, 1932; Schönberg and Rupp, *Naturwiss.*, 1933, **21**, 561; Koch, *J.*, 1949, 394, 401.

hexaphenylethane in solution to give a monosulphide.[12] Stronger physicochemical evidence is that hot solutions of di(benzothiazol-2-yl) disulphide in toluene are paramagnetic,[13] but Cutforth and Selwood [13] have pointed out that even this is not critical since excitation of the disulphide to a triplet state would produce a comparable effect. No evidence is available [14] that simple alkyl or aryl disulphides display paramagnetism at temperatures up to 140°.

Discussion of the homolysis of S–S bonds in the sulphur molecule, $S_8$, and in organic polysulphides is especially relevant. Gee and his co-workers [14, 15] have described the increase in molecular complexity of liquid sulphur which occurs quite abruptly at 159° in terms of the formation of a linear polymeric diradical form of sulphur which is in equilibrium with $S_8$ rings:

$$S_8 + \cdot S_x\cdot \rightleftharpoons \cdot S_{x+8}\cdot \qquad (17)$$

for which confirmation is provided by recent paramagnetic studies of liquid sulphur at 189° and above.[16] However, the existence of diradical forms of sulphur at $\geqslant 159°$ cannot be offered as evidence that a significant concentration of such species is present in olefinic solutions at $\sim 140°$, as required by the free-radical chain mechanism of Farmer *et al.*[1] Sulphur and organic polysulphides are as reactive as disulphides towards hydrocarbon radicals, *e.g.*, alkyl and alkenyl radicals derived from alkyl- or alkenyl-phenyltriazens.[17] By contrast with disulphides, sulphur inhibits the free-radical polymerisation of vinylic monomers,[18] this being ascribed to homolysis of the S–S bond in the $S_8$ molecule by the polymeric radical [reaction (18)], giving a persulphenyl radical incapable of re-initiating polymerisation:

$$R_n\cdot + S_8 \longrightarrow R_nS_x\cdot \qquad (18)$$

Organic polysulphides, $R'S_xR'$ ($x > 2$), also act as polymerisation inhibitors [7] and do not initiate vinyl polymerisation even under photolytic conditions.* No explanation appears to have been offered for the reduced reactivity of $R'S_x\cdot$ ($x \geqslant 2$) compared with $R'S\cdot$ in initiating vinyl polymerisation, but one is probably revealed by recent work [15] which suggests that $R'S_x\cdot$ radicals are partly stabilised by a resonance structure containing a "three-electron bond": $R{-}\underset{..}{\overset{..}{S}}{-}\underset{..}{\overset{..}{S}}{-}\underset{..}{\overset{..}{S}}\cdot \longleftrightarrow R{-}\underset{..}{\overset{..}{S}}{-}\overset{..}{S}\overset{..}{\cdots}\underset{..}{\overset{..}{S}}$. Gee *et al.*[15] consider this stabilisation to be responsible for the heat of scission of the S–S bond in a polymeric diradical sulphur chain being <35 kcal./mole, compared with a heat of atomisation of about 428 kcal./mole for the $S_8$ ring (equivalent to a heat of scission of 53 kcal. per S–S bond in the ring), and point out that in organic polysulphides it will lead to an S–S bond stability sequence in $R'{-}S\overset{a}{-}S\overset{b}{-}S{-}S{-}R'$ of $a > b$, if interactions involving the group R′ are neglected.

To summarise: purely thermal homolysis of S–S bonds in sulphur and organic di- and poly-sulphide molecules at temperatures below 140° has not yet been conclusively demonstrated; such fission occurs only when induced photolytically or by a radical displacement reaction such as (15) and (18).

*Heterolysis of* S–S *Bonds*.—The S–S bonds in sulphur and organic polysulphides are readily broken by nucleophilic reagents, as represented by (19):

$$X^- + {-}S{-}\underset{..}{\overset{..}{S}}{-}\underset{..}{\overset{..}{S}}{-} \longrightarrow {-}S{-}\underset{..}{\overset{..}{S}}{-}X + {}^{-}\underset{..}{\overset{..}{:S}}{-} \qquad (19)$$

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* Birch *et al.*[7] state that di-*tert.*-butyl trisulphide is an exception in this respect, since it photolytically initiates polymerisation of acrylonitrile.

[12] Lecher, *Ber.*, 1920, **53**, 577.

[13] Cutforth and Selwood, *J. Amer. Chem. Soc.*, 1948, **70**, 278.

[14] See Gee, *Trans. Faraday Soc.*, 1952, **48**, 515.

[15] Fairbrother, Gee, and Merrall, *J. Polymer Sci.*, 1955, **16**, 459; Gee, *Sci. Progr.*, 1955, **43**, 193.

[16] Gardner and Fraenkel, *J. Amer. Chem. Soc.*, 1954, **76**, 5891; 1956, **78**, 3279.

[17] Tinyakova, Dolgoplosk, and Tikhomolova, *J. Gen. Chem.* (*U.S.S.R.*), 1955, **25**, 1333 (U.S. transl.).

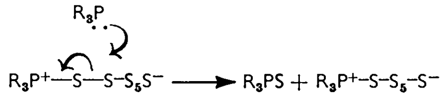
[18] Bartlett and Trifan, *J. Polymer Sci.*, 1956, **20**, 457 and references therein; Kice, *J. Amer. Chem. Soc.*, 1954, **76**, 6274; *J. Polymer Sci.*, 1956, **19**, 123.

