697. *Oxidation of Organic Sulphides. Part XIII.*[1] *The Antioxidant Action of Sulphoxides and Thiolsulphinates in Autoxidizing Squalene.*

By L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen.

Sulphoxides of certain structures, and thiolsulphinates in general, inhibit the autoxidation of squalene in a novel manner, namely, by suppressing the homolytic decomposition of the hydroperoxide which otherwise serves to initiate the reaction. These sulphinyl compounds are ineffective when oxy- or peroxy-radicals are supplied independently as initiating species, and also in autoxidations not involving hydroperoxides as intermediates or products (*e.g.*, of styrene). The inhibitory activity arises from a peculiar kind of complex-formation; this can be suppressed, and its effect reduced or destroyed, by addition of a bonding agent for SO groups such as stearic acid; this complex-formation is highly sensitive to the detailed character of the SO group. Structural factors bearing on this effect are discussed, especially the correlation with E_i-type elimination to which "active" sulphoxides are particularly prone.

It was shown in Parts X [2] and XII [1] that the autoxidation of squalene at moderate temperatures is strongly retarded by small amounts of certain organic mono- and di-sulphides, and, more remarkably, that the actual antioxidants are not these sulphides, but the corresponding sulphoxides and thiolsulphinates which are formed initially on absorption of a very small, in some cases a barely detectable, amount of oxygen. We now consider the basis of this hitherto unsuspected reactivity of these sulphinyl compounds and the structural specificity for high antioxidant activity, especially in sulphoxides.

[1] Part XII, Cain and Cunneen, *J.*, 1962, 2959.
[2] Barnard, Bateman, Cain, Colclough, and Cunneen, *J.*, 1961, 5339.

Under conditions relevant to the present work, a non-conjugated olefin reacts with oxygen by the following basic free-radical chain mechanism: [3]

Initiation:	$RH + O_2 \longrightarrow$	(1′)
	$RO_2H \longrightarrow$ Generation of R· or RO_2	(1″)
	$2RO_2H \longrightarrow$	(1‴)
Propagation:	$R\cdot + O_2 \longrightarrow RO_2\cdot$	(2)
	$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$	(3)
Termination:	$2RO_2\cdot \longrightarrow$ Non-propagating species	

where RH represents the olefin with an α-methylenic hydrogen atom. Reaction (1′) must be the initial step when the olefin is completely free from hydroperoxide or other catalyst (*e.g.*, a metal compound), but is exceedingly difficult to observe and still remains to be characterized because it is rapidly superseded by the easier radical-generating processes (1″) and (1‴). The bimolecular reaction (1‴) is generally predominant, and is to be understood as the " initiation reaction " unless otherwise stated. With many olefins, kinetically equivalent variants are superimposed on the above mechanism; thus the propagation stage in squalene consists of a double pair of reactions equivalent to (2) and (3).[4] However, it is unnecessary to introduce these complications here as the simplified scheme embraces the essential reactivity principles involved.

Inhibition of autoxidation reflects suppression of either the initiation or the propagation processes, alternatives which can be distinguished by distinctively changing the mode of initiation. If inhibitory activity of an additive is restricted to certain well-defined modes, then its association with the initiation step is evident; if such activity is not so restricted, then association with the invariable propagation sequence can be deduced. Side reactions of the additive sometimes obscure clean differentiation, so it is useful to augment such evidence with independent knowledge of its reactivity towards the initiating and the propagating species.

By these criteria, the inhibition of autoxidizing squalene by sulphoxides and thiolsulphinates is clearly seen to be the suppression of the initiation. Thus, di-t-butyl sulphoxide, 1,3-dimethylbut-2-enyl isopropyl sulphoxide, isopropyl t-butyl sulphoxide, 4,4-dimethyl-1-t-butylsulphinylpentan-3-one, and the thiolsulphinate derived from di-t-butyl disulphide typify strong inhibitors for this autoxidation which, in contrast with a phenolic-type inhibitor, are without effect when the decomposition of added azoisobutyronitrile, *t*-butyl phenylperacetate or benzoyl peroxide replaces reaction (1‴), as the initiation step (Fig. 1). If, however, t-butyl hydroperoxide is added as initiator, then the inhibitory action of the sulphinyl compounds is fully operative (Fig. 1). It is evident, therefore, that inhibition results when initiation arises directly from hydroperoxide molecules, as in reactions (1″) and (1‴) and not when alkyl and alkylperoxy-radicals (from the azo-compound), benzyl and t-butoxy-radicals (from the perester), and phenyl and benzoate radicals (from benzoyl peroxide) are generated in the system. This insensitivity to free radicals is further apparent from the observation that active sulphoxides * have little or no effect on the autoxidation of styrene (Fig. 2). Under the experimental conditions adopted, this autoxidation proceeds by a chain mechanism formally similar to that set out above, in which alkyl and alkylperoxy-radicals are also involved in the propagation step although that corresponding to (3) is one of addition to the double bond leading to 1 : 1

