Oxidation of Organic Sulphides. Part III. A Survey of the Autoxidizability of Monosulphides.*

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The reactivity of a variety of organic monosulphides towards molecular oxygen has been investigated at temperatures from 45° to 75°. Formally saturated sulphides by themselves are inert, allylic acyclic sulphides react initially much faster than comparable unsaturated hydrocarbons, and allylic and vinylic cyclic sulphides are still more reactive. Oxygen absorption is promoted by light, by the free-radical catalyst αα'-azo*iso*butyronitrile, and by certain metallic compounds, but not by peroxides. The azo-compound is sufficiently active to catalyse the oxidation of saturated sulphides having C–H bonds adjacent to the sulphur atom, while aryl alkyl sulphides also respond to photo-catalysis.

A notable feature of these autoxidations is the self-inhibition or strong retardation which generally becomes apparent at small oxygen uptakes.

Certain mechanistic details which can be deduced from the experimental findings are discussed.

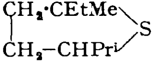
The reactivity of organic sulphides towards molecular oxygen has not hitherto been investigated despite its relevance to important industrial problems. Chief amongst these is the oxidative ageing of ordinary (sulphur-cured) rubber vulcanisates, and here the omission has been partly deliberate in the sense that a rational approach has only become possible with recent advances in the understanding of the mode of sulphur combinations (see Bateman, Glazebrook, Moore, and Saville, Proc. Third Internat. Rubber Tech. Conf., London, 1954, in the press).

This paper reports a survey of autoxidizability of a number of saturated and unsaturated, cyclic and acyclic, monosulphides. We propose later to consider the influence of multi-sulphur linkages, the nature of the oxidation products, and the olefin–sulphide co-oxidation system which a sulphur vulcanisate exemplifies.

Experimental

Alkyl- and Phenyl-substituted Sulphides.—Dibutyl, dibenzyl, and diphenyl sulphides were commercial specimens purified by conventional methods. Benzyl *n*-propyl, methyl 1-phenylethyl, and diphenylmethyl methyl sulphides were synthesized by standard methods. *n*-Butyl methyl and *cyclo*hexyl methyl sulphides and 2-ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane were kindly provided by Mr. J. Ford, Dr. D. Barnard, and Mr. R. W. Glazebrook, respectively. The purified sulphides (see below) were characterized physically as shown in Table 1; their purity was checked by analysis in all cases, but these data are given for the new compounds only.

Table 1.

			C (%)		H (%)		S (%)	
	B. p./mm.	n_D^{20}	Found	Reqd.	Found	Reqd.	Found	Reqd.
$Bu^n{\cdot}SMe$	122·5°/760	1·4475	—	—	—	—	—	—
$Bu^n{\cdot}SBu^n$	71°/14	1·4525	—	—	—	—	—	—
cyclo-$C_6H_{11}{\cdot}SMe$	62·5°/13	1·4945	—	—	—	—	—	—
 (I)	87°/10	1·4760	—	—	—	—	—	—
$Ph{\cdot}SPh$	95°/0·02	1·6320	—	—	—	—	—	—
$Ph{\cdot}CH_2{\cdot}SPr^n$	110°/12	1·5429	72·2	72·2	8·5	8·5	19·5	19·6
$Ph{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph$	(M. p. 49·5°)	—	—	—	—	—	—	—
$Ph{\cdot}CHMe{\cdot}SMe$	89°/12	1·5510	71·1	71·1	8·0	7·9	21·1	21·0
$Ph_2CH{\cdot}SMe$	(M. p. 33°)	—	78·6	78·5	6·7	6·6	15·0	15·0

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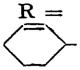
* Part II, *Proc. Roy. Soc.*, 1954, *A*, **224**, 399.

Allylic Acyclic Sulphides.—These were prepared by treatment of the corresponding allylic chloride or bromide with the sodium salt of the appropriate thiol in alcohol. Where necessary the chlorides were subjected to high-efficiency fractionation to ensure isomeric homogeneity (tested by infra-red spectroscopy). Conditions of halide replacement were chosen to ensure direct (S_N2) substitution. No difficulty was experienced with concomitant alcoholysis. The sulphides were washed with water and then fractionated through high-efficiency columns, and contained no detectable amounts of possible isomers as revealed by their infra-red spectra. Their preparation by reaction of a halide with a suspension of the sodium salt of a thiol in benzene or toluene is to be avoided as the sulphide–hydrocarbon azeotropes often obtained on subsequent fractionation are difficult to separate.

The *cyclo*hexenyl and cinnamyl sulphides were kindly provided by Dr. F. W. Shipley (see following paper) and Dr. D. Barnard, respectively.

