

**1053. The Oxidation of Organic Sulphides. Part X.<sup>1</sup> The Co-oxidation of Sulphides and Olefins.**

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Certain organic mono- and di-sulphides retard the autoxidation of squalene. This retardation has been shown to be due, not to the sulphides themselves, but to the derived sulphoxides and thiolsulphinates, which are highly active when critical structural requirements are fulfilled.

PREVIOUS papers in this series have dealt with the oxidation of various types of organic sulphide by oxygen,<sup>2</sup> hydroperoxides,<sup>3</sup> and ozone.<sup>1</sup> We now describe the effect exerted by such sulphides on autoxidising hydrocarbons, that is, systems in which hydroperoxides could be formed *in situ* and which could exhibit distinctive features associated with co-oxidation phenomena.

Considerable interest attaches to the beneficial action exerted by organic sulphides on the stability of, for example, polyethylene<sup>4</sup> and lubricating oils<sup>5</sup> under oxidising conditions. This action has been ascribed to the ability of the sulphides,<sup>6</sup> or of the derived sulphonic acids,<sup>7</sup> to interact with and effectively to destroy the hydroperoxides which normally function as initiators of the free-radical oxidation chain process. We have found: (i) a highly specific dependence of inhibitory activity on sulphide structure which is inconsistent with the above postulate in its simplest form; and (ii) that it is not in fact the sulphides themselves which are active in this respect but certain oxygenated derivatives.

## EXPERIMENTAL

*Squalene*.—Basking-shark liver oil was twice distilled in a falling-film short-path still<sup>8</sup> and successively chromatographed, as a 2% solution in light petroleum (b. p. 30—40°), on alumina, activated charcoal, and alumina.

*Ethyl Linoleate*.—Material supplied by the Hormel Foundation and described as the pure *cis-cis*-isomer with less than 0.12% of conjugated diene was used as purchased.

*But-2-enylbenzene*.—A "research" grade supplied by Phillips Petroleum Co. was used without further purification.

*Sulphur Compounds*.—Except for the new compounds listed below, these were either commercial samples or were synthesised by standard methods. All were purified by fractional distillation or crystallisation.

*1,3-Diphenylallyl t-Butyl Sulphide*.—1,3-Diphenylallyl alcohol (0.1 mole) and 2-methylpropane-2-thiol (0.1 mole) were heated *in vacuo* at 75° for 16 hr. in a sealed tube. The product was dissolved in light petroleum (1 l.; b. p. 40°), dried (MgSO<sub>4</sub>), and eluted from alumina (1.5 × 50 cm.). After removal of solvent the residual *sulphide* was distilled and had b. p. 166—168°/0.002 mm.,  $n_D^{20}$  1.5991 (Found: C, 81.1; H, 7.90; S, 11.1. C<sub>18</sub>H<sub>22</sub>S requires C, 81.4; H, 7.6; S, 11.0%),  $\lambda_{\max}$  (in cyclohexane) 2570 Å ( $\epsilon$  21,400).

*1,3-Diphenylallyl Phenyl Sulphide*.—Prepared as above from 1,3-diphenylallyl alcohol and thiophenol, the *product* recrystallised from ethanol as colourless needles, m. p. 75.5—76° (Found: C, 83.0; H, 6.2; S, 10.5. C<sub>21</sub>H<sub>18</sub>S requires C, 83.5; H, 6.0; S, 10.6%),  $\lambda_{\max}$  (in cyclohexane) 2570 Å ( $\epsilon$  24,900).

*Preparation of Sulphoxides*.—A standard procedure<sup>9</sup> for the oxidation of the parent

<sup>1</sup> Part IX, Barnard, *J.*, 1957, 4547.

<sup>2</sup> (a) Bateman and Cunneen, *J.*, 1955, 1596; (b) Bateman and Shipley, *J.*, 1955, 1996; (c) Bateman, Cunneen, and Ford, *J.*, 1956, 3056; (d) Bateman, Cunneen, and Ford, *J.*, 1957, 1539.

<sup>3</sup> (a) Bateman and Hargrave, *Proc. Roy. Soc.*, 1954, A, 224, 389; (b) Bateman and Hargrave, *ibid.*, p. 399; (c) Hargrave, *ibid.*, 1956, A, 235, 55; (d) Barnard, *J.*, 1956, 489.