* Since most thiolsulphinates, in contrast to sulphoxides, are polymerisation-inhibitors and are sensitive to attack by styryl radicals [5] their effects in this system are not critical. Actually, t-butyl 2-methylpropane-2-thiolsulphinate shows some inhibitory action though much less than in autoxidizing squalene (retardation ratios [2] of 8 and 140, respectively), while isopropyl 1-propane-2-thiolsulphinate is completely without effect.

[3] Bateman, *Quart. Rev.*, 1954, **8**, 147.
[4] Bolland and Hughes, *J.*, 1949, 492.
[5] Barnard and Percy, unpublished work.

co-polymerization of styrene and oxygen.[6] The significant differences are that the polymeric peroxide $[\cdot CHPh\cdot CH_2\cdot O_2\cdot]_n$ is a relatively weak free-radical initiator, producing only a minor degree of autocatalysis, that the direct styrene–oxygen reaction corresponding to (1′) occurs more readily and is an important initiating process, and that reactions corresponding to (1″) and (1‴) are necessarily absent as hydroperoxide is not formed. The

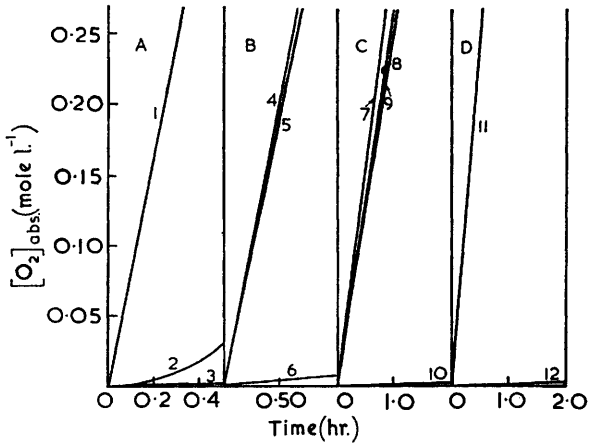


FIG. 1.

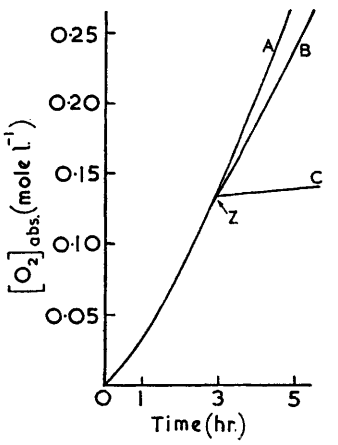


FIG. 2.

FIG. 1. Effect of various additives (0·01M) on the catalysed (0·1M) autoxidation of squalene, (A), (B), and (C) in chlorobenzene at 60°, (D) without solvent at 75°.

Curve	Catalyst	Squalene concn. (% by wt.)	Additive
1	αα′-Azoisobutyronitrile	20	No addition, or Bu^t_2SO, or $Bu^t\cdot SO\cdot Pr^i$, or $CMe_2{:}CH\cdot CH\cdot Me\cdot SO\cdot Pr^i$, or $Bu^t\cdot CO\cdot[CH_2]_2\cdot SO\cdot Bu^t$, or $Bu^t\cdot SO\cdot S\cdot Bu^t$
2	αα′-Azoisobutyronitrile	20	β-Naphthol
3	αα′-Azoisobutyronitrile	20	2,6-Di-t-butyl-*p*-cresol
4	t-Butyl phenylperacetate	50	$Bu^t\cdot SO\cdot Pr^i$
5	t-Butyl phenylperacetate	50	No addition, or Bu^t_2SO
6	t-Butyl phenylperacetate	50	β-Naphthol
7	Benzoyl peroxide	50	No addition
8	Benzoyl peroxide	50	$Bu^t\cdot SO\cdot Pr^i$
9	Benzoyl peroxide	50	Bu^t_2SO
10	Benzoyl peroxide	50	β-Naphthol
11	t-Butyl hydroperoxide	100	No addition
12	t-Butyl hydroperoxide	100	Bu^t_2SO

FIG. 2. Effect of additives (0·01M) added at (Z) on the autoxidation of styrene at 75°. (A) No addition, or $Bu^t\cdot SO\cdot Pr^i$, or $CMe_2{:}CH\cdot CHMe\cdot SO\cdot Pr^i$. (B) Bu^t_2SO. (C) 2,6-Di-t-butyl-*p*-cresol.

lack of inhibitory action by the added sulphoxide can only be attributed to the last feature. These findings provide the first proved example of the inactivation of hydroperoxide by molecular interaction. Such an effect has previously been proposed in order to explain the antioxidant properties of certain organic sulphides,[7] although we now know that, at

[6] Miller and Mayo, *J. Amer. Chem. Soc.*, 1956, **78**, 1017.