Common examples include the attack of $SO_3^{2-}$, $CN^-$, $RS^-$, or $HS^-$ ions on sulphur and di- and poly-sulphides [19] and reactions with Grignard reagents (RMgX) and lithium aluminium hydride [20] are probably other examples, the respective nucleophilic species being $R^-$ and $AlH_4^-$. More recently, evidence has been offered that the non-ionic nucleophiles $R_3N\colon$ and $R_3P\colon$ participate in $S_N2$ reactions at S–S bonds. Jennen and Hens [21] and Krebs [22] formulate the reaction of molecular sulphur with tertiary amines as:

$$R_3N\colon + S_8 \longrightarrow R_2N^+{-}S{-}S_6{-}S^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

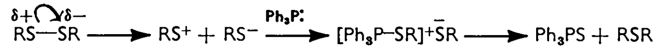
and Bartlett and Meguerian [23] obtained kinetic evidence that the reaction of sulphur with triphenylphosphine, to give triphenylphosphine sulphide, involves an initial rate-determining $S_N2$ heterolysis of $S_8$ [reaction (21)], followed by a rapid sequence of comparable reactions typified by (22):

$$R_3P\colon + S_8 \longrightarrow R_3P^+{-}S{-}S_6{-}S^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$



$$R_3P^+{-}S{-}S{-}S_5S^- \longrightarrow R_3PS + R_3P^+{-}S{-}S_5{-}S^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

The reaction of triphenylphosphine with diallyl disulphide has also been interpreted [24] as a polar process [reaction (23)], contrary to the free-radical postulate of Schönberg *et al.*[11, 25]:



$$\overset{\delta+\ \ \delta-}{RS{-}SR} \longrightarrow RS^+ + RS^- \xrightarrow{Ph_3P\colon} [Ph_3P{-}SR]^+\bar{S}R \longrightarrow Ph_3PS + RSR \quad . \; . \; . \; . \quad (23)$$

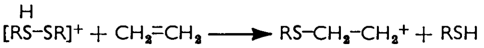
and a similar view is taken of the reaction of triethyl phosphite with diethyl disulphide: [26]

$$(EtO)_3P\colon + EtS{-}SEt \longrightarrow [EtS{\cdot}P^+(OEt)_3]S^-Et \longrightarrow EtS{\cdot}P\colon O(OEt)_2 + EtSEt \quad . \; . \; . \quad (24)$$

The relevance of reactions (20) and (21) to the function of vulcanisation accelerators and zinc salts in increasing the rate of sulphur–olefin reactions will be discussed elsewhere.

Electrophilic fission of S–S bonds, as is now envisaged in olefin sulphuration, is less well authenticated. One example is thought to be the acid-catalysed interaction of alkyl disulphides with olefins to give bismonosulphides, as in the chain sequence (25)—(28): [27]

$$RS{-}SR + H^+ \longrightarrow [\overset{H}{RS{-}SR}]^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$



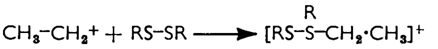
$$[\overset{H}{RS{-}SR}]^+ + CH_2{=}CH_2 \longrightarrow RS{-}CH_2{-}CH_2^+ + RSH \quad . \; . \; . \; . \; . \; . \quad (26)$$

$$RS{-}CH_2{-}CH_2^+ + RS{-}SR \longrightarrow RS{-}CH_2{-}CH_2{-}SR + RS^+ \quad . \; . \; . \; . \; . \; . \quad (27)$$

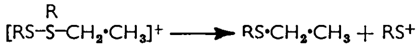
$$RS^+ + CH_2{=}CH_2 \longrightarrow RS{-}CH_2{-}CH_2^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (28)$$

To explain the formation of monosulphides as minor products when *strong* acids such as hydrofluoric acid are used, reactions (29)—(31) are then postulated as an additional chain-initiation process:

$$CH_2{=}CH_2 + H^+ \longrightarrow CH_3{-}CH_2^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (29)$$



$$CH_3{-}CH_2^+ + RS{-}SR \longrightarrow [RS{-}\overset{R}{S}{-}CH_2{\cdot}CH_3]^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (30)$$



$$[RS{-}\overset{R}{S}{-}CH_2{\cdot}CH_3]^+ \longrightarrow RS{\cdot}CH_2{\cdot}CH_3 + RS^+ \quad . \; . \; . \; . \; . \; . \; . \quad (31)$$

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[19] Foss, *Acta Chem. Scand.*, 1950, **4**, 404; Bertozzi, Davis, and Fettes, *J. Polymer Sci.*, 1956, **19**, 17.

[20] Arnold, Lien, and Alm, *J. Amer. Chem. Soc.*, 1950, **72**, 731; Bordwell and McKellin, *ibid.*, 1951, **73**, 2251.

[21] Jennen and Hens, *Compt. rend.*, 1956, **242**, 786.

[22] Krebs, *Gummi u. Asbest*, 1955, **8**, 68.

[23] Bartlett and Meguerian, *J. Amer. Chem. Soc.*, 1956, **78**, 3710.

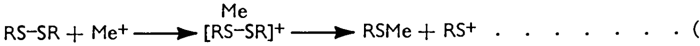
[24] Challenger and Greenwood, *J.*, 1950, 26.

[25] Schönberg, *Ber.*, 1935, **68**, 163.

[26] Jacobsen, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.

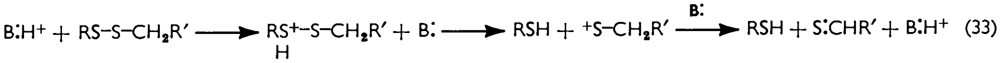
[27] Lien, McCaulay, and Proell, General Papers, Division of Petroleum Chem., Amer. Chem. Soc., 1952, No. 28, p. 169.

Reactions comparable to (27) and (30)—(31) have been advanced to explain the formation of monosulphides from the thermal reaction of dialkyl disulphides with betaine ($Me_3N^+{\cdot}CH_2{\cdot}CO{\cdot}O^-$) which acts as a source of $Me^+$ cations [reaction (32)]: [28]



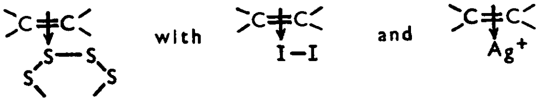
$$RS{-}SR + Me^+ \longrightarrow [RS\overset{Me}{-}SR]^+ \longrightarrow RSMe + RS^+ \quad \ldots\ldots\ldots (32)$$

Similarly, the fission of S–S bonds in carboxyl-substituted alkyl disulphides by dimethylformamide (B:) has been formulated as an acid–base-catalysed reaction: [29]