<sup>4</sup> Hawkins, Lanza, Loeffler, Matreyek, and Winslow, *J. Polymer Sci.*, 1958, 28, 439.

<sup>5</sup> Denison, *Ind. Eng. Chem.*, 1944, 36, 477; Kennerly and Patterson, *ibid.*, 1956, 48, 1917.

<sup>6</sup> Denison and Condit, *Ind. Eng. Chem.*, 1945, 37, 1102.

<sup>7</sup> Leonardi, Oberright, Orkin, and White, *Preprints Div. of Petroleum Chem., Amer. Chem. Soc.*, 1957, 2 (No. 1), 35.

<sup>8</sup> Farmer and Sutton, *J. Soc. Chem. Ind.*, 1946, 65, 164.

<sup>9</sup> Barnard, Fabian, and Koch, *J.*, 1949, 2442.

sulphides with hydrogen peroxide in acetone was employed for the preparation of the following compounds.

	B. p./mm.	$n_D^{20}$	Purity from SO content <sup>10</sup> (%)
Bu <sup>t</sup> :SO:Bu <sup>t</sup> .....	(M. p. 63.5—65°)	—	98.0
Et:CH:CH:CH <sub>2</sub> :SO:Me .....	43—44°/0.01	1.5038	97.8
CH <sub>2</sub> :CH:CHMe:SO:Bu <sup>n</sup> .....	55°/0.005	1.4935	97.5
Et:CH:CH:CHMe:SO:Me .....	50°/0.01	1.4970	97.1
Cyclohex-2-enyl t-butyl sulphoxide .....	*	—	97.6

\* Purified by counter-current distribution between light petroleum and water.

*t*-Butyl 2-Methylpropane-2-thiolsulphinatc.—2-Methylpropane-2-sulphinic acid (22 g.), obtained by the reaction of *t*-butylmagnesium chloride with sulphur dioxide, was treated with thionyl chloride (25 ml.) to give 2-methylpropane-2-sulphinyl chloride (19.8 g.), b. p. 62°/15 mm.,  $n_D^{18}$  1.4840 (Found: C, 34.2; H, 6.4; Cl, 25.8; S, 23.1. C<sub>4</sub>H<sub>9</sub>ClOS requires C, 34.1; H, 6.4; Cl, 25.2; S, 22.8%). Slow addition of a mixture of 2-methylpropane-2-thiol (1 mol.) and pyridine (1 mol.) to the sulphinyl chloride (1 mol.) in ether gave the thiolsulphinatc, b. p. 55°/0.05 mm.,  $n_D^{21}$  1.5060 (Found: C, 49.0; H, 9.3; S, 32.4. C<sub>8</sub>H<sub>18</sub>OS<sub>2</sub> requires C, 49.5; H, 9.4; S, 32.9%).

Di-[*p*-(phenylsulphinylthio)phenyl] Ether.—Benzenesulphinyl chloride (18.4 g.) in ether (200 ml.) was added slowly to a stirred suspension of bis-4-mercaptophenyl ether (12.8 g.), prepared by Marvel and Caesar's method,<sup>11</sup> in pyridine (9.05 g.) and ether (200 ml.) at -10°. After warming to room temperature the mixture was diluted with chloroform (150 ml.) to give a clear yellow solution. This was washed with 2*N*-sulphuric acid (150 ml.), dried (CaCl<sub>2</sub>), and evaporated, to give a yellow solid (26.6 g.) which had a purity, as the expected thiolsulphinatc, of 79.5%.<sup>12</sup> Recrystallisation from methanol-chloroform gave a product of purity 95%, as thiolsulphinatc, m. p. 100—102° (decomp.) (Found: C, 59.7; H, 3.7; S, 26.5. C<sub>24</sub>H<sub>18</sub>O<sub>3</sub>S<sub>4</sub> requires C, 59.7; H, 3.8; S, 26.6%).

1,3-Dimethylbut-2-enyl 1-ethyl-2-methylpropyl sulphide, 1,3-dimethylbut-2-enyl 1,1-dimethylbutyl sulphide, bis-(1,3-dimethylbut-2-enyl) sulphide and disulphide, and bis-(1,1-dimethylbutyl) disulphide were kindly presented by Dr. B. Saville.