[7] Denison, *Ind. Eng. Chem.*, 1944, **30**, 477; Denison and Condit, *ibid.*, 1945, **37**, 1102; Kennerly and Patterson, *ibid.*, 1956, **48**, 1917; Berry, Toettcher, and Knowles, Div. Petroleum Chem., Amer. Chem. Soc., Symposium on Additives in Lubricants, Atlantic City, N.J., Sept., 17—21, 1956, p. 70; Oberright, Leonardi, and Kozacik, *ibid.*, p. 115; Leonardi, Oberright, Orkin, and White, Div. Petroleum Chem., Amer. Chem. Soc., General Papers, Miami, Fla., April 7—12, 1957, p. 35; Harle, *ibid.*, p. 51.

least under conditions comparable to those being considered, the sulphides are merely precursors of the true antioxidants and do not themselves interact in the manner required with hydroperoxide (see below).

The action of the sulphinyl compounds might be ascribed to their inducing a very rapid decomposition of the hydroperoxide by a non-radical mechanism. Although this would be a novel reaction since other accelerated decompositions of hydroperoxide (*e.g.*, by acids or metal compounds) often enhance the free-radical reactivity, it is reasonable *a priori* (*a*) because SO groups are known to be powerful hydrogen-bonding sites for O_2H-groups,[8] and (*b*) because a broad correlation is evident between inhibitor activity and the power to accelerate hydroperoxide decomposition. Representative data are given in Fig. 3 to illustrate the facts that, whereas SO compounds with little or no antioxidant activity [2]

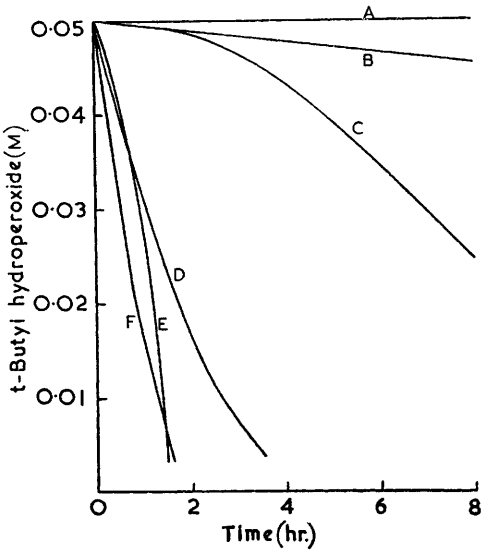


FIG. 3. Decomposition of t-butyl hydroperoxide by sulphoxides (0·05M) and thiolsulphinates (0·05M) in benzene at 75°.

(A) No addition, or Me_2SO, or Et_2SO, or Pr^i_2SO, or Bu^n_2SO, or $[Ph{\cdot}CH_2{\cdot}CH_2]_2{\cdot}SO$, or 2,6-di-t-butyl-*p*-cresol (0·05M).
(B) $Bu^t{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}SO{\cdot}Me$, or $Me{\cdot}CO[CH_2]_3{\cdot}SO{\cdot}Me$, or $Bu^t{\cdot}CO{\cdot}[CH_2]_3{\cdot}SO{\cdot}Bu^t$.
(C) $Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Me$.
(D) $Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$
(E) Bu^t_2SO.
(F) $Bu^t{\cdot}SO{\cdot}S{\cdot}Bu^t$.

only slightly affect the rate of decomposition of t-butyl hydroperoxide, similar compounds with high activity increase this rate considerably. However, even this increase in rate is insufficient to account for the speed and the degree at which inhibition is imposed since adding di-t-butyl sulphoxide, isopropyl t-butyl sulphoxide, 1,3-dimethylbut-2-enyl isopropyl sulphoxide, 4,4-dimethyl-1-t-butylsulphinylpentan-3-one, or t-butyl 2-methylpropane-2-thiolsulphinate to autoxidizing squalene reduced the rate of oxygen absorption immediately to near zero, whereas the fall in hydroperoxide content occurs much more slowly (Fig. 4).