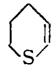
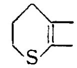
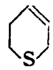
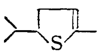
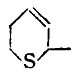
Physical properties and analyses are recorded in Table 2.

TABLE 2.

			C (%)		H (%)		S (%)	
	B. p./mm.	n_D^{20}	Found	Reqd.	Found	Reqd.	Found	Reqd.
$CH_2{:}CH{\cdot}CH_2{\cdot}SBu^n$	73°/14	1·4677	—	—	—	—	—	—
$(CH_2{:}CH{\cdot}CH_2)_2S$	33°/16	1·4905	—	—	—	—	—	—
$CH_2{:}CH{\cdot}CHMe{\cdot}SBu^n$ ...	61°/15	1·4655	—	—	—	—	—	—
$CHMe{:}CH{\cdot}CH_2{\cdot}SMe$ ...	126°/760	1·4780	58·9	58·8	9·9	9·9	31·1	31·3
$CHMe{:}CH{\cdot}CH_2{\cdot}SBu^n$ ...	72°/14	1·4742	—	—	—	—	—	—
$CHMe{:}CH{\cdot}CH_2{\cdot}SPh$ ...	50°/0·1	1·5695	—	—	—	—	—	—
$CHMe{:}CH{\cdot}CHMe{\cdot}SMe$	138°/749	1·4707	62·0	62·0	10·4	10·4	27·6	27·6
$CHMe{:}CH{\cdot}CHMe{\cdot}SPr^n$	60°/13	1·4688	66·4	66·6	11·2	11·1	22·3	22·3
$CHMe{:}CH{\cdot}CHMe{\cdot}SPr^i$	55°/17	1·4650	66·4	66·6	11·2	11·1	22·2	22·3
$CHMe{:}CH{\cdot}CHMe{\cdot}SBu^n$	81°/15	1·4688	68·2	68·3	11·5	11·4	20·1	20·3
$CHMe{:}CH{\cdot}CHMe{\cdot}SBu^t$	66·5°/13	1·4660	68·1	68·3	11·3	11·4	20·2	20·3
$CHMe{:}CH{\cdot}CHMe{\cdot}SPh$	118°/14	1·5542	73·9	74·1	7·9	7·9	18·1	18·0
R =  $R{\cdot}SMe$	64·5°/14	1·5210	—	—	—	—	—	—
$R{\cdot}SEt$	76°/14	1·5140	—	—	—	—	—	—
$R{\cdot}SPr^i$	84°/14	1·5062	—	—	—	—	—	—
$R{\cdot}SBu^t$	97°/14	1·5015	—	—	—	—	—	—
$R{\cdot}SPh$	82°/0·005	1·5929	—	—	—	—	—	—
$CHPh{:}CH{\cdot}CH_2{\cdot}SBu^n$ ...	100°/0·05	1·5660	—	—	—	—	—	—
$CHPh{:}CH{\cdot}CH_2{\cdot}SPh$ ...	(M. p. 77—78°)	—	—	—	—	—	—	—

Unsaturated Cyclic Sulphides.—The unsubstituted thia*cyclo*hexenes were prepared by Mr. J. Ford according to published procedures; the synthesis of the remaining examples will be described elsewhere (Bateman and Glazebrook, forthcoming publication) : see Table 3.

TABLE 3.

	B. p./mm.	n_D^{20}		B. p./mm.	n_D^{20}
 (II)	142·5°/758	1·5330	 (IV)	66°/10	1·5280
 (III)	36°/12	1·5346	 (V)	64°/10	1·4932
	50°/10	1·5258			

Treatment of Sulphides with Alumina.—Immediately before use, the neat sulphides were run through alumina contained in a silica tube under an atmosphere of oxygen-free nitrogen. The treatment eliminated variable induction periods and minor variations in oxidation rates.

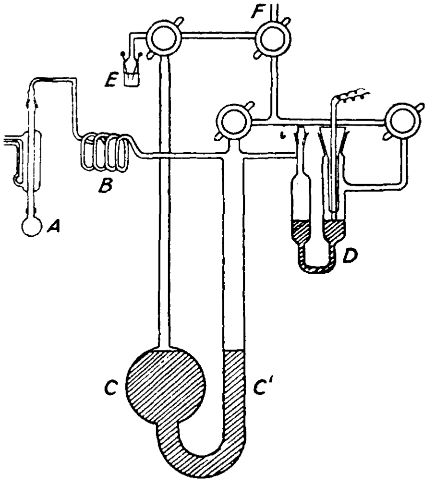
Other Materials.—*n*-Butyl cinnamyl sulphoxide, prepared and purified as described by Barnard and Hargrave (*Analyt. Chim. Acta*, 1951, **5**, 536), had m. p. 66°. Cinnamaldehyde (n_D^{20} 1·6195) and dibutyl disulphide (n_D^{20} 1·4934) were commercial samples purified by fractionation. 4-Ethylthiobutan-2-one (n_D^{20} 1·4724) and 3-ethylthiobutanal (n_D^{20} 1·4750) were prepared by addition of ethanethiol to methyl vinyl ketone and crotonaldehyde, respectively.