*Oxidation Apparatus and Procedure.*—The absorption of oxygen was measured in a constant-pressure apparatus, essentially as described by Bateman and Cunneen.<sup>2a</sup> To ensure reproducibility of results it was necessary to pass both the olefins and liquid sulphur compounds through columns of alumina under a nitrogen atmosphere immediately before use. A standard concentration (0.25*M*) of sulphur compound in olefin and a standard temperature (75°) of oxidation were adopted, except in the case of certain of the more active materials when concentrations of 0.01*M* or less were used.

*Expression of Results.*—The usual plots of extent of oxidation *versus* either time or rate of oxidation were complex and no single parameter could be derived to express the effect of the additive. An arbitrary "retardation ratio" has been adopted, *viz.*, the ratio of the times taken for 1% (w/w) (or in certain specified cases 0.1%) of oxygen to be absorbed by the olefin plus additive, and by the pure olefin, respectively. The larger the ratio the better the performance of the additive as a retarder of oxidation.

## RESULTS AND DISCUSSION

The effect of a wide variety of saturated and unsaturated mono- and di-sulphides and of other sulphur compounds on the autoxidation of squalene is expressed by the retardation ratios given in Tables 1—4. From these it will be seen that most monosulphides are without effect on the autoxidation under the conditions stated, but that a few exert a marked retardation. For highest activity the critical structural requirements are (a) that one substituent on the sulphur atom be a *t*-butyl (or other *t*-alkyl) group, and (b) that the second substituent be another *t*-butyl group (as in di-*t*-butyl sulphide) or an allyl group alkylated at the 1- and the 3-position (as in *t*-butyl 1,3,3-trimethylallyl and *t*-butyl cyclohexenyl sulphide). The reverse is apparent with the disulphides examined; that is, most show retarder activity but this is at its highest with simple alkyl disulphides and is

<sup>10</sup> Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 536.

<sup>11</sup> Marvel and Caesar, *J. Amer. Chem. Soc.*, 1951, **73**, 1097.

<sup>12</sup> Barnard and Cole, *Analyt. Chim. Acta*, 1959, **20**, 540.

TABLE 1.  
Saturated monosulphides.

Sulphide (0.25M)	Retardn. ratio	Sulphide (0.25M)	Retardn. ratio	Sulphide (0.25M)	Retardn. ratio
Bu <sup>n</sup> <sub>2</sub> S .....	1.7 *	2-Ethyl-1,2,3,4-tetrahydro-5-		Bu <sup>t</sup> <sub>2</sub> S .....	256
C <sub>6</sub> H <sub>11</sub> SMe .....	3.4 *	isopropyl-2-methylthiophen	3.7 *	Bu <sup>t</sup> S·CCl <sub>3</sub> .....	0.8
Thiacyclo-		Bu <sup>t</sup> ·SMe .....	1.4	Bu <sup>t</sup> ·SPh .....	1.4
hexane .....	4.5 *	Bu <sup>t</sup> ·SPr <sup>i</sup> .....	2.1	Ph <sub>3</sub> C·SPh .....	0.7

\* At 400 mm. oxygen pressure, otherwise at 760 mm.

TABLE 2.  
Unsaturated monosulphides.