A more direct demonstration that hydroperoxide decomposition is not determinative is provided by the following experiments. Pure squalene (1·48 g.) was oxidised at 55° for 5·4 hours, absorbing 2·0% w/w (0·536 mol.) of oxygen; its rate of oxidation was then $5{\cdot}4 \times 10^{-5}$ mole $l.^{-1}$ $sec.^{-1}$. Di-t-butyl sulphoxide (0·2 mol.) was added, whereupon the rate immediately became immeasureably small (cf. Fig. 4). After 15 min. the reaction mixture was dissolved in light petroleum (20 ml.) and washed with water (10 × 10 ml.) to remove the sulphoxide, and the infrared absorption spectrum in the region 3200—3600 $cm.^{-1}$ was determined. The absorption corresponded exactly to that given by a similar sample of squalene oxidized to the same extent but not otherwise treated (Fig. 5) and is characteristic of the complex peroxide–hydroperoxide grouping present in squalene hydroperoxide. The relative intensities indicate that the latter is present in the inhibited product to ~70% of that in the control experiment. But even this amount is not the correct

[8] Barnard, Hargrave, and Higgins, *J.*, 1956, 2845.

minimum because if di-n-butyl sulphoxide (which is an "inactive" sulphoxide with negligible inhibitory power under conditions of these experiments) is added to the untreated oxidized squalene and the mixture, after being kept at 55° for 15 min. in nitrogen, is extracted with water as described above, then the absorption spectrum becomes almost identical with that of the hydroperoxidic product from the inhibited system (Fig. 5). When the sulphoxide is washed out, some of the hydroperoxide is evidently removed as well, as is reasonable. The oxidized squalenes, after the removal of both sulphoxides, were found to react further with oxygen at the same rate ($3{\cdot}5 \times 10^{-5}$ mole $l.^{-1}$ $sec.^{-1}$). This was 65% of the rate observed before sulphoxide addition (Fig. 6), this ratio corresponding closely to the difference in hydroperoxide content as determined spectroscopically (Fig. 5) and iodometrically. Clearly the di-t-butyl sulphoxide (in an amount substantially

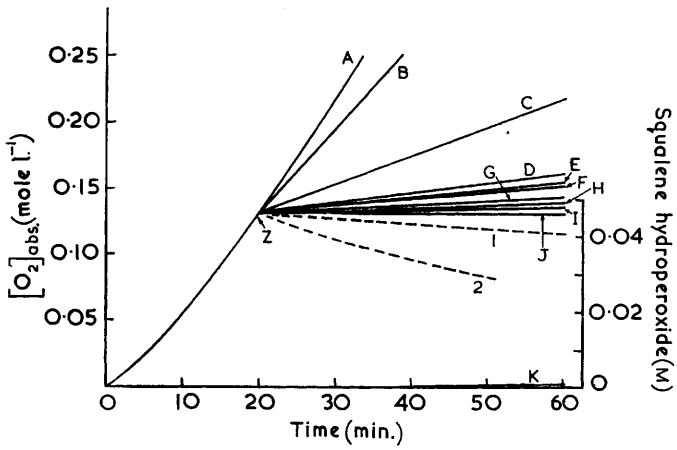


FIG. 4. Effect of various additives added at (Z) on the autoxidation of autoxidizing squalene at 75°.

(A) No addition, or $Bu^t{\cdot}SO{\cdot}Me$ (0·25M), or $Bu^t{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}SO{\cdot}Me$ (0·01M) added initially.
(B) $Bu^t{\cdot}SO{\cdot}S{\cdot}Bu^t$ (0·005M), or $CMe_2{:}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr^i$ (0·005M), or $Bu^t{\cdot}SO{\cdot}Pr^i$ (0·05M) and stearic acid (0·05M).
(C) $CMe_2{:}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr^i$ (0·05M) and stearic acid (0·25M).
(D) $Bu^t{\cdot}SO{\cdot}Pr^i$ (0·05M), or $Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$ (0·05M) and stearic acid (0·25M).
(E) Bu^t_2SO (0·05M) and stearic acid (0·25M).
(F) β-Naphthol (0·005M).
(G) $CMe_2{:}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr^i$ (0·05M).
(H) Bu^t_2SO (0·005M) or $Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$ (0·05M or 0·005M).
(I) $Bu^t{\cdot}SO{\cdot}S{\cdot}Bu^t$ (0·05M).
(J) Bu^t_2SO (0·05M).
(K) $Bu^t{\cdot}SO{\cdot}Pr^i$ (0·008M) or Bu^t_2SO (0·008M), both added initially.
(1) Variation of hydroperoxide content for $Bu^t{\cdot}SO{\cdot}Pr^i$ (0·05M) or $CMe_2{:}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr$ (0·05M).
(2) Variation of hydroperoxide content for $Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$ (0·05M) or Bu^t_2SO (0·05M).

greater than that required to give marked inhibition) interferes with the initiating action of the hydroperoxide without otherwise affecting it.