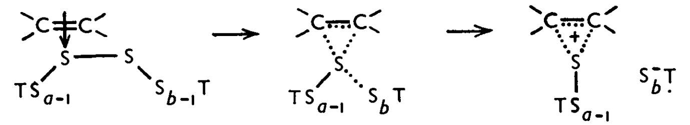


$$B{:}H^+ + RS{-}S{-}CH_2R' \longrightarrow \underset{H}{RS^+}{-}S{-}CH_2R' + B{:} \longrightarrow RSH + {}^+S{-}CH_2R' \xrightarrow{B:} RSH + S{:}CHR' + B{:}H^+ \quad (33)$$

*Interaction of* S–S *Bonds with Olefinic Double Bonds.*—Reaction (6) has been formally represented as the dissociation of a polysulphide into free persulphenyl ions, which in the prevailing non-polar medium must be associated either as an ion-pair or as constituting a highly polarised molecule. Species of this kind have been postulated in other polar reactions in non-polar solvents where solvation forces cannot provide the large amount of energy necessary for separation (as distinct from formation) of two unlike ions.[30] Polarisation of S–S bonds in sulphur and polysulphide molecules will be promoted by the electron-donor activity of olefinic double bonds, just as this promotes complex formation with iodine,[31] silver ions,[31,32] and various metallic salts,[32,33] cf.:



Such association is essentially similar to, although of a lower order than, the nucleophilic attack of tertiary amines [21,22] and triarylphosphines [23] on sulphur. A truer representation of reactions (6) and (7) is therefore:



....(34)

Initial state (IV) Transition state (V) (VI) Final state (ion-pair)

The sulphuration process as represented by reaction (34) is thus mechanistically analogous to other reactions involving the addition of electrophilic reagents to olefins in non-polar media, *e.g.*, halogen addition [34] and " allylic " chlorination,[35] ozonolysis,[36] and addition of sulphenyl halides.[37] The cationic moiety of (VI), formulated as a bridged persulphonium ion by analogy with comparable structures [38] and because of certain reactivity characteristics discussed below, appears to be the dominant intermediate in determining the course and products of the overall sulphuration process. The highly complex nature of the products [39] can be related logically to the various possibilities of reaction of this

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[28] Challenger, Taylor, and Taylor, *J.*, 1942, 48; Challenger, *Quart. Rev.*, 1955, **9**, 255.

[29] Schöberl and Gräfje, *Naturwiss.*, 1956, **43**, 445.

[30] Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1265 and references therein; Ingold, *Proc. Chem. Soc.*, 1957, 279.

[31] Evans, *J. Chem. Phys.*, 1956, **24**, 1244 and references therein.

[32] Chatt, in " Cationic Polymerization," Ed. Plesch, Heffer, Cambridge, 1953, pp. 40 *et seq.*

[33] Douglas, " The Chemistry of the Co-ordination Compounds," Ed. Bailar, Reinhold Publ. Corp., New York, 1956, pp. 487 *et seq.*

[34] de la Mare, *Quart. Rev.*, 1949, **3**, 126.

[35] Taft, *J. Amer. Chem. Soc.*, 1948, **70**, 3364; Salomon, *Proc. Inst. Rubber Ind.*, 1956, **3**, 176.

[36] See Waters, *Ann. Reports*, 1952, **49**, 111.

[37] Hogg and Kharasch, *J. Amer. Chem. Soc.*, 1956, **78**, 2728.

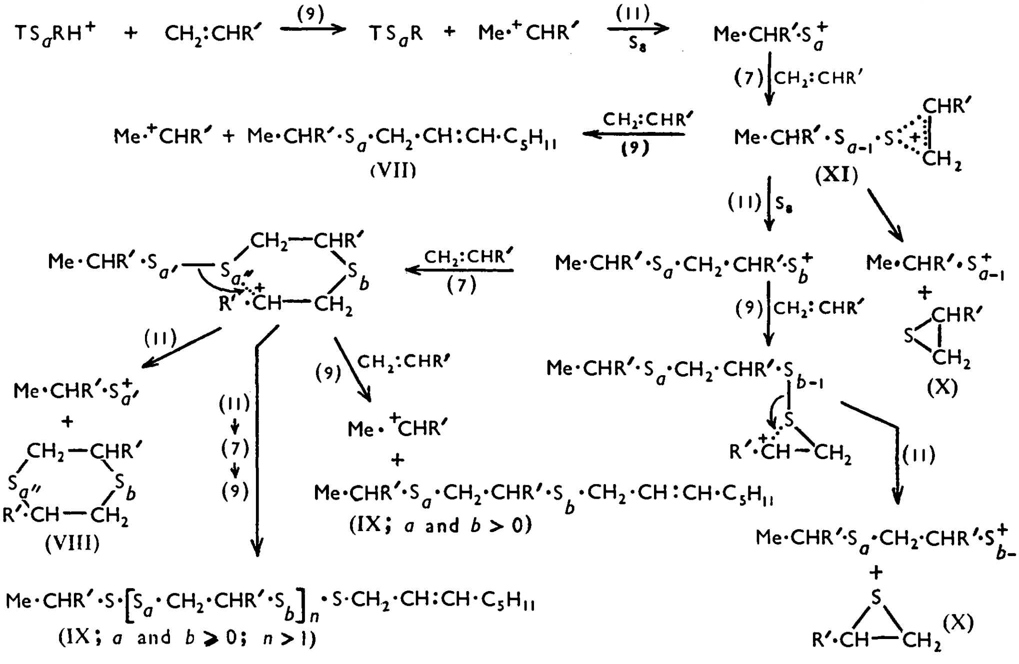
[38] Winstein and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828; Winstein and Ingraham, *ibid.*, 1952, **74**, 1160.

[39] Bateman, Glazebrook, Moore, Porter, Ross, and Saville, *J.*, 1958, 2838; Bateman, Glazebrook, and Moore, *J.*, 1958, 2846.

cation, *viz.*, combination with the associated anion or with a sulphur molecule, and proton- or hydride-ion-exchange with an olefin molecule, the differences in product compositions in different olefinic systems reflecting changes in the relative importance of these competing reactions as detailed below.