Sulphide (0.25M)	Retardn. ratio	Sulphide (0.25M)	Retardn. ratio
CH <sub>2</sub> :CH·CH <sub>2</sub> ·SBu <sup>n</sup> .....	1.4 *	CMe <sub>2</sub> :CH·CHMe·S·CMe <sub>2</sub> Pr <sup>n</sup> .....	357
CH <sub>2</sub> :CH·CH <sub>2</sub> ·SBu <sup>t</sup> .....	1.5	CMe <sub>2</sub> :CH·CMe <sub>2</sub> ·SBu <sup>t</sup> .....	110
CHMe:CH·CH <sub>2</sub> ·SMe .....	1.3 *	CHPh:CH·CH <sub>2</sub> ·SBu <sup>n</sup> .....	6.3, * 3.5
CH <sub>2</sub> :CH·CHMe·SBu <sup>n</sup> .....	4.1 *	CHPh:CH·CHPh·SBu <sup>t</sup> .....	1.2
CHMe:CH·CHMe·SMe .....	3.8, * 3.1	CHPh:CH·CHPh·SPh .....	2.3
CHMe:CH·CHMe·SPr <sup>i</sup> .....	24.3	Cyclohex-2-enyl methyl sulphide...	2.4 *
CHMe:CH·CHMe·SBu <sup>n</sup> .....	40.5, * 15.3	Cyclohex-2-enyl t-butyl sulphide...	480, * 150
CHMe:CH·CHMe·SBu <sup>t</sup> .....	310, * 93	1-Thiacyclohex-3-ene .....	3.8
CHMe:CH·CHMe·SPh .....	270 *	1-Thiacyclohex-2-ene .....	6.9 *
CMe <sub>2</sub> :CH·CHMe·S·CHEt·CHMe <sub>2</sub> ...	110	2,3-Dihydro-2-isopropyl-5-methyl-	
CMe <sub>2</sub> :CH·CHMe·S·CHMe·CH:Me <sub>2</sub> ..	4.4	thiophen .....	3.6 *
CMe <sub>2</sub> :CH·CHMe·S·CMe <sub>2</sub> ·CH:CHMe	5.0	MeS·CH:CH·CHMe·S·Me .....	1.1
CMe <sub>2</sub> :CH·CHMe·SBu <sup>t</sup> .....	276		

\* At 400 mm. oxygen pressure, otherwise at 760 mm.

TABLE 3.  
Di- and poly-sulphides.

Sulphide (0.25M)	Retardn. ratio	Sulphide (0.25M)	Retardn. ratio	Sulphide (0.25M)	Retardn. ratio
MeS·SMe .....	9	Dicyclohex-2-enyl di-		CH <sub>2</sub> Ph·S·S·CH <sub>2</sub> Ph ...	8
Pr <sup>i</sup> S·SPr <sup>i</sup> .....	66	sulphide .....	20	Dibenzothiazol-2-yl	
Bu <sup>n</sup> S·SBu <sup>n</sup> .....	121, 90 †	(Me·[CH <sub>2</sub> ] <sub>4</sub> ·CH <sub>2</sub> ·S) <sub>2</sub> ...	51	disulphide .....	5
Bu <sup>t</sup> S·SBu <sup>t</sup> .....	1.6	(Me·[CH <sub>2</sub> ] <sub>2</sub> ·CMe <sub>2</sub> ·S) <sub>2</sub> ...	1.7	1,2-Dithian .....	7
C <sub>6</sub> H <sub>11</sub> :S·S·C <sub>6</sub> H <sub>11</sub> ...	106	(CMe <sub>2</sub> :CH·CHMe·S) <sub>2</sub> ...	9	Pr <sup>i</sup> S·S·S·SPr <sup>i</sup> .....	79
		PhS·SPh .....	2		

† At 760 mm. oxygen pressure, otherwise at 400 mm.

TABLE 4.  
Miscellaneous sulphur compounds.

Compound	Retardn. ratio	Compound	Retardn. ratio
Sulphur (0.25M) .....	107	2,5-Diphenyl-1,4-dithiin 1-oxide	
Ph·SO <sub>3</sub> H (0.01M) .....	1.8	(0.25M) .....	17
" (0.1M) .....	1.4	(Me <sub>2</sub> N·CS <sub>2</sub> ) <sub>2</sub> Zn (0.25M) .....	128
Bu <sup>t</sup> ·SO <sub>3</sub> H (0.01M) .....	1.0 *	(Me <sub>2</sub> N·CS <sub>2</sub> ) <sub>2</sub> Zn (0.01M) .....	28
Bu <sup>t</sup> ·SO <sub>3</sub> H (0.01M) .....	0.6 *	[Me <sub>2</sub> N·CS <sub>2</sub> ] <sub>2</sub> (0.01M) .....	17
Et <sub>2</sub> SO <sub>3</sub> (0.01M) .....	1.3 *	Thiourea (0.01M) .....	11
Ph·SO·OMe (0.25M) .....	1.0	Phenothiazine (0.004M) .....	415 *
2,5-Diphenyl-1,4-dithiin (0.25M) .....	8		

\* At 760 mm. oxygen pressure, otherwise at 400 mm.

lost almost completely in the case of di-t-alkyl and diaryl disulphides. Among the miscellaneous sulphur compounds (Table 4), only sulphur itself, zinc dimethyldithiocarbamate (a powerful antioxidant <sup>13</sup>), and phenothiazine are strong retarders. Representatives of more conventional classes of antioxidant, phenyl-β-naphthylamine and β-naphthol, at concentrations of 0.01M gave comparable retardation ratios of about 100.