This conclusion, that the primary source of the inhibition lies, not in removal of hydroperoxide, but in some form of molecular association between the SO compound and the hydroperoxide, is consistent with the further fact that addition of stearic acid, which bonds strongly with sulphoxides and thiolsulphinates and can thus disrupt their complex-formation with hydroperoxide, counteracts their inhibitory action. The extent to which this effect occurs depends, as would be expected, on the power of the inhibitor. With isopropyl t-butyl sulphoxide, an equivalent amount of stearic acid almost eliminates the inhibition; with the more active 1,3-dimethylbut-2-enyl isopropyl sulphoxide a higher

proportion of acid achieves the same result, while very active compounds such as di-t-butyl sulphoxide and 4,4-dimethyl-1-t-butylsulphinylpentan-3-one are considerably more resistant (Fig. 4). Consistently, any given SO compound inhibits more efficiently the earlier it is added during autoxidation, its concentration relative to hydroperoxide being then greater, and this ratio must usually be about unity for substantial inhibition to result. The exceptions are di-t-butyl sulphoxide and 4,4-dimethyl-1-t-butylsulphinylpentan-3-one which are similarly active when the ratio is about 0·1—an anomaly of obvious theoretical and practical significance which has yet to be understood.

The main problem remaining is to ascertain why inhibitory activity depends so greatly

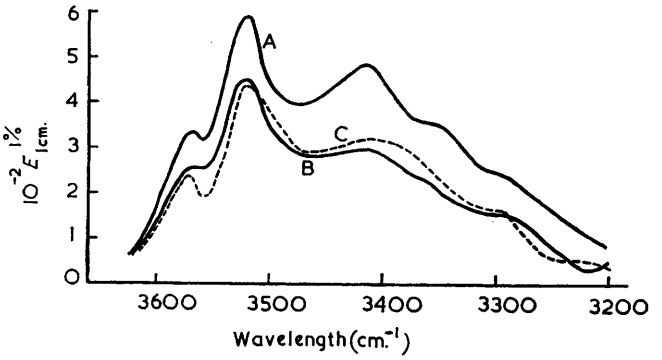


FIG. 5.

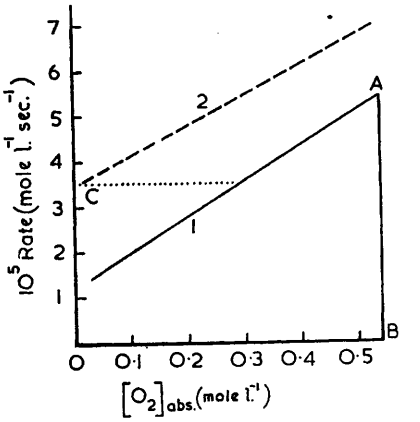


FIG. 6.

FIG. 5. Infrared spectra of autoxidized squalene.

(A) Autoxidised squalene (2·0% of combined oxygen by wt.).
(B) Product from (A) treated for 15 min. with Bu^t_2SO (0·2M) at 55° in oxygen (no absorption) and then washed with water.
(C) Product from (A) treated for 15 min. with Bu^n_2SO (0·2M) at 55° in nitrogen and then washed with water.

FIG. 6. Autoxidation at 55° of squalene and of oxidized squalene after treatment with sulphoxides.

(1) Squalene alone. Addition of Bu^t_2SO at (A) immediately reduced rate to zero (B).
(2) (i) Product from above system after rate reduced to zero as at (B), freed from sulphoxide. Also
(ii) product from system similar to 1 but with Bu^n_2SO which has no effect on the rate, added instead of Bu^t_2SO at (A), also freed from sulphoxide.

Note: The high rate at (C) compared with zero at (B) results simply by removal of the active sulphoxide. The rate at (C) corresponds to the rate on curve 1 at the same hydroperoxide content.

on the substituents R′ and R″ in R′·SO·R″. In sulphoxides, R′ must be a t-alkyl or a 1,3-dialkylallyl group and R″ a t- or an s-alkyl group for high activity; if R′ = R‴S, as in thiolsulphinates, then activity is more generally possessed, though it is greater with alkyl than with aryl substituents. Perhaps even more striking is that in keto-sulphoxides,[1] R′·SO·$[CH_2]_n$·CO·R″, high activity appears when $n = 2$ but is generally absent when $n = 1$ or 3. As yet no relation is discernible between these very marked and critically determined differences and other known properties of the respective SO groups, *e.g.*, their hydrogen-bonding propensity or ionic character as determined spectroscopically. The only recognisable correlation is that high inhibitory activity goes in hand with (*a*) the

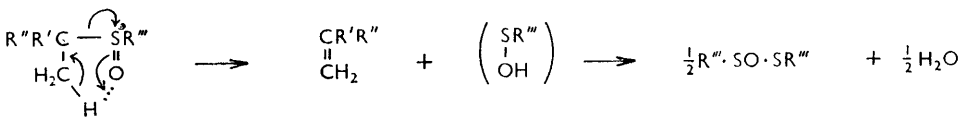
power to promote hydroperoxide decomposition (p. 3573), and (*b*) thermal instability (see Table).

