

616. *Oxidation of Organic Sulphides. Part XIV.¹ The Antioxidant Effect of Organic Sulphur Compounds Structurally Related to Cross-links in Natural Rubber Vulcanisates.*

By M. E. CAIN and J. I. CUNNEEN.

Organic di- and poly-sulphides structurally related to cross-links in natural rubber vulcanisates may retard both thermal and $\alpha\alpha'$ -azodi-isobutyronitrile-initiated oxidation of squalene. Their action differs from that previously described for organic sulphides since free-radical chain termination is involved. Elemental sulphur also shows chain-terminating activity, and the relation of these observations to ageing behaviour of natural rubber vulcanisates is discussed.

EARLIER papers in this series have shown that unsaturated mono- and saturated disulphides² and saturated γ -keto-sulphides³ retard the thermal autoxidation of squalene through the formation of the corresponding sulfoxides or thiolsulphinates, which do not affect the free-radical chain process of autoxidation but act by suppressing initiation by squalene hydroperoxide.¹ Concurrent work in these laboratories on the chemistry of vulcanisation⁴ has led to considerable elucidation of the structures of cross-links in different vulcanisates, and to the preparation of "model" sulphur compounds of related structure.⁵ The effect of these "model" cross-links on both thermal and $\alpha\alpha'$ -azodi-isobutyronitrile-initiated oxidations of squalene has now been examined in order to clarify the part played by the sulphurated network structures in vulcanisate ageing.

¹ Part XIII, Bateman, Cain, Colclough, and Cunneen, *J.*, 1962, 3570.

² Barnard, Bateman, Cain, Colclough, and Cunneen, *J.*, 1961, 5339.

³ Cain and Cunneen, *J.*, 1962, 2959.

⁴ Bateman, Glazebrook, Moore, Porter, Ross, and R. W. Saville, *J.*, 1958, 2838; Bateman, Glazebrook, and Moore, *J.*, 1958, 2846; Evans, Higgins, Moore, Porter, B. Saville, and Watson, unpublished work.

⁵ B. Saville, *Proc. Chem. Soc.*, 1962, 18; Evans, Higgins, B. Saville, and Watson, *J.*, 1962, 5045; B. Saville, *J.*, 1962, 5040; Milligan, B. Saville, and Swan, *J.*, 1961, 4850; Evans, Higgins, and B. Saville, unpublished work; Moore and Trego, *Tetrahedron*, 1962, 18, 205.

Experimental.—Materials. Squalene² and $\alpha\alpha'$ -azodi-isobutyronitrile¹ were purified as previously described. Chlorobenzene was redistilled to greater than 99.9% purity (gas-liquid chromatography). Sulphur compounds were prepared by Drs. B. Saville and Shephard, and Messrs. Lee, Watson, and Trego by methods described elsewhere.^{5,6} Sulphur was used in the form of commercial "flowers of sulphur" and after its purification.⁷

Oxidations. These were carried out in a constant-pressure apparatus³ at 760 mm. oxygen pressure, thermal autoxidations at 75°, and initiated runs at 60°. Liquids were freed from peroxidised material by passage through small columns of chromatographic alumina before use. Additives were weighed directly into the oxidation vessels, squalene being added to give a standard concentration (0.25M) of additive. For initiated runs a 20% w/w solution of squalene in chlorobenzene was obtained by the addition of a 0.5% solution of $\alpha\alpha'$ -azodi-isobutyronitrile in chlorobenzene, giving an initiator concentration of 0.1M based on squalene.

Results and Discussion.—Thermal autoxidations. Relative antioxidant efficiencies are compared in Table 1 by means of the arbitrary "retardation ratio," *i.e.*, the ratio of

TABLE 1.
Relative antioxidant efficiencies of sulphur compounds (0.25M) in squalene at 75°.