<sup>13</sup> Dunn and Scanlan, *Trans. Proc. Inst. Rubber Ind.*, 1958, **34**, 228.

*Basis of the Retarding Activity.*—If, as has been postulated,<sup>6</sup> the retarding activity merely reflects the reduction of olefin hydroperoxide by sulphide, then it would be predicted from detailed studies of this interaction<sup>3a,b</sup> that activity would be a maximum, not a minimum, with a di-n-alkyl monosulphide and would, in any case, be of a low order at the moderate temperatures employed.

What is truly responsible can be deduced from careful studies of the course of retarded reactions in the very early stages. Retardation was found to be imposed only after a

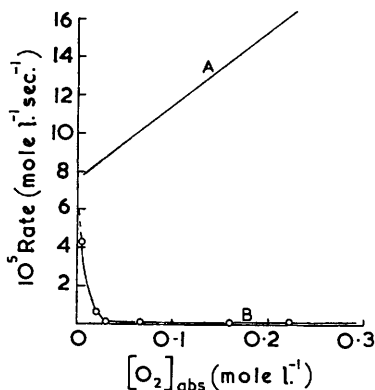


FIG. 1. Co-oxidation of squalene and cyclohexenyl t-butyl sulphide (0.25M) at 75° and 760 mm. oxygen pressure. (A) Squalene alone; (B) squalene plus sulphide.

FIG. 2. Co-oxidation of squalene and di-n-butyl disulphide (0.25M) at 75° and 400 mm. oxygen pressure. (A) Squalene alone; (B) squalene plus sulphide.

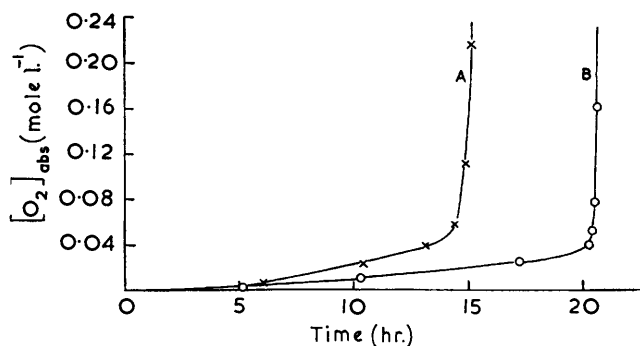
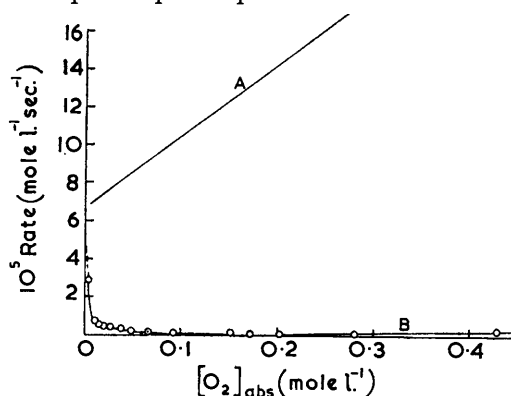


FIG. 3. Co-oxidation of squalene with (A) di-t-butyl sulphoxide (0.01M), and (B) n-butyl butanethiolsulphinat (0.005M) at 75°.

very small but quite definite absorption of oxygen (Figs. 1 and 2) implying that it is not the sulphides themselves but one or more oxidized derivatives which are the actual retarders and that these are of high potency. By direct test of the possible oxygenated derivatives, including sulfoxides, sulphones, thiolsulphinates, thiolsulphonates, disulphones, sulphinic and sulphonic acids, only those sulphoxides derived from the "active" monosulphides, and thiolsulphinates were found to be highly active. From the data in Table 5 and typical oxidation curves (Fig. 3) it will be seen that: (a) these derivatives are effective as retarders at much lower concentrations than are the parent sulphides; (b) retardation occurs from the earliest stages of reaction—there is no measurable initial absorption of oxygen necessary as with the sulphides; and (c) there is a much more abrupt ending of the induction period than with the sulphides (cf. Figs. 1 and 2). The length of the induction period is partly, at least, determined by the thermal instability of the retarder, which, especially for the sulphoxides,<sup>14</sup> runs parallel to activity. This instability is one