Comparison of the thermal decomposition of sulphoxides heated at 75° for 16 hours with their effect on the autoxidation of squalene at 75°.

Sulphoxide	Decompn. (%)	Retardation [2] ratio *	Sulphoxide	Decompn. (%)	Retardation ratio *
Me_2SO	0	1	$Bu^t{\cdot}SO{\cdot}Pr^i$	15	120
Et_2SO	0	1	$CMe_2{\cdot}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr^i$	47	310
Pr^i_2SO	0	1	$Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$	48	90
Bu^n_2SO	0	1	$Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Me$...	76	120
$(Ph{\cdot}CH_2{\cdot}CH_2)_2{\cdot}SO$	0	1	Bu^t_2SO	100	144
$Bu^t{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}SO{\cdot}Me$	<5	1			

* Calc. from the time to 0·1% oxygen uptake at an additive concn. of 0·01M.

As already discussed, the inhibition is not directly explicable as decomposition of the initiating hydroperoxide, but appears to reflect a looser interaction of which the induced decomposition is a further and fuller manifestation—this is under investigation. In sulphoxides, ease of thermal decomposition appears to require that a suitably activated C–H bond be in the β-position to the SO group so that intramolecular hydrogen-transfer can occur: [9]



The possibility thus raised that sulphoxides act merely as a source of thiolsulphinates is disproved by the fact that addition of an active sulphoxide to an autoxidizing olefin causes *immediate* inhibition, and that some sulphoxides are more active than the thiolsulphinates derived from them (cf. curves H and B of Fig. 4).

In dialkyl sulphoxides, the sulphur and α-carbon atoms must be heavily alkylated, as in di-t-butyl sulphoxide, for this decomposition to proceed most easily. It is apparently necessary to combine the inductive influence of one t-butyl group on the polarization of the S=O bond with the proneness to olefin-elimination in the other to secure the required driving force. The importance of the second contribution is evident from the activity of 1,3-substituted allyl and γ-keto-sulphoxides in which H-atom transfer is promoted by the greater urge towards elimination of a conjugated diene or vinyl ketone, respectively, with the nature of R''' less critical:

Indicative of electronic interaction leading to the transition state formulated is that a γ-keto-sulphoxide containing a CMe_2 group, and not a CH_2 group, adjacent to the keto-group is of much greater thermal stability (see Table), is relatively unreactive towards hydroperoxides (Fig. 3), and does not inhibit the autoxidation of squalene (Fig. 4). There is thus strong evidence that this electronic interaction is the source of, or is intimately connected with, the distinctive properties of the active sulphoxides. Since the inhibitory action of these compounds involves association with hydroperoxide molecules and since stearic acid interferes with this, there can be no doubt that the SO group is the functional site in the inhibition—a conclusion consistent with the exactly parallel behaviour of thiol-sulphinates as oxidation inhibitors (a parallelism which does not extend to vinyl polymerisations, which are inhibited by thiolsulphinates but not by sulphoxides—reflecting

[9] Colclough and Cunneen, *Chem. and Ind.*, 1960, 626.

the availability of a sulphidic-sulphur atom in the former for polymer-radical attack).[5] Why such a subtle modification of the SO group as is imposed by the postulated activation process or by an adjacent sulphur atom is required for an inhibition reaction of the type envisaged remains inexplicable, although it becomes understandable that this reaction should also be sensitive to the nature of the hydroperoxide and to experimental conditions such as temperature.[2] For efficacy in this reaction, the choice of SO compound for a given system under given conditions will therefore vary and be limited.

Experimental

Oxidation Procedure.—Measurements of oxygen absorption were carried out at 760 mm. oxygen pressure in an apparatus previously described.[10] The method used for studying the effect of antioxidants on autoxidizing squalene involved interruption of the oxidation. Freshly chromatographed squalene (*ca.* 0·5 g.) was autoxidized for 20·0 min. at 75·0° and then added to a second oxidation vessel containing the additive, and the autoxidation was restarted. Curve A in Fig. 4 corresponds to an uninterrupted autoxidation of squalene. It was found that interruption caused a slight retardation (*ca.* 2 min.) on the overall time to an absorption of 0·27 mole $l.^{-1}$.