Commercial specimens of quinol (m. p. 170·5°), 2 : 6-di-*tert.*-butyl-*p*-cresol (OH = 1) (m. p. 69·5—70·5°), α-naphthol (m. p. 94·5°), and phenyl-β-naphthylamine (m. p. 107·5°) were recrystallized to constant m. p. αα′-Azo*iso*butyronitrile was purified by successive precipitations from chloroform solutions with light petroleum. Benzoyl peroxide was purified first by crystallization from ether and then by precipitations from chloroform solution with methanol. *tert.*-Butyl and *cyclo*hex-2-enyl hydroperoxides were of the purity described by Barnard and Hargrave (*ibid.*, p. 479).

Cobalt stearate was purchased from Messrs. Boake Roberts Ltd. and was used directly. The iron and copper phthalocyanines were highly purified samples, kindly supplied by Professor R. P. Linstead.

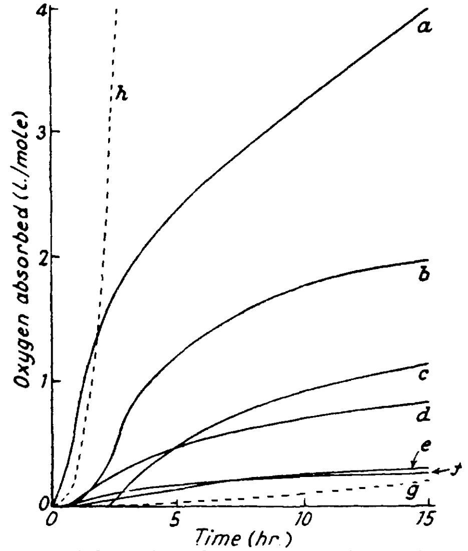
Oxidation Procedure.—A constant-pressure type of apparatus was employed as shown in Fig. 1. As certain of the cyclic sulphides and those containing the 1 : 3-dimethylallyl group showed a sensitivity to the nature of the containing vessel and possibly also to mercury vapour, all the measurements now reported were made by using a transparent silica reaction vessel and an involatile silicone as the manometric fluid.

FIG. 1. *Apparatus for measuring oxygen absorption.*



A, Silica reaction vessel; B, glass spiral; C, burette with silicone fluid; D, pressure-control device with sodium nitrite in trimethylene glycol as conducting fluid; E, gas generator for pressure equalization; F, outlet to pumps and oxygen supply. A was immersed in a thermostat at the required temperature, the remainder of the apparatus in a tank at 25·00° ± 0·05°. *Rise in limb C′ measured by cathetometer.*

FIG. 2. *Autoxidation of* Bu^{n}SR *at* 75°.



R = (*a*) $CHPh{:}CH{\cdot}CH_2{\cdot}$, (*b*) $CHMe{:}CH{\cdot}CHMe{\cdot}$, (*c*) $CH_2{:}CH{\cdot}CHMe{\cdot}$, (*d*) $CHMe{:}CH{\cdot}CH_2{\cdot}$, (*f*) $CH_2{:}CH{\cdot}CH_2{\cdot}$. *Curves* (*e*), (*g*), *and* (*h*) *refer to diallyl sulphide, methyl oleate, and ethyl linoleate respectively.*

Sulphoxide Estimations.—The oxidized mixtures were analysed for sulphoxide by Barnard and Hargrave's titanous chloride method (*loc. cit.*).

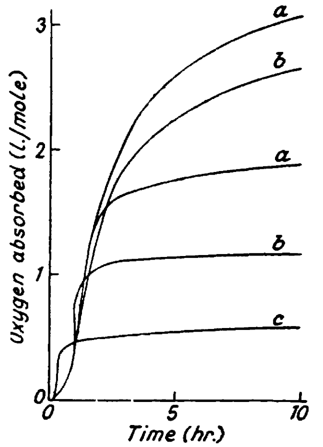
Peroxide Estimations.—The formation of hydroperoxides in the autoxidizing sulphide was tested by the sensitive ferrous thiocyanate method (Bolland, Sundralingam, Sutton, and Tristram, *Trans. Inst. Rubber Ind.*, **1941**, **17**, 29) and was found to be too small for accurate estimation.