No.	Structure	Retardation ratio	No.	Structure	Retardation ratio
1	(CMe ₂ :CH·CHMe) ₂ S	4.4 *	14	(CMe ₂ :CH·CHMe) ₂ S ₂	9.0 *
2	CMe ₂ :CH·CHMe·S·CMe ₂ :CH·CHMe	5.0 *	15	CMe ₂ :CH·CHMe·S·S·CH ₂ ·CMe:CHEt	15
3	CMe ₂ :CH·CHMe·S·CH ₂ ·CMe:CHEt	2.0	16	(CHEt:CMe·CH ₂) ₂ S ₂	24
4	(CHEt:CMe·CH ₂) ₂ S	1.8	17	CMe ₂ :CH·CHMe·S·SPri ⁱ	25
5	CHEt:CMe·CH ₂ ·S·CHEt:CMe:CH ₂	1.8	18	CMe ₂ :CH·CHMe·S·SBu ^t	20
6	CMe ₂ :CH·CHMe·SMe	27	19	CHEt:CMe·CH ₂ ·S·SEt	30
7	CMe ₂ :CH·CHMe·S·CHEtPri ⁱ	110 *	20	CHEt:CMe·CH ₂ ·S·SPri ⁱ	34
8	CMe ₂ :CH·CHMe·SBu ^t	276 *	21	(CMe ₂ :CH·CHMe) ₂ S ₃	20
9	CMe ₂ :CH·CHMe·S·CMe ₂ Pri ⁿ	357 *	22	(CHEt:CMe·CH ₂) ₂ S ₃	65
10	CHEt:CMe·CH ₂ ·SBu ^t	2.8	23	Et ₂ S ₃	140
11	(CMe ₂ Pri ⁿ) ₂ S ₂	1.7 *	24	(CHEt:CMe·CH ₂) ₂ S ₄	36
12	(CHEtPri ⁿ) ₂ S ₂	3.5	25	Sulphur	43
13	(CMeEtPri ⁿ) ₂ S ₂	1.8			

* From ref. 2.

the times for the absorption of 1% w/w of oxygen by squalene containing the additive and by squalene alone.² Some values previously obtained² are included for completeness.

The dialkenyl monosulphides (1—5) had small antioxidant effects which decreased as the amount of substitution at α -carbon decreased. This, together with the shape of the oxidation curves obtained for the most effective of this class (Fig. 1), suggests that they may form rather unstable sulphoxides having some antioxidant activity.² The effects of the alkenyl alkyl monosulphides (6—10) varied considerably with structure, as previously reported,² the oxidation curves again indicating the formation of an active antioxidant during the initial stages of the reaction (Fig. 1). The negligible effect of 2-methylpent-2-enyl t-butyl sulphide (10) is not surprising since it has a primary carbon attached to the sulphur atom, and the presence of labile β -hydrogen atoms has been noted as essential for antioxidant activity in alkenyl alkyl sulphoxides.¹

The three dialkyl disulphides (11—13) had only minor effects on the autoxidation. This agrees with the observation that di-t-alkyl disulphides are apparently inactive owing to their low rate of conversion into thiolsulphinates by squalene hydroperoxide,² and the same argument may apply to the extremely sterically hindered di-s-alkyl disulphide (12) used here.

The dialkenyl and alkenyl alkyl disulphides (14—16 and 17—20, respectively) showed somewhat different behaviour. Their retarding effects were of the same order as a

¹ Lee and Shephard, unpublished work.

² Bacon and Finelli, *Ind. Eng. Chem.*, 1942, **34**, 1043.

moderately active alkenyl alkyl monosulphide (e.g., 6), but the oxidation curves showed no evidence of secondary antioxidant formation, the reaction proceeding autocatalytically but at a much reduced rate (Fig. 2). The variation of activity with structure was not large in this series, the 2-methylpent-2-enyl structure, with primary carbon attached to

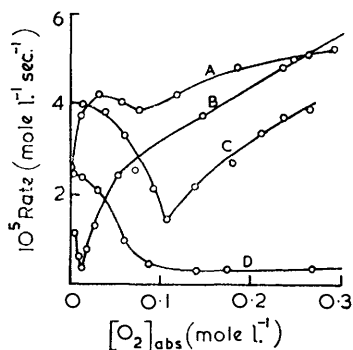


FIG. 1. Thermal autoxidation of squalene containing dialkenyl and alkenyl alkyl monosulphides (0.25M) at 75° and 760 mm.

- A, $\text{CHEt}:\text{CMe}:\text{CH}_2:\text{SBU}^t$.
 B, $\text{CMe}_2:\text{CH}:\text{CHMe}:\text{S}:\text{CMe}_2:\text{CH}:\text{CHMe}$.
 C, $(\text{CMe}_2:\text{CH}:\text{CHMe})_2\text{S}$.
 D, $\text{CMe}_2:\text{CH}:\text{CHMe}:\text{SMe}$.