The persulphenyl anion, $TS_b^-$, does not appear to participate in the olefinic sulphuration, although it may well facilitate the breaking of the $S_8$ ring, in keeping with the known ability of sulphenyl anions to induce S–S bond scission,[19] and it will certainly engage in exchange reactions with the polysulphide products.[19] There is no evidence for the addition of this anion to an olefin, this being in accord with the fact that base-catalysed addition of thiols to double bonds occurs only when the latter are activated by electron-attracting substituents ($CO_2R$, CHO, CN).[40]

*Sulphuration of Oct-*1-*ene.*—2-Methylheptyl oct-2-enyl sulphides (VII; $a \geqslant 1$), the cyclic compounds (VIII; $a''$ and $b \geqslant 1$), and the polymeric material (IX; $a$ and $b \geqslant 0$; $n \geqslant 1$) are major products, and 1 : 2-epithio-octane (X) a minor product, of this reaction.[39] The formation of these compounds (which are not obviously related) and their derivation from common intermediates can be rationalised on the basis of the arguments developed in the last section, as indicated in the annexed reaction scheme, where $R' = C_6H_{13}$ and the numbers refer to reactions already designated.



Important features of this scheme are:

(i) The reactions leading to the different products are the propagation steps in the basic chain mechanism (pp. 2867—8), or kinetically equivalent variants which generate carbonium or persulphenium ionic-type intermediates in the product-forming reactions (to give VIII—X). This justifies kinetic analysis in terms of the basic mechanism, notwithstanding the complexity of the product.[4]

(ii) The bridged persulphonium ion (XI) appears to react mainly (*a*) by combining with sulphur, to give subsequently (VIII), (IX), and (X), and (*b*) by transferring a proton to an olefin, thereby giving (VII). The effect of (*b*) is to cause the sulphur chain in (VII) to

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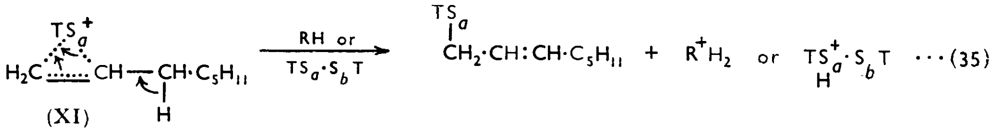
[40] Schöberl and Wagner, " Methoden der Organischen Chemie," Houben-Weyl, Georg Thieme, 1955, Vol. IX, pp. 123 *et seq.*

be attached to the secondary position of the alkyl unit and to the primary position in the alkenyl unit, as is found experimentally.[39]

(iii) The unsaturation pattern in (VII) is that of an allyl sulphide. This strongly suggests that proton elimination occurs in a process specifically involving the bridged persulphonium unit and a $\beta$-$CH_2$ group (reaction 35):



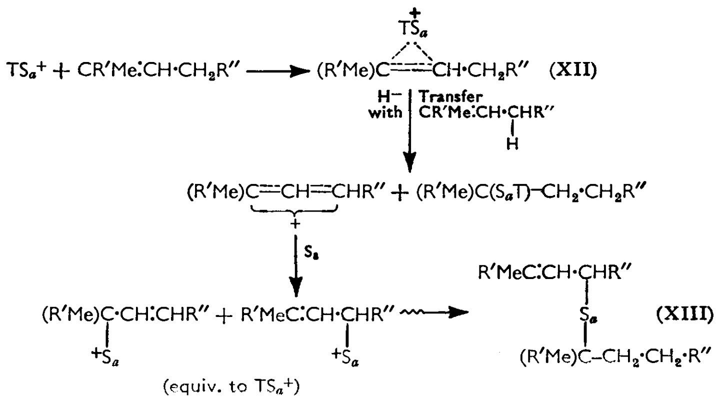
(XI) · · · (35)

rather than from the carbonium ion $TS_a{-}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}C_5H_{11}$, which would be expected to give at least a proportion of the more stable vinyl isomer, $TS_a{-}CH{:}CH{\cdot}CH_2{\cdot}C_5H_{11}$.[39,41] This mode of deprotonation and its structural consequences are also evident in the di-isoprenoid system (p. 2877).

(iv) Hydride-ion transfer (reaction 8) appears not to occur to an appreciable extent. Its occurrence would generate the mesomeric cation $\overbrace{CH_2\text{==}CH\text{==}CH}^{+}{\cdot}C_5H_{11}$, which should lead to a small but readily detectable amount of the 1-vinylhexyl sulphide structure, $CH_2{:}CH{\cdot}CH(C_5H_{11}){\cdot}S_a{-}$ in the alkenyl unit of the octenyl octyl polysulphide—which is contrary to fact.[39] With other olefins, however, this reaction is of considerable importance.

(v) Neither the detailed structure of any given product nor the different types of product formed can be explained by the free-radical reaction mechanism of Farmer and his co-workers.[1]

*Sulphuration of Di- and Tri-alkylethylenes.*—In passing from oct-1-ene to *cyclo*hexene and then to trialkylethylenes the following trends are observed: (i) the rate of sulphuration increases;[4] and (ii) similar products are formed but the proportion of alkenyl alkyl polysulphide increases considerably at the expense of cyclic and polymeric compounds typified by (VIII) and (IX).[39] In the alkenyl alkyl polysulphides obtained from trialkylethylenes, the unsaturation is mainly of the type $CR'R''{:}CHR'''$, and the attachment of the sulphur to the alkyl unit is at the tertiary carbon atom ($-S-CR'R''{\cdot}CH_2R'''$),[39] as depicted in (XIII). The second structural feature is compatible with proton-exchange (reaction 9) equivalent to that detailed for oct-1-ene, but the first feature is not, since complete replacement of the original unsaturation pattern by the types $CH_2{:}CR'R''$ and $CHR'{:}CHR''$ (which are found to only a minor extent) would then be required. It appears therefore that in the sulphuration of trialkylethylenes, reaction 9 is of little importance compared with the competitive hydride-ion transfer (8), whose detailed course can be represented as:



(XII)

(XIII)

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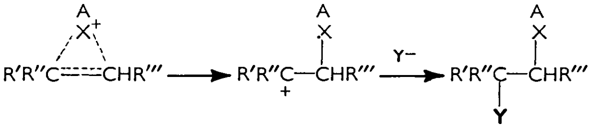
[41] Tarbell and McCall, *J. Amer. Chem. Soc.*, 1952, **74**, 48; Tarbell and Lovett, *ibid.*, 1956, **78**, 2259.