The disappearance of hydroperoxides added to the sulphides as potential catalysts was followed by the stannous chloride method (Barnard and Hargrave, *loc. cit.*)

RESULTS

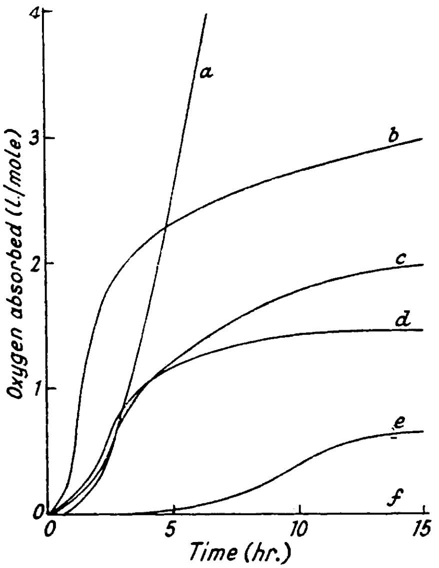
General Characteristics.—Most unsaturated sulphides react readily with oxygen at 75°—much more readily initially than a comparable mono-olefin, and somewhat similarly to a 1 : 4-diolefin (see Fig. 2). In contrast to behaviour with olefins, however, a marked retardation develops at an early stage in the reaction, and oxygen absorption often ceases when only a small fraction of a mole of oxygen has been absorbed. Such intense autoinhibition appears to be unique for autoxidations, although a milder form is not uncommon and is associated with the formation of inhibitory substances as a result of decomposition of the primary product. Two processes therefore contribute to the overall oxidation picture : the first, predominating in the earlier stages, is the interaction between the substrate and oxygen; the second, of increasing importance as reaction proceeds, is the interference caused by the secondary reaction products.

FIG. 3. *Autoxidation of* CHMe:CH·CHMe·SMe *at* 75°.



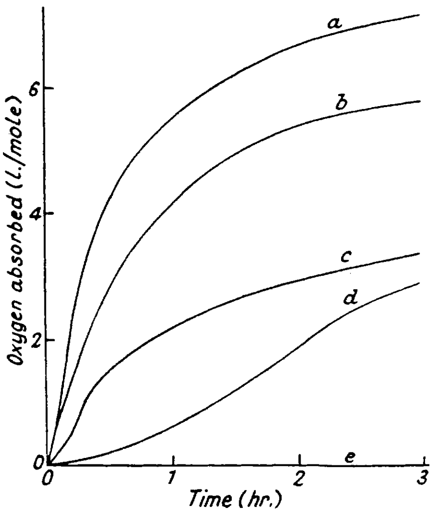
(*a*) *In silica reaction vessel;* (*b*) *in glass reaction vessel;* (*c*) *in the presence of powdered glass.*

FIG. 4. *Autoxidation of* CHMe:CH·CHMe·SR *at* 75°.



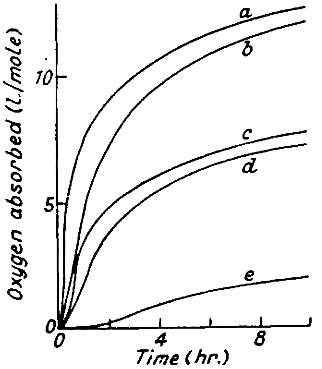
R = (*a*) Ph, (*b*) Me, (*c*) Bu^n, (*d*) Pr^n, (*e*) Pr^i, (*f*) Bu^t (*no uptake*).

FIG. 5. *Autoxidation of* cycloC$_6$H$_9$SR *at* 75°.



R = (*a*) Me, (*b*) Et, (*c*) Ph, (*d*) Pr^i, (*e*) Bu^t (*no uptake*).

FIG. 6. *Autoxidation of unsaturated cyclic sulphides at* 55°.



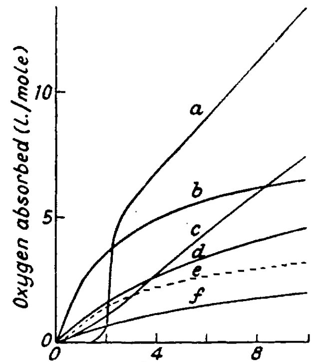
(*a*) 2-*Methyl*-5-iso*propylthia*cyclo*pent*-2-*ene*.
(*b*) 2-*Methylthia*cyclo*hex*-2-*ene*.
(*c*) *Thia*cyclo*hex*-2-*ene*.
(*d*) *Thia*cyclo*hex*-3-*ene*.
(*e*) 2 : 3-*Dimethylthia*cyclo*hex*-2-*ene*.

Only brief reference will be made to the latter here since its detailed consideration requires full product analysis (to be reported later); our present concern is mainly with the response of the primary reaction to structural changes and to catalysts and inhibitors.