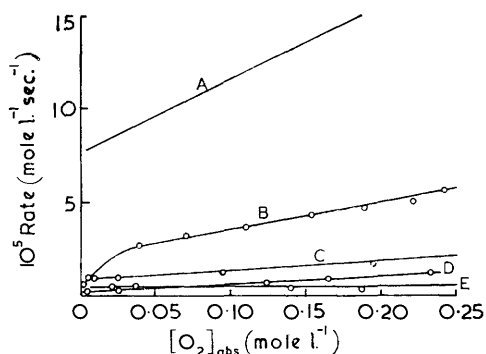


FIG. 2. Thermal autoxidation of squalene containing dialkenyl and alkenyl alkyl disulphides (0.25M) at 75° and 760 mm.

- A, No addition. B, $\text{CHEt}:\text{CMe}:\text{CH}_2:\text{S}:\text{SPr}^t$.
 C, $(\text{CMe}_2:\text{CH}:\text{CHMe})_2\text{S}_2$.
 D, $(\text{CHEt}:\text{CMe}:\text{CH}_2)_2\text{S}_2$.
 E, $\text{CMe}_2:\text{CH}:\text{CHMe}:\text{S}:\text{SPr}^t$.

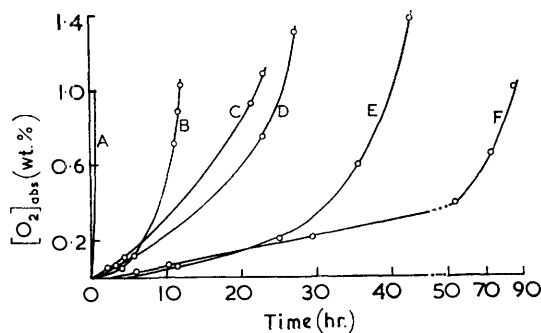


FIG. 3. Thermal autoxidation of squalene containing polysulphides and elemental sulphur (0.25M) at 75° and 760 mm.

- A, No addition. B, $(\text{CMe}_2:\text{CH}:\text{CHMe})_2\text{S}_3$.
 C, $(\text{CHEt}:\text{CMe}:\text{CH}_2)_2\text{S}_4$. D, Sulphur.
 E, $(\text{CHEt}:\text{CMe}:\text{CH}_2)_2\text{S}_3$. F, Et_2S_3 .

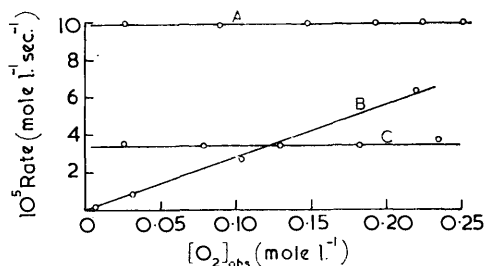


FIG. 4. Azodi-isobutyronitrile (0.1M)-initiated oxidation of squalene containing sulphide and phenol antioxidants at 60° and 760 mm.

- A, No addition.
 B, 2,6-Di-*t*-butyl-*p*-cresol (0.01M).
 C, Et_2S_3 (0.25M).

sulphur, conferring higher activity in both classes. The alkenyl *t*-alkyl disulphide (18) was the least effective, a further difference from previously observed trends.²

The higher efficiency of 2-methylpent-2-enyl structures is also apparent in the dialkenyl trisulphides (21, 22), the structural effects being greater than in the disulphides, the di-*n*-alkyl trisulphide being the most effective. Increase of sulphur chain length to four gave a somewhat less effective antioxidant (24). The polysulphides again gave autocatalytic oxidation curves, the two most effective giving definite induction periods of several hours. The effect of elemental sulphur was similar to that of the polysulphides, with no evidence of secondary antioxidant formation (Fig. 3).

αα'-Azodi-isobutyronitrile-initiated oxidations. The divergences from the previously established pattern of sulphide antioxidant behaviour suggest that some of the compounds studied may possess a different type of antioxidant action, and the autocatalytic curves and occasional observation of definite induction periods suggest the intrusion of free-radical chain-terminating reactions. Such reactions may be detected in a system in which autocatalysis by hydroperoxide decomposition is rendered trivial by addition of a free-radical chain initiator such as *αα'*-azodi-isobutyronitrile. Under the conditions used (60°, 0.1M-initiator, chlorobenzene solution) a horizontal rate-extent plot is obtained for squalene (Fig. 4), confirming the absence of autocatalysis, the time to absorb 1% w/w of oxygen being 45 minutes, compared with 37 minutes for the thermal autoxidations at 75°.

The introduction of representative compounds from each of the classes of sulphide examined under thermal conditions gave similar horizontal rate curves, and the steady rate values obtained are compared in Table 2. The conventional inhibitor, 2,6-di-*t*-butyl-*p*-cresol, gave an induction period of one hour in this system at 0.01M-concentration, and the subsequent rate curve was not horizontal (Fig. 4).