Olefins are known to participate in hydride-ion transfers of this type,[42] which will be promoted by alkyl substitution at the far side of the adjacent double bond owing to the greater resonance stabilisation of the resultant allylic carbonium ion (cf. the comparable influence in free-radical olefin autoxidation [3]). Such substitution can thus be expected to facilitate the above sequence of reactions, and in doing so to repress relatively the alternative reactions of the bridged persulphonium ion involving proton-transfer and addition of sulphur. The rate and product changes through the olefin series detailed above are, therefore, mutually consistent and understandable. In the case of the particular trialkylethylene, 2 : 6-dimethylocta-2 : 6-diene, there is a specific consequence of hydride-ion transfer (p. 2877).

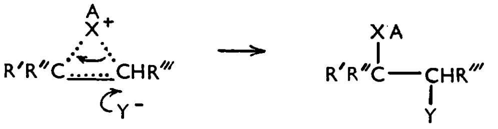
One special feature of the hydride-ion transfer represented above may be noted, *viz.*, the attachment of the hydride ion to the least substituted carbon atom of the bridged persulphonium ion (XII), leading to the *tert.*-alkylperthio-linkage in (XIII). The opening of the bridged persulphonium ion (XII) in this way, which in effect is contrary to Markownikoff's rule for polar addition of the electrophile $TS_a^+$ to a double bond, is unusual but not unique. The usual direction of opening of bridged 'onium ions (XIV; AX = $NR_2$, SR, or OH, etc.) by attack of a nucleophilic reagent $Y^-$, recognised in numerous reactions,[38,43] is that leading to (XV), and is attributed [44] to the preferential formation of the tertiary carbonium ion by ring fission of (XIV) before attachment of the addendum $Y^-$:



(XIV) (XV) . . . . . (36)

The reaction conditions are generally those conducive to this essentially $S_{\rm N}1$ type, two-stage process.

An alternative, $S_{\rm N}2$ type process is possible, however, in which ring fission occurs synchronously with nucleophilic attack by $Y^-$ preferentially at the least substituted carbon atom:



. . . . . (37)

Reactions believed to illustrate this process, and certainly to involve migration of a group (AX) from a less to a more substituted carbon atom, are: (i) the reaction of 3-chloro-1-ethylpiperidine (XVI) with benzylamine to give 2-(benzylaminomethyl)-1-ethylpyrrolidine (XVII) [45] (reaction 38); and (ii) the displacement of chlorine from 2-chloropropyl methyl sulphide (XVIII) by sulphite ions to give (XIX) (reaction 39).[46] Particularly pertinent examples are the reactions of chlorine and of bromine with propylene sulphide in anhydrous chloroform and carbon tetrachloride, which are formulated [47] as shown (for chlorine). It is to be noted that this series of reactions, in which opening of the episulphide ring

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[42] Bartlett, Condon, and Schneider, *J. Amer. Chem. Soc.*, 1944, **66**, 1531; Schneider and Kennedy, *ibid.*, 1951, **73**, 5013, 5017, 5024; Moore and Waight, *J.*, 1952, 4237; Baddeley and Pickles, *J.*, 1953, 3726.

[43] Fuson, Price, and Burness, *J. Org. Chem.*, 1946, **11**, 475; Kharasch and Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724; Davies and Savige, *J.*, 1950, 317; 1951, 774; Kerwin, Ullyot, Fuson, and Zirkle, *J. Amer. Chem. Soc.*, 1947, **69**, 2961.

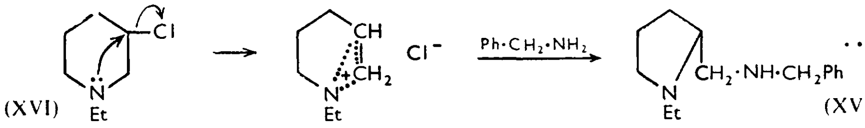
[44] Alexander, " Ionic Organic Reactions," Wiley, New York, 1950, pp. 97 *et seq.*

[45] Reitsema, *J. Amer. Chem. Soc.*, 1949, **71**, 2041.

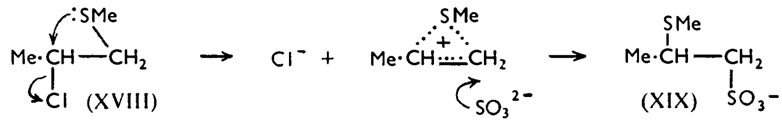
[46] Marvel and Weil, *ibid.*, 1954, **76**, 61.

[47] Stewart and Cordts, *ibid.*, 1952, **74**, 5880.

occurs exclusively to give sulphur attachment at the more substituted carbon atom, proceeds in non-solvating media where $S_N2$ type interaction of the postulated ionic inter-

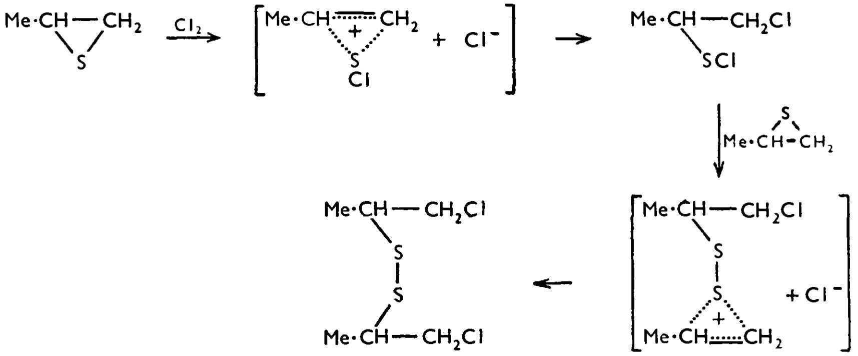


(XVI) (XVII) ···(38)

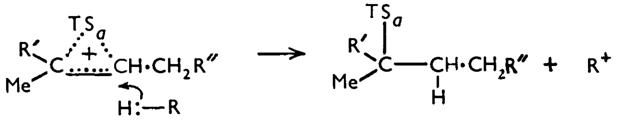


(XVIII) (XIX) ·····(39)

mediate will be favoured, whereas ring-opening in which a bridged sulphonium ion is first converted into a much more labile carbonium ion will not.