Infrared Spectra.—These were recorded on a Hilger H.800 double-beam spectrometer.

Analytical Procedures.—t-Butyl hydroperoxide was estimated by the stannous chloride method of Barnard and Hargrave,[11] except that iodine was used instead of potassium dichromate to estimate the excess of stannous chloride. Experiments with synthetic mixtures of the hydroperoxide and sulphur compounds showed that quantitative results were obtained by this method.

Squalene hydroperoxide in the presence of sulphur compounds was estimated iodometrically [12] (Fig. 4); similar results were obtained colorimetrically by the oxidation of ferrous to ferric thiocyanate,[4] but variable results were obtained by the stannous chloride method.[11]

Decomposition of t-Butyl Hydroperoxide.—Aliquot parts (5 ml.) of benzene solutions of the hydroperoxide and additives were degassed, sealed *in vacuo*, and heated at 75°. If the reactions were carried out in the presence of air the rate of hydroperoxide decomposition was slightly increased.

Thermal Decomposition of Sulphoxides.—Aliquot parts (5 ml.) of carbon tetrachloride solutions (*ca.* 0·1M) of the sulphoxides were sealed under nitrogen and heated at 75°. They were analysed either volumetrically [11] or spectroscopically from the sulphoxide bands at: 1038 $cm.^{-1}$ (Bu^t_2SO); 1045 $cm.^{-1}$ ($Bu^t{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}SO{\cdot}Me$); 1046 $cm.^{-1}$ ($Bu^t{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Bu^t$); 1048 $cm.^{-1}$ ($Bu^t{\cdot}SO{\cdot}Pr^i$); 1054 $cm.^{-1}$ ($CMe_2{:}CH{\cdot}CHMe{\cdot}SO{\cdot}Pr^i$); or 1060 $cm.^{-1}$ ($Me{\cdot}CO{\cdot}[CH_2]_2{\cdot}SO{\cdot}Me$.) No correction was made for bond overlap or hydrogen bonding, the percentage decomposition being obtained directly from the ratios of optical densities before and after heating.

Squalene.—This was purified as previously described.[2]

αα′-Azoisobutyronitrile and Benzoyl Peroxide.—These were purified by successive precipitations from chloroform solution with light petroleum (b. p. <40°), and methanol, respectively.

t-Butyl Hydroperoxide.—This was purified through its sodium salt [13] until it was 98—100% pure, as estimated by the stannous chloride method.[11] This purity was confirmed by gas–liquid chromatography with dinonyl phthalate as stationary phase.

t-Butyl Phenylperacetate.—The perester (Found: C, 70·0; H, 7·7. Calc. for $C_{12}H_{16}O_3$: C, 69·3; H, 7·7%) was prepared as previously described.[14]

Sulphoxides and Keto-sulphoxides.—Except for the new keto-sulphoxide described below, all the sulphoxides and keto-sulphoxides were prepared as described in Parts X [2] and XII [1] and had the physical characteristics given therein.

2,2,4,4-Tetramethyl-1-methylsulphinylpentan-3-one.—The Grignard reagent obtained from 2-chloro-2-methylpropane (5·0 mole) and magnesium (5·0 g.-atom) in dry ether (1·2 l.) was cooled to −30° and a solution of 2-methylpropanal (4·9 mole) in dry ether (500 ml.), cooled to −10°, was added with stirring during 3 hr. The complex was decomposed by addition to

[10] Bateman and Cunneen, *J.*, 1955, 1596.
[11] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 536.
[12] Bateman and Hughes, *J.*, 1952, 4594.
[13] Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205.
[14] Bartlett and Hiatt, *J. Amer. Chem. Soc.*, 1958, **80**, 1398.

