Electron Spin Resonance Studies of Radicals formed during the Thermolysis and Photolysis of Sulphoxides and Thiolsulphonates

By **Chrysosstomos Chatgilialoglu, Bruce C. Gilbert,*** and **Barbara Gill**, Department of Chemistry, University of York, Heslington, York YO1 5DD
Michael D. Sexton, PARAMINS Technology Division, Esso Chemicals Ltd., Esso Research Centre, P.O. Box No. 1, Abingdon, Oxfordshire OX13 6BB

E.s.r. spectroscopy has been employed to characterize radical pathways in the thermal and photolytic decomposition of a variety of diaryl sulphoxides and aryl arenethiolsulphonates ($ArSO_2SAr$). For the sulphoxides, S–C bond cleavage leads to the formation of the delocalized and relatively unreactive sulphinyl radicals ($ArSO\cdot$); their subsequent reaction evidently involves disproportionation to sulphonyl ($ArSO_2\cdot$) and thiyl ($ArS\cdot$) radicals. This pair of radicals is also formed directly in the homolysis of the thiolsulphonates, and the subsequent formation of sulphinyl radicals has been investigated. The results are analysed in terms of the products of the reactions and the efficacy of some of the parent substrates as antioxidants.

In a recent study [1] of the antioxidant action of some alkyl and aryl sulphides in the decomposition of 1-methyl-1-phenylethyl hydroperoxide it was demonstrated that the effective catalyst is sulphur dioxide. It was also shown that the thermal chemistry of sulphur–oxygen compounds (sulphoxides, thiolsulphinates [RS(O)SR], thiolsulphonates [$RS(O)_2SR$]) formed from the sulphides determines whether or not a particular sulphide will catalyse hydroperoxide decomposition.

The products formed from the thermolysis of sulphoxides depend critically upon the structure of the sulphoxide, and in particular, on whether or not there is a β-hydrogen atom. Thus sulphoxides with β-hydrogens undergo predominantly a *syn*-β-elimination to form alkenes [see *e.g.* reaction (1) [2]] and sulphenic acids,[3] as well as thiolsulphinates.[4] In contrast, methyl phenylmethyl sulphoxide gives [2a] benzaldehyde and methanethiol on pyrolysis [reaction (2)]. Homolytic S–C bond cleavage in (1) [reaction (3)] has been proposed [5] to account not only for the formation of the sulphenate (2), thiolsulphonate (3), and 1,2-diphenylethane but also for the racemization of the parent sulphoxide. Diaryl sulphoxides are more stable, and thermal racemization at 473 K is believed to involve a pyramidal inversion mechanism.[6]

Thiolsulphinates are compounds of relatively low thermal stability; as with sulphoxides, the modes of decomposition are structurally dependent, and both β-elimination [7] and disproportionation to thiolsulphonate and disulphide [8] [possibly *via* a radical process, reaction (4)] have been reported. We have previously [9] employed e.s.r. spectroscopy to confirm the production of thiyl and sulphinyl radicals during the thermal (and photochemical) decomposition of some thiolsulphinates and also during peroxidation reactions of thiolsulphinates.

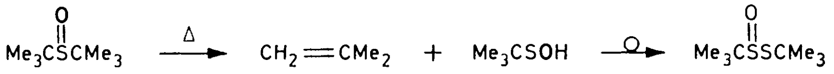
It has been reported that whereas aryl arenethiolsulphonates ($ArSO_2SAr$) are relatively stable to thermolysis,[10a] alkyl alkenethiolsulphonates and alkyl arenethiolsulphonates decompose readily on heating and yield sulphur dioxide and the corresponding monosulphide (together with small amounts of disulphide).[10b] On the basis of kinetic evidence, it was concluded [10b] that the decomposition is not free-radical in nature. On the other hand, as indicated in our preliminary report of the work to be described here,[11] radicals can be detected by e.s.r. spectroscopy during thermolysis reactions of some thiolsulphonates.

Reports of studies of the photolytic decomposition of sulphur–oxygen compounds are less common. One detailed account [12] identifies the products obtained from the direct and sensitized photolysis of a range of dialkyl, dialkenyl, and aryl sulphoxides; the products (which include sulphides, alkanes, disulphides, and alcohols) can be explained in terms of the reactions of initially formed alkyl ($R\cdot$) and sulphinyl radicals ($RSO\cdot$), with the subsequent mediation of sulphenate esters (RSOR) indicated by the identification of products which appear to be derived from reactions of thiyl ($RS\cdot$) and alkoxyl ($RO\cdot$) radicals [including, *e.g.* the photochemical equivalent of reaction (2), in which benzaldehyde and methanethiol are again formed]. E.s.r. studies [13] have confirmed that alkanesulphinyl radicals ($RSO\cdot$) can be detected during the photolysis of dialkyl sulphoxides.

In view of the interest in the thermal and photochemical decomposition of sulphoxides and thiolsulphonates, and since radicals have been proposed as intermediates in many of their reactions, we have carried out an e.s.r. investigation into the *in situ* decomposition of these compounds. Particular emphasis has been placed on the reactions of the diaryl compounds, especially those