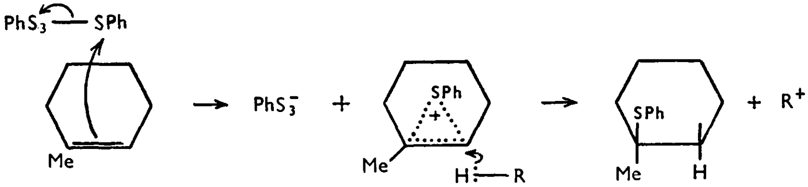


The hydride-ion transfer step in the sulphuration process can reasonably be regarded as analogous to the above reactions in being a bimolecular substitution at the least substituted carbon atom of (XII) (reaction 40):



······(40)

where H–R is the olefin and the hydride ion transferred is α-methylenic. This interpretation of the reaction not only rationalises the present findings but allows apparently anomalous data in the literature to be understood. Thus, Bloomfield[48] found that the main product from the thermal reaction of 1-methyl*cyclo*hexene and diphenyl tetra-



·····(41)

sulphide was 1-methyl*cyclo*hexyl phenyl sulphide, and was unable to account for the addition of the elements of PhSH, or addition in accord with Markownikoff's rule, having regard to the belief in the free-radical nature of sulphuration processes then current.[1] The reaction appears now to be analogous to the reaction of a trialkylethylene with sulphur, with hydride-ion transfer proceeding as specified above (reaction 41).

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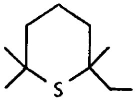
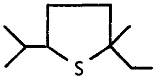
[48] Bloomfield, *J.*, 1947, 1547.

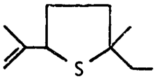
*Sulphuration of* 2 : 6-*Dimethylocta*-2 : 6-*diene*.—The products of this reaction are the triene (XX), a cyclic sulphide mixture, consisting mainly of (XXI) and (XXIII), with some (XXII); (XXIV) appears in greater amount at the expense of (XXIII) as reaction proceeds, and complex polysulphides whose composition also changes with reaction time.[39] In the early stages of reaction, there is a predominance of acyclic polysulphidic structures typified by (XXV) and (XXVI), but compounds containing cyclic sulphide units and having short sulphide cross-links ($S_1$ or $S_2$) as in (XXVII) and (XXVIII) ($a = 1$ or 2, and the dotted lines represent alternative positions of the sulphur linkage and possible sites of unsaturation) are later formed to an increasing extent.

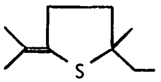
It was previously believed that the cyclic sulphides (XXI)—(XXIII) were primary products.[49] Thus, (XXIII) was thought to result from direct attack of sulphur at one double bond of the diene followed by cyclisation of an intermediate perthiol (reaction 42). Oxidation of the perthiol to liberate hydrogen sulphide ($2R{\cdot}S_xH \xrightarrow{S} R{\cdot}S_{2x}{\cdot}R + H_2S$) which can then add in a polar manner to the diene to give a mono-olefinic tertiary thiol susceptible to intermolecular addition was held to be the origin of the saturated sulphides (XXI) and (XXII). However, recent evidence does not accord with the participation of thiols as intermediates in these reactions,[4] and it is now believed that the acyclic polysulphides are the sole primary products and that the cyclic sulphides, both free and combined in later formed polysulphides, arise wholly from secondary reactions similar in type and kinetically equivalent to the primary product-forming steps.

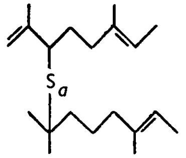

(XX)

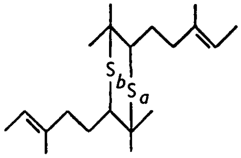

(XXI)

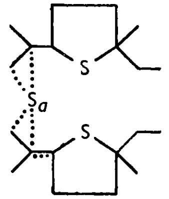

(XXII)

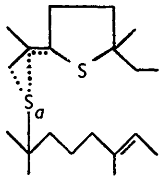

(XXIII)

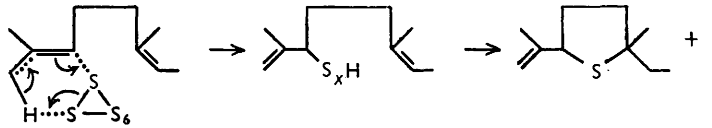

(XXIV)


(XXV)


(XXVI)

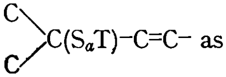

(XXVII)


(XXVIII)



·····(42)

Reactions leading to the primary polysulphides in accordance with the sulphuration mechanism now advanced are set out on p. 2877. Only the more important possibilities for isomerism are given; it is to be understood that deprotonation of the persulphonium ion, $TS_a{}^+RH$, for example, may lead to some unsaturated sulphide units of the type



$\begin{smallmatrix}C\\ \\C\end{smallmatrix}\!\!>\!C(S_aT){-}C{=}C{-}$ as well as the terminal vinyl type present in (XXV).

Whereas stabilisation of the bridged persulphonium ion, $TS_a{}^+RH$, appears to occur predominantly by proton transfer in oct-1-ene and by hydride-ion transfer in singly unsaturated trialkylethylenes, both these processes can be recognised in the di-isoprenic