Reproducibility.—Care being given to synthesis and purification and to the pre-treatment with alumina immediately before use, no trouble was experienced with most of the sulphides in obtaining reproducible rates and extents of oxygen absorption. A few cases presented difficulties, however, which are illustrated for the worst example (1 : 3-dimethylallyl methyl sulphide) in Fig. 3. In Pyrex vessels, large variations in the total absorptions were observed, with comparatively minor differences in the initial rates of absorption. The use of silica vessels led to a more reproducible but essentially the same initial rate, and reduced, but did not eliminate, the variability in uptake. The addition of powdered glass had a more profound effect, the initial rate being considerably increased and the total uptake being reduced. The glass presumably catalyses the decomposition of a primary product so that inhibitors are formed at an earlier stage than otherwise. 1 : 3-Dimethylallyl *n*-propyl sulphide, but-2-enyl methyl sulphide, and thia*cyclo*hex-2-ene behaved similarly but to a lesser degree; the sensitivity in this respect of the remainder of the sulphides examined was very small. All the results now reported, however, pertain to silica reaction vessels.

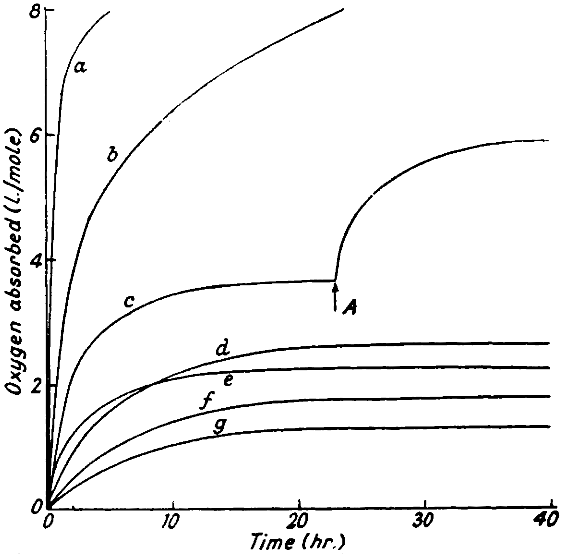
Sulphide Structure and Oxidizability.—Saturated sulphides. The alkyl and phenyl sulphides listed in Table 1 absorbed no oxygen during 24 hr. at 75°. More surprisingly (see below), the benzyl- and diphenylmethyl-substituted compounds were found to be similarly inert. The catalysed oxidation of these sulphides is discussed below.

FIG. 7. *Catalysed autoxidations of* $\mathrm{CHPh{:}CH{\cdot}CH_2{\cdot}SBu^n}$ *at* 75° (1% *by wt. of additive*).



(*a*) *Iron phthalocyanine.*
(*b*) *αα′-Azo*iso*butyronitrile.*
(*c*) *Cobalt stearate.*
(*d*) *Copper phthalocyanine.*
(*e*) *No catalyst, or* cyclo*hex-2-enyl hydroperoxide or* tert.*-butyl hydroperoxide.*
(*f*) *Benzoyl peroxide.*

FIG. 8. *Autoxidation of sulphides catalysed by αα′-azo*iso*butyronitrile* (1% *by wt.*) *at* 75°.



(*a*) cyclo*Hex-2-enyl methyl sulphide.*
(*b*) $\mathrm{CHPh{:}CH{\cdot}CH_2{\cdot}SBu^n}$.
(*c*) $\mathrm{CHMe{:}CH{\cdot}CHMe{\cdot}SMe}$.
(*d*) 2-*Ethyl-2-methyl-5-*iso*propylthia*cyclo*pentane.*
(*e*) $\mathrm{CHMe{:}CH{\cdot}CHMe{\cdot}SBu^t}$.
(*f*) $\mathrm{Ph{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph}$.
(*g*) $\mathrm{MeSBu^n}$. *At A a further* 1% *of catalyst was added.*

Acyclic allylic sulphides. (*a*) Effect of substitution on the allyl system. Allyl *n*-butyl sulphide and diallyl sulphide react rather slowly with oxygen at 75° and reaction virtually ceases at about 0·3 l./mole (Fig. 2). Marked increases in both the rate and extent of absorption occur on progressive substitution of methyl and phenyl into the allyl unit (Fig. 2). The differences are qualitatively parallel to those associated with analogous substitutional changes in unsaturated hydrocarbons (Bolland, *Trans. Faraday Soc.*, 1950, **46**, 358).