<sup>14</sup> Colclough and Cunneen, *Chem. and Ind.*, 1960, 626; and unpublished work.

cause of the non-linear dependence of retardation efficiency on concentration, and undoubtedly is involved in the more puzzling feature that in certain cases the retardation ratios pass through a maximum as the concentration is increased, behaviour which has been observed with other antioxidants.<sup>15</sup>

The identity of the true retarder was confirmed by isolating the sulphoxide from a large-scale oxidised mixture of squalene and cyclohexenyl *t*-butyl sulphide after counter-current distribution of the products between squalene and aqueous methanol. Only those fractions containing sulphoxide were immediately effective in producing an induction period when added to autoxidising squalene. In a similar experiment, in which squalene containing di-*n*-butyl disulphide (0.25M) was autoxidised until the maximum degree of retardation was achieved and the mixture then eluted in light petroleum from a column of silica gel, it was found that the recovered squalene, which still contained the major part of the disulphide, behaved as the original mixture, *i.e.*, retardation developed only after more oxygen was absorbed. The small amount of material eluted from silica gel with methanol caused immediate but short-lived (1 hr.) retardation of autoxidation when added to fresh squalene. *n*-Butyl butanethiolsulphinatate was shown to be present in the eluate by paper-chromatography.<sup>12</sup> It was confirmed in separate experiments that thiolsulphinates are normal products of the reaction of disulphides with hydroperoxides in the temperature range of present interest—their formation when peracids are the oxidants is well known.<sup>16</sup>

The conclusion is reached, therefore, that the co-oxidation of squalene with a mono- or di-sulphide commences with the normal formation of squalene hydroperoxide,<sup>17</sup> and that the latter, or intermediate peroxy-radicals, then react with the sulphide to yield the sulphoxide or thiolsulphinatate. Oxygen uptake is then depressed to a value determined by (i) the efficiency of the sulphoxide or thiolsulphinatate as inhibitor, (ii) the ease with which these compounds are formed under the oxidation conditions, and (iii) the readiness with which they undergo thermal decomposition under the same conditions.

*Structural Features Affecting the Retarding Activity of Sulphoxides and Thiolsulphinates.*—The data in Tables 1—3 and 5 show that all mono- and di-sulphides which are retarders yield sulphoxides and thiolsulphinates of high activity, but that the converse is not necessarily true. For example, diaryl and di-*t*-alkyl disulphides are inactive while the corresponding thiolsulphinates would be rated as active and highly active, respectively. The explanation for this lies in the relative resistance of these sulphides to oxidation by peroxides. More puzzling is the inactivity of isopropyl *t*-butyl sulphide even though its sulphoxide is one of the most active examined and its rate of oxidation by hydroperoxide is only slightly less than that of di-*t*-butyl sulphide. This apparent anomaly suggests a delicate interplay of the three factors mentioned above in determining sulphide activity.

In general, however, relations between structure and activity in the sulphoxides and thiolsulphinates parallel those in the parent sulphides, as discussed earlier. While all the thiolsulphinates examined show largely similar activities, there is a critical dependence on structure in the sulphoxides with the same combinations of *t*-alkyl and substituted allyl substituents required for high activity as in the monosulphides. This is to be expected as the latter are active only as a consequence of their oxidation to an active sulphoxide. The possible significance of the particular sulphoxide structures which confer high retarder activity will be discussed in a later paper.

*Effect of Reaction Conditions on Retarding Activity.*—Reduction of the temperature below 75° generally led to an increase in the retardation ratio. For sulphoxides and thiolsulphinates this can be attributed to their longer life at the lower temperatures. For sulphides the situation is more complex since the rate of formation of the active retarder will now influence the overall effect. For example, with di-*n*-butyl disulphide a lower

<sup>15</sup> Shelton, *Rubber Chem. Technol.*, 1957, **30**, 1251.

<sup>16</sup> Small, Bailey, and Cavallito, *J. Amer. Chem. Soc.*, 1947, **69**, 1711.

<sup>17</sup> Bolland and Hughes, *J.*, 1949, 492.

TABLE 5.