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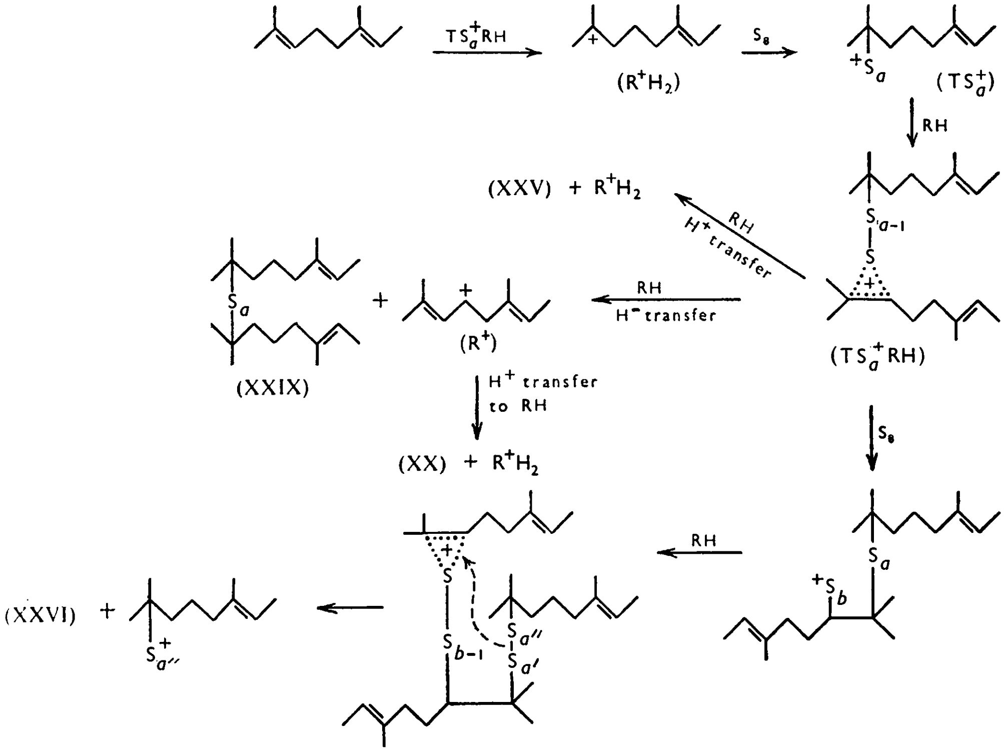
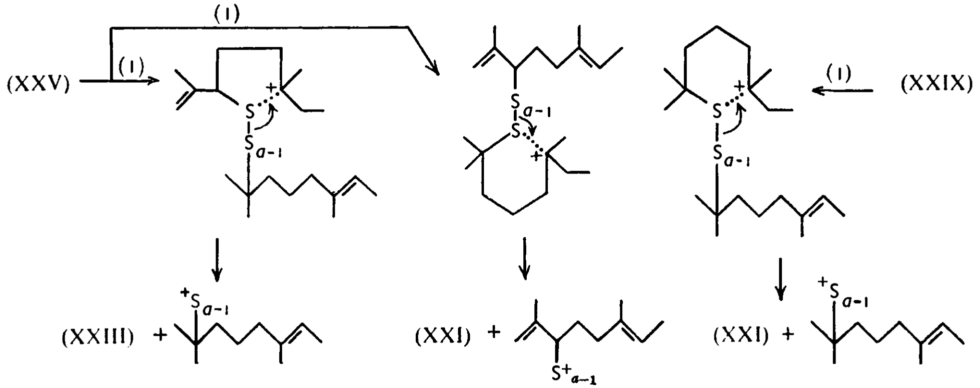
[49] Bateman, Glazebrook, Moore, and Saville, Proc. 3rd Rubber Techn. Conf., London, 1954, p. 298.

system. Indicative of the first is the formation of vinylic unsaturated units $CH_2{:}CR'R''$ (cf. below), as in the polysulphide (XXV) and the derived cyclic sulphide (XXIII) (see p. 2878), while strong evidence for the second is the formation of the triene (XX). The latter feature further indicates an understandable difference in reactivity of the allylic carbonium ions formed by loss of a hydride ion from the structures $CMe_2{:}CH{\cdot}CH_2R$ and $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CHMe$; in the first case, combination with sulphur ensues to give a persulphenium ion (p. 2873); in the second, the unsaturation pattern provides a strong driving force for a preferential deprotonation, and thus the formation of the highly resonance-stabilised conjugated triene (XX). This triene undoubtedly competes with the diene in the overall sulphuration and is probably the source of the small amount of conjugated diene unsaturation detected in the cross-linked polysulphidic mixture.[39]



The cyclic sulphides (XXI) and (XXIII) can be derived from the primary polysulphides (and also from isomers resulting from initial protonation at the other double bond in the diene) by intramolecular reactions induced by, and involving, active intermediates analogous to those postulated for the primary sequence of reactions as exemplified in the annexed scheme. The allylic sulphide (XXIII) is known [39] to undergo a sulphur-catalysed isomerisation to the vinylic isomer (XXIV), and would be expected to undergo other reactions leading to the saturated thia*cyclo*pentane (XXII) and to polysulphidic-cyclic sulphide structures such as (XXVII) and (XXVIII): analogous reactions applied to cross-linked polysulphides of type (XXVI) lead to similar polysulphidic-cyclic sulphide structures. The formation of (XXVIIb) accords with the finding of conjugated vinylic sulphide units in these structures although they are absent from the acyclic polysulphides.[39]