(*b*) Influence of the alkyl substituent in allyl alkyl sulphides. Changes in the saturated or quasi-saturated component in an allyl alkyl sulphide can produce large changes in reactivity, as illustrated for 1 : 3-dimethylallyl and *cyclo*hexenyl compounds in Figs. 4 and 5 respectively. Through the series, methyl, ethyl, *iso*propyl, *tert.*-butyl, the oxidizability decreases progressively until with the last substituent the compounds behave as though they were saturated, *i.e.*, are of negligible reactivity under the experimental conditions. The possibility that the more bulky substituents sterically hinder the approach of reactants to the activated methylene group adjacent to the sulphur atom was shown to be of limited validity by the comparable response of the nalogous amethyl and *tert.*-butyl compounds to catalysis by azo*iso*butyronitrile (see Fig. 8).

It thus appears that the decrease in autoxidizability reflects some intrinsic antioxidant activity by the sulphide itself.

Cyclic sulphides. Compared with comparable acyclic compounds, unsaturated cyclic sulphides are oxidized much more rapidly and show less intense auto-inhibition (see Fig. 6, which gives absorption characteristics at 55°, not 75°, as for the acyclic sulphides). This is especially so for a substituted thia*cyclo*pentene with vinylic unsaturation.

Catalysts and Inhibitors.—Effect of different catalyst types. The oxidation of *n*-butyl cinnamyl sulphide is promoted by a number of common oxidation catalysts (Fig. 7). The important and significant exceptions are benzoyl peroxide, *tert.*-butyl hydroperoxide, and *cyclo*hex-2-enyl hydroperoxide. The following experiments show that the catalytic inactivity of the peroxides cannot be attributed to abnormally rapid destruction in the sulphides. (i) *n*-Butyl cinnamyl sulphide (10 ml.), containing *tert.*-butyl hydroperoxide (0·1034 g.), was heated at 75° in the presence of oxygen. Samples withdrawn at intervals of 1, 2, and 6 hr. after mixing had the following proportions of the original peroxide content present: 46, 28, and 15%, respectively. (ii) The above sulphide (10 ml.), containing benzoyl peroxide (0·5 g.), when heated at 75° for 1 hr. had a peroxide content equal to 10% of the original solution.

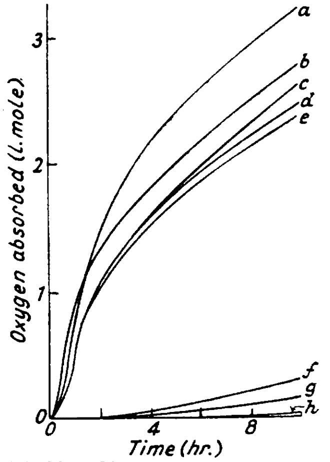


FIG. 9. *Autoxidation of* $CHPh{:}CH\cdot CH_2\cdot SBu^n$ *in the presence of various additives at* 75° (*b—e*, 1% *by wt.*; *f—h*, 0·1% *by wt.*).

(*a*) *No addition.*
(*b*) $CHPh{:}CH\cdot CH_2\cdot SO\cdot Bu^n$.
(*c*) $CHPh{:}CH\cdot CHO$ *or* $Bu^n{}_2S_2$ *or* $EtS\cdot CH_2\cdot CH_2\cdot COMe$.
(*d*) H_2O.
(*e*) $EtS\cdot CHMe\cdot CH_2\cdot CHO$.
(*f*) 2 : 6-*Di*-tert.-*butyl*-p-*cresol.*
(*g*) *Phenyl-β-naphthylamine.*
(*h*) *Quinol or α-naphthol.*

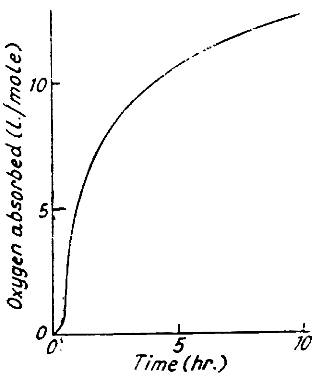


FIG 10. *Autoxidation of* $CHPh{:}CH\cdot CH_2\cdot SPh$ *at* 75°.

*Effect of αα′-azo*iso*butyronitrile on different sulphide types.* As shown in Fig. 8, azo*iso*butyronitrile not only promotes the oxidation of unsaturated sulphides but catalyses the oxidation of otherwise inert saturated types. This is also true of the unsaturated *tert.*-butyl-substituted sulphides, *e.g.*, $CHMe{:}CH\cdot CHMe\cdot SBu^t$. Diphenyl sulphide, which has no alkyl-type C–H bonds, provides an exception in not responding to such catalysis. The function of the azo-compound as a chain initiator is strikingly shown in example (*c*) (Fig. 8), where a reaction which stops when the added catalyst has wholly decomposed re-starts at almost the same rate on the addition of further catalyst (this has been repeated successively several times).