The inhibitory effects of the oxidation products of mono- and di-sulphides on the autoxidation of squalene at 75°.

Additive	Concn. (M)	Retardn. ratio †	Additive	Concn. (M)	Retardn. ratio †
CHMe:CH·CH <sub>2</sub> ·SO·Me	0.26	5	Bu <sup>n</sup> ·SO·SBu <sup>n</sup>	0.005	248, 32 *
CH <sub>2</sub> :CH·CHMe·SO·Bu <sup>n</sup>	0.26	3	Et·SO·SEt	0.004	145, 48 *
CHMe:CH·CHMe·SO·Me	0.26	7	"	0.25	337, 83 *
CMe <sub>2</sub> :CH·CHMe·SO·Me	0.01	50, 11 *	Bu <sup>t</sup> ·SO·SBu <sup>t</sup>	0.004	140, 140 *
CMe <sub>2</sub> :CH·CHMe·SO·Pr <sup>i</sup>	0.01	310, 60 *	Ph·SO·SPh	0.005	40, 14 *
Cyclohex-2-enyl t-butyl sulphoxide	0.26	69	"	0.01	68, 24 *
"	0.005	112	"	0.05	372, 132 *
Bu <sup>n</sup> ·SO·Bu <sup>n</sup>	0.01	1, 1 *	"	0.15	487, 225 *
Et·SO·Bu <sup>t</sup>	0.01	1, 1 *	"	0.25	575, 240 *
Pr <sup>i</sup> ·SO·Bu <sup>t</sup>	0.006	120, 90 *	"	0.40	737, 156 *
Bu <sup>t</sup> ·SO·Bu <sup>t</sup>	0.01	144, 24 *	Di-[ <i>p</i> -(phenylsulphinylthio)-phenyl] ether	0.005	33, 26 *
"	0.03	95, 30 *	Ph·SO <sub>2</sub> ·SPh	0.25	1, 0.7 *
"	0.06	59, 9 *	Et·SO <sub>2</sub> ·SEt	0.01	1, 1 *
Bu <sup>t</sup> ·SO·CCl <sub>3</sub>	0.005	1, 1 *	Ph·SO <sub>2</sub> ·SO·Ph	0.05	10, 20 *
Bu <sup>t</sup> ·SO <sub>2</sub> ·Bu <sup>t</sup>	0.01	1, 1 *	Ph·SO <sub>2</sub> ·SO <sub>2</sub> ·Ph	0.25	1, 1 *
Cyclohex-2-enyl t-butyl sulphone	0.25	1, 1 *			

\* Retardation ratio calculated on times to 1% oxygen uptake.

† Retardation ratio calculated on times to 0.1% oxygen uptake. This often corresponds approximately to the end of the induction period.

temperature results in a poorer performance at low extents of oxidation but a superior performance at higher extents when thiolsulphinate has accumulated.

Retardation ratios found at 400 and 760 mm. oxygen pressure often differ appreciably (Tables 1 and 2), although the induction periods given by sulphoxides and thiolsulphinates are insensitive to this variation. The rate of autoxidation of squalene is nearly, but not quite independent of oxygen pressure in this range (at the pressures mentioned the times

TABLE 6.

Retardation ratios of sulphur compounds in various olefins at 75°.

Additive (0.25M)	Squalene	Retardation ratio But-2-enylbenzene	Et linoleate
Di-n-butyl disulphide	90	15	1.7
Di-t-butyl sulphide	256		36
Cyclohexenyl t-butyl sulphide	150	16	32
Phenyl benzenethiolsulphinate	240	6	8

for the absorption of 1% w/w of oxygen are 42 and 36 minutes, respectively). It appears, therefore, that this slight difference in rate is sufficient to disturb what is clearly a critical balance in the relative build up of hydroperoxide and retarder. Some support for this view is that the time taken for maximum retardation to be produced by di-n-butyl disulphide is more affected by changes in oxygen pressure than is the actual degree of retardation.

*Effect of Olefin Structure.*—In certain olefins other than squalene the various sulphur compounds exert a much reduced activity under the present conditions (Table 6). This is in accord with the view that the olefin hydroperoxide is involved not only in the formation of retarder but also in the mechanism of retardation and that, therefore, its specific reactivity greatly influences the overall effect. A fuller discussion of this point will be presented later.

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