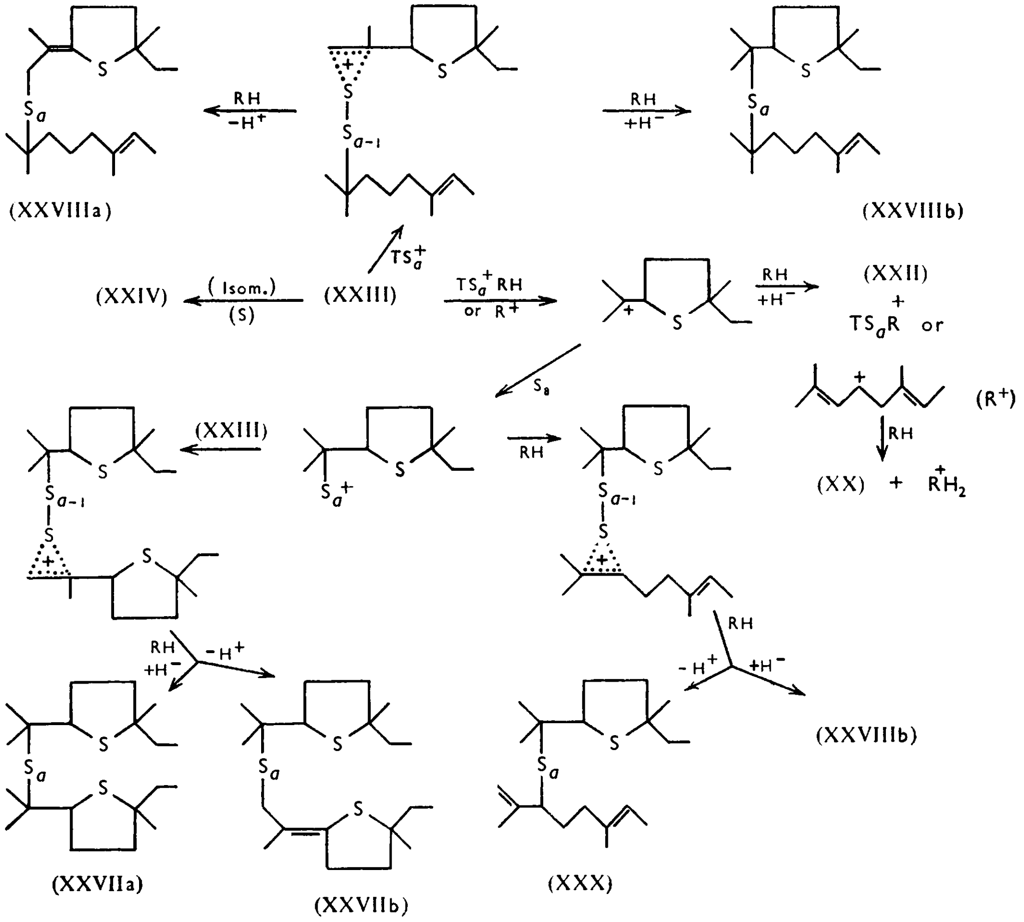
The basic sulphuration mechanism thus explains the formation and nature of the numerous products detailed above. Conversely, it definitely implies the formation of a complex mixture of products which changes in composition as sulphuration proceeds as a result of successive reactions involving products as well as primary reactants and yet conforming to a single kinetic pattern. One significant kinetic distinction between the



(I) $H^+$ transfer from $TS_a^+RH$ or $R^+$.

1 : 5-diene and the mono-olefin system is associated with cyclic sulphide formation in the former, as discussed below (p. 2879).

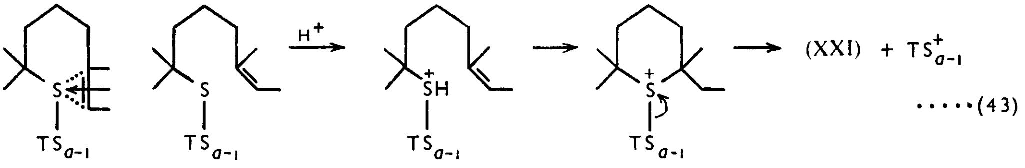
*Sulphuration of Polyisoprenes.*—The cross-linking (vulcanisation) of natural rubber



by sulphur alone at 140° is a very inefficient reaction; each effective cross-link requires the combination of some 40—60 atoms of sulphur.[49, 50] This has been attributed [51] to the incorporation of the sulphur (*a*) in multi-atom cross-links ($S_4$—$S_8$), and (*b*) in cyclic sulphide (non-cross-linking) structures; to these must now be added (*c*) in adjacent cross-links, as in (XXVI), which act physically as a single cross-link. The present work throws light on three aspects of this technologically important and hitherto little understood subject.

First, contrary to earlier ideas, [49, 51] no acceptable mechanism can be advanced to explain the formation of cyclic sulphide independently of, and yet competitive with, the formation of polysulphide. Secondly, although acyclic polysulphides are now held to be the precursors of the cyclic sulphides, this conversion does not result in the ultimate destruction of a cross-link (cf. ref. 51); a persulphenium ion, $TS_a^+$, is concurrently produced and this forms a new cross-link by reaction with the polyisoprene. The inefficient use of sulphur in this sense is in fact more subtle than previously supposed; [51] it involves, not the destruction of cross-links, but the diversion of carbonium and bridged persulphonium ion intermediates ($R^+$ and $TS_a^+RH$, respectively) from reactions which directly create cross-links to those giving cyclic sulphides. Thus, protonation of double bonds vicinal to sulphur attachments by the species $R^+$ or $TS_a^+RH$ (p. 2878) leads to cyclic sulphide rather than to the cross-linking which directly follows the protonation of other double bonds. In the formation of cyclic sulphide, a carbonium ion is in effect transformed into a persulphenium ion without combination of sulphur. It is this transformation which is held responsible for the lower rate of sulphuration of 1 : 5-dienes compared with comparable mono-olefins,[4] an otherwise peculiar feature of these reactions.

The third point to be made is that the mechanism now proposed for cyclic sulphide formation in a di-isoprene does not readily explain an important feature of the polyisoprene system, *viz.*, the formation of many *isolated* cyclic sulphide structures (*i.e.*, not associated with cross-linking units), as inferred from the low cross-linking efficiency of vulcanisation. Protonation at a double bond vicinal to a polysulphide linkage has been postulated as a prerequisite for formation of a cyclic sulphide. In a polymeric olefin such as natural rubber, random protonation would be expected greatly to outweigh this directed protonation, unless special factors come into play. Two possible factors are: (i) polarisation of specific double bonds, creating an enhanced affinity for protons, by interaction with neighbouring sulphur atoms (*e.g.*, XXXI) (cf. p. 2871); (ii) preferred protonation of the polysulphidic chain, followed by attack of the resultant persulphonium ion (XXXII) at an adjacent double bond (reaction 43) (cf. ref. 27).



(XXXI) (XXXII) ·····(43)

The effect on these reactions of the technologically important "accelerators" and other auxiliary vulcanising agents for rubbers will be discussed elsewhere; a major effect is to increase the importance of persulphenyl anions ($TS_b^-$) relative to the persulphenium ions in promoting combination of sulphur and in favouring cross-linking.

The work described in this paper and in Parts VIII—X forms part of the programme of research undertaken by the Board of the British Rubber Producers' Research Association.

The British Rubber Producers' Research Association,
48—56, Tewin Road, Welwyn Garden City, Herts.
[*Received, December* 23*rd*, 1957.]

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[50] Moore and Ross, unpublished work.

[51] Bloomfield, *J. Soc. Chem. Ind.*, 1949, **68**, 66.