Photocatalysis. Irradiation with a mercury-vapour lamp through silica or Pyrex glass increases the rate of oxygen uptake and reduces auto-inhibition in those sulphides which autoxidize in the dark. Of those which are inert in the dark (p. 1600), benzyl sulphides, but not dialkyl or diphenyl sulphides, undergo photo-oxidation.

Inhibitors. The common amine and phenolic types of oxidation inhibitor strongly retard the autoxidation of *n*-butyl cinnamyl sulphide (Fig. 9). 4-Ethylthiobutan-2-one, a type of compound claimed to be an anti-oxidant for unsaturated natural fats (Thompson, *Ind. Eng. Chem.*, 1951, **43**, 1638), and the related 3-ethylthiobutanal exert little effect, as do the major oxidation products of the sulphide, *viz.*, *n*-butyl cinnamyl sulphoxide, cinnamaldehyde, dibuty disulphide, and water (Barnard, unpublished results; also cf. Bateman and Shipley, *J.*, in the press).

Sulphoxide Formation.—The oxygen uptakes and sulphoxide contents of the various sulphides after reaction with oxygen for 24 hr. under the conditions of the absorption measurements recorded in Figs. 2, 4, 5, 6, and 10, are shown in Table 4. The sulphoxide yields vary with the temperature of oxidation, the trend being illustrated in Table 5.

TABLE 4.

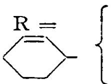
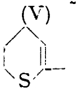
Sulphide	O_2 absorbed (l./mole)	Sulphoxide content (% of absorbed O_2)	Sulphide	O_2 absorbed (l./mole)	Sulphoxide content (% of absorbed O_2)
CHPh:CH·CH_2·SBu^n ...	4·84	23·9	CHMe:CH·CH_2·SBu^n ...	0·78	5·6
CHMe:CH·CHMe·SBu^n	2·33	5·0	$(CH_2$:CH·$CH_2)_2S$	0·36	11·8
CH_2:CH·CHMe·SBu^n ...	1·40	6·6	CH_2:CH·CH_2·SBu^n	0·27	23·0
CHMe:CH·CHMe·SPh ...	6·71	5·7	CHMe:CH·CHMe·SBu^n	2·33	5·0
CHMe:CH·CHMe·SMe ...	3·18	5·5	CHMe:CH·CHMe·SPr^i	0·78	11·0
CHMe:CH·CHMe·SPr^n ...	1·57	5·0	CHPh:CH·CH_2·SPh ...	15·1	9·8
 R·SMe	7·94	13·4	(V)	15·93	17·5
R·SEt	6·40	13·2		13·10	15·0
R·SPh	3·93	4·6	(II)	8·90	20·2
$R·SPr^i$	3·83	13·2	(III)	7·85	52·5
			(IV)	4·52	9·4

TABLE 5. *Yields of sulphoxide in autoxidation of* cyclo*hex-2-enyl methyl sulphide.*

Temp.	Time (hr.)	O_2 absorbed (l./mole)	Sulphoxide content (% of O_2 absorbed)	Temp.	Time (hr.)	O_2 absorbed (l./mole)	Sulphoxide content (% of O_2 absorbed)
35°	73	6·14	24·8	75°	28	7·94	13·4
55	23	8·74	21·3	95	5·5	4·44	13·5

DISCUSSION

The free-radical chain character of the autoxidations is clearly revealed by the catalysis by azo*iso*butyronitrile and by light, and the strong retardation by small additions of common oxidation inhibitors. It follows that the remarkable autoretardation and autoinhibition effects must be attributed to specific interference in the chain initiation or propagation steps by one or more of the reaction products. Details of these processes are at present under investigation.

The relative rates of oxidation of a mono-olefin, a 1 : 4-diolefin, and an allylic sulphide (see Fig. 2) suggest that the doubly activated methylene group is the primary reactive centre in the sulphide; cf. C:C·CH·S with C:C·CH·C:C. Critical support for this conclusion is afforded by cinnamyl phenyl sulphide, which is autoxidized very readily (Fig. 10) and possesses only the above type of potentially active C–H bonds. These considerations discount attack by free radicals at the double bond in the allyl unit (in the primary stage), as does other evidence. First, the effect of substitution in the allyl unit (Fig. 2) parallels the relative changes in α-methylenic activity in olefins (Bolland and Gee, *Trans. Farday Soc.*, 1946, **42**, 224; Bolland, *loc. cit.*; Bateman, *Quart. Reviews*, 1954, **8**, 147); secondly, by suitable catalysis, saturated sulphides—with diphenyl sulphide as a significant exception—can be induced to oxidize similarly to their unsaturated counterparts; thirdly, the formation of polymeric products, which would be expected to result if double-bond attack occurred, is inappreciable in allylic sulphides so far examined, but is substantial in the vinylic sulphide, thia*cyclo*hex-2-ene (Ford, unpublished results), where such attack would be expected.