TABLE 2.

Rates (10^{-5} mole l.⁻¹ sec.⁻¹) of *αα'*-azodi-isobutyronitrile-initiated oxidations of squalene at 60° in the presence of sulphur compounds.

No.	Additive	Rate	No.	Additive	Rate
	None	9.9	20	CHEt:CMc·CH ₂ ·S·SPr ¹	5.8
2	CMe ₂ :CH·CHMe·S·CMe ₂ CH:CHMe	9.9	21	(CMe ₂ :CH·CHMe) ₂ S ₃	5.8
8	CMe ₂ :CH·CHMe·SBu ^t	9.9	22	(CHEt:CMc·CH ₂) ₂ S ₃	3.4
12	(CHEtPr ¹) ₂ S ₂	9.9	23	Et ₂ S ₃	3.4
16	(CHEt:CMc·CH ₂) ₂ S ₂	5.1	25	Sulphur	7.4
18	CMe ₂ :CH·CHMe·S·SBu ^t	9.1		Sulphur, "purified"	6.8

The dialkenyl and alkenyl alkyl mono- and di-alkyl disulphides had no effect on the oxidation rate, as would be expected if their antioxidant action depends entirely on the formation of sulfoxide or thiolsulphinates which themselves have no chain-terminating activity.² As inferred from their behaviour under thermal conditions, all the other types had a retarding effect, indicating some chain-terminating activity. These effects are small compared with that of a phenolic inhibitor such as 2,6-di-*t*-butyl-*p*-cresol. It seems likely that the activity observed could easily account for the somewhat larger effects observed in the thermal autoxidation, although it is not possible to exclude completely direct reaction between the sulphur compound and olefin hydroperoxide as a contributing factor.

The mechanism of the chain-terminating process is also not clear, although it is unlikely to involve hydrogen donation to the chain-propagating radicals since the radicals formed from saturated and unsaturated sulphides are known to propagate autoxidation.⁸ Attack at the sulphur atoms by alkyl or alkylperoxy-radicals therefore seems more likely, and this conclusion is supported by the similar behaviour shown by elemental sulphur.

The observation of chain-terminating activity with both samples of sulphur examined is contrary to the recent suggestion by Hawkins and Sautter⁹ that it is first oxidised to sulphur dioxide, which then destroys the hydroperoxide initiator. However, at the elevated temperatures (120–140°) used by them, some oxidation of this type is presumably feasible, although radical attack on sulphur leading to polysulphide formation with chain termination seems more likely. It seems certain that conversion into sulphur dioxide is not responsible for the effects observed under our milder conditions.¹⁻³

It is now possible to draw some conclusions about the effect of network structures

⁸ Bateman and Cunneen, *J.*, 1955, 1596; Bateman and Shipley, *J.*, 1955, 1996; Bateman, Cunneen, and Ford, *J.*, 1956, 3056; 1957, 1539.

⁹ Hawkins and Sautter, *Chem. and Ind.*, 1962, 1825.

alone on the ageing behaviour of natural rubber vulcanisates. Dialkenyl monosulphidic cross-links would have little effect on oxidation resistance, whereas alkenyl alkyl monosulphidic and any disulphide groups could give rise to some "built-in" antioxidant action either by chain termination or by formation of secondary antioxidants. Polysulphide cross-links would be expected to show chain-terminating activity, although, if the activity of the "model" polysulphides studied is due to radical attack at the sulphur bridge with S-S or C-S bond cleavage, this could lead to destruction of the cross-links in a vulcanisate with consequent increase in the rate of ageing as measured by the stress-relaxation technique.¹⁰ Perhaps the most important finding is that any protective effect is likely to be small compared with those obtained from conventional amine or phenol antioxidants, and the likelihood of producing a sulphur-bridged network with inherent high ageing resistance is small. Comparison of the present results with those obtained in our laboratories from the study of both vulcanisation chemistry and the oxidative stress relaxation of highly purified natural rubber vulcanisates has led to a clearer understanding of ageing behaviour,¹¹ and that work will be reported later.

THE NATURAL RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48-56 TEWIN ROAD,
WELWYN GARDEN CITY, HERTS. [Received, January 24th, 1963.]

¹⁰ Tobolsky, Prettyman, and Dillon, *J. Appl. Phys.*, 1944, **15**, 380.

¹¹ Cain and Cunneen, *Rev. Gen. Caoutch.*, 1962, **39**, 1940.