hydrochloric acid (600 ml.), water, and ice, and the product isolated in the usual way. Distillation gave a large fore-run, followed by 2,2,4-trimethylpentan-3-ol (116 g.), b. p. 78·5—82°/60 mm., n_D^{20} 1·4288 (Found: C, 74·2; H, 14·3. Calc. for $C_8H_{18}O$: C, 73·8; H, 13·9%), purity 98% by gas–liquid chromatography. This alcohol (0·57 mole) was oxidized by the method of Lauchenauer and Schinz; [15] it was heated with aluminium isopropoxide (0·19 mole) at 130°/500 mm. for 2 hr., then at 140°/400 mm. for a further 2 hr. Cinnamaldehyde (1·15 mole) was added during 45 minutes, during which the bath-temperature was raised to 180° and the pressure lowered to 300 mm. The pressure was finally lowered to 100 mm. until no more product distilled. The mixture so obtained was heated under reflux for 3 hr. with an excess of benzoyl chloride. Distillation gave 2,2,4-trimethylpentan-3-one (27 g.), b. p. 134—137°, n_D^{20} 1·4076 (Found: C, 74·8; H, 12·8. Calc. for $C_8H_{16}O$: C, 74·9; H, 12·6%), purity 99·9% by gas–liquid chromatography. Finely powdered sodamide (0·16 mole) was added slowly to 2,2,4-trimethylpentan-3-one (0·16 mole) in boiling benzene (175 ml.), and refluxing continued for a further 2½ hr., during which a gelatinous yellow precipitate appeared. Chloromethyl methyl sulphide (0·16 mole) was added slowly to the refluxing mixture, the precipitate changing to white. The cooled mixture was poured into water (250 ml.), the layers were separated, and the aqueous layer was saturated with salt and washed with ether (4 × 30 ml.). The combined benzene and ether layers were washed with 2N-sulphuric acid and water, and dried ($MgSO_4$). Distillation of the solvent residue gave *2,2,4,4,-tetramethyl-1-methylthiopentan-3-one* (8 g.), b. p. 103—103·5°/10 mm., n_D^{20} 1·4750 (Found: C, 63·6; H, 10·5; S, 17·3. $C_{10}H_{20}OS$ requires C, 63·8; H, 10·7; S, 17·0%), purity 92 area % by gas–liquid chromatography; the impurities were not identified. Oxidation of the sulphide with hydrogen peroxide in acetone [16] gave a product which on distillation at 50°/0·001 mm. from a pot still on to a cold-finger at −80° yielded *2,2,4,4,-tetramethyl-1-methylsulphinylpentan-3-one*, a colourless liquid, n_D^{20} 1·4853 (Found: S, 15·4; SO 23·5. $C_{10}H_{20}O_2S$ requires S, 15·7, SO 23·5%).

Decomposition of Di-t-butyl Sulphoxide.—Decomposition of the sulphoxide for 28 hr. at 75° under a stream of nitrogen gave water and isobutene. The latter was characterised by treatment with 2,4-dinitrobenzenesulphenyl chloride; the derivatives so obtained had m. p. 86° (Found: C, 41·1; H, 3·7; Cl, 12·4; S, 11·2. Calc. for $C_{10}H_{11}ClN_2O_4S$: C, 41·3; H, 3·8; Cl, 12·2; S, 11·0%) after crystallization from ethanol.[17] The residue consisted of t-butyl 2-methylpropane-2-thiolsulphinate (86%) and unchanged sulphoxide (14%) (Found: C, 50·1; H, 9·5; S, 30·1. Calc. for the mixture: C, 50·9; H, 9·6; S, 30·9%). Sulphoxide was removed from the residue by extraction with water and the thiolsulphinate so obtained was purified by crystallization from light petroleum (b. p. <40°) at *ca.* −45°. Its infrared spectrum was identical with that of the synthetic compound.[2]

The rate of decomposition of the sulphoxide at 75° was followed in chloroform and in carbon tetrachloride by measurement of the intensity of absorption due to SO (at 1008 cm.$^{-1}$ in chloroform and at 1038 cm.$^{-1}$ in carbon tetrachloride). Concurrently the formation of t-butyl 2-methylpropane-2-thiolsulphinate was estimated from the intensity of absorption due to SO·S (at 1050 cm.$^{-1}$ in chloroform and 1078 cm.$^{-1}$ in carbon tetrachloride). The rate of decomposition was of the first-order in both solvents (carbon tetrachloride, $k = 7·5 \times 10^{-5}$ sec.$^{-1}$ at initial concn. of 0·11 and 0·44M; chloroform, $k = 2·5 \times 10^{-5}$ sec.$^{-1}$ at an initial concn. of 0·12M), and *ca.* 0·5 mole of thiolsulphinate was obtained for each molecule of sulphoxide decomposed.

On decomposition of the sulphoxide for 16 hr. in benzene at 75°, 0·48 mole of water (determined by titration with the Karl Fischer reagent) was formed for each mole of sulphoxide decomposed.

The authors are indebted to Mr. G. Higgins for the spectroscopic data.

The Natural Rubber Producers' Research Association,
48–56, Tewin Road,
Welwyn Garden City, Herts. [*Received, February 27th*, 1962.]

[15] Lauchenauer and Schinz, *Helv. Chim. Acta*, 1949, **32**, 1265.
[16] Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 476.
[17] Kharasch and Buess, *J. Amer. Chem. Soc.*, 1949, **71**, 2724.