The inhibitory activity of quinol and related substances demonstrates that peroxy- or oxy-free radicals are involved in the propagation step of the autoxidation, and it is therefore reasonable, and consistent with other features such as product composition (Bateman and

Shipley, *loc. cit.*) and substitutional effects, to envisage an autoxidation mechanism comprising the following reactions :

$$
\begin{aligned}
\mathrm{CHR{:}CH{\cdot}CH_2{\cdot}SR}\ (\mathrm{A}) &\xrightarrow{(-\mathrm{H})} \mathrm{B} && (1)\\
\mathrm{B} + \mathrm{O_2} &\longrightarrow \mathrm{BO_2} && (2)\\
\mathrm{BO_2} + \mathrm{A} &\longrightarrow \mathrm{BO_2H} + \mathrm{B} && (3)\\
\mathrm{BO_2H} &\longrightarrow \mathrm{BO} + \mathrm{OH} && (4)\\
\mathrm{A} + \mathrm{OH} &\longrightarrow \mathrm{B} + \mathrm{H_2O} && (5)\\
\mathrm{BO} &\longrightarrow \mathrm{CHR{:}CH{\cdot}CHO} + \mathrm{RS} && (6)\\
2\mathrm{RS} &\longrightarrow \mathrm{R_2S_2} && (7)
\end{aligned}
$$

where B represents the radical $\mathrm{CHR{:}CH{\cdot}\dot{C}H{\cdot}SR}$, and BO, $\mathrm{BO_2}$, and $\mathrm{BO_2H}$ are the derived radicals and compound. The last would be expected to be highly unstable, of merely transitory existence, decomposing with ease into the aldehyde, water, and disulphide as suggested in reactions (4), (5), (6), and (7).

The formation of sulphoxides as reaction products, sometimes in substantial amount (Table 4), has still to be explained. For this, two supplementary processes are possible. First, since hydroperoxides are known to oxidize sulphides molecularly under conditions comparable with those of autoxidation (Part II, *loc. cit.*), the unstable compound ($\mathrm{BO_2H}$) may react very rapidly with the substrate according to :

$$\mathrm{BO_2H} + \mathrm{A} \longrightarrow \mathrm{BOH} + \mathrm{CHR{:}CH{\cdot}CH_2{\cdot}SOR} \qquad (8)$$

Secondly, the peroxy-radicals may oxidize the combined sulphur atoms, liberating the oxy-radicals (BO) which can then react as in reaction (10) as well as in (6) :

$$
\begin{aligned}
\mathrm{BO_2} + \mathrm{A} &\longrightarrow \mathrm{BO} + \mathrm{CHR{:}CH{\cdot}CH_2{\cdot}SOR} && (9)\\
\mathrm{BO} + \mathrm{A} &\longrightarrow \mathrm{BOH} + \mathrm{B} && (10)
\end{aligned}
$$

Common to both possibilities is that the hemithioacetal (BOH), rather than $\mathrm{BO_2H}$, is the precursor of the oxidation scission products (see above), which is not unreasonable having regard to our meagre knowledge of hemithioacetals (Levi, *Gazzetta*, 1932, **62**, 775; Schubert, *J. Biol. Chem.*, 1936, **114**, 341; Kipnis and Ornfelt, *J. Amer. Chem. Soc.*, 1952, **74**, 1068).

The significant mechanistic feature introduced by reactions (9) and (10) is the designation of the oxy-radical (BO) as the dehydrogenating chain carrier, and this may well be responsible for certain special characteristics of sulphide autoxidation which are at present difficult to explain. Thus, just as the greater oxidizability of aldehydes compared with olefins seems to reflect the greater reactivity of acylperoxy- compared with alkenylperoxy-radicals (Bateman and Morris, *Trans. Faraday Soc.*, 1953, **49**, 1026), so the ease of oxidation of unsaturated sulphides may reflect mainly the high reactivity of BO radicals in reaction (10). This in turn is undoubtedly connected with the surprising lack of catalytic activity by peroxides despite the normal behaviour of azo*iso*butyronitrile. It has been shown that this difference cannot be attributed to rapid destruction of the peroxides in the reaction system, and appears to be explicable only in terms of highly specific reactivity of the radicals derived from the various additives. The inactivity of benzoyl peroxide, which is so generally a free-radical catalyst, is puzzling but not unique, for it fails to promote the decarbonylation of aldehydes whereas alkoxy-radicals are effective (Waters, *Nature*, 1952, **170**, 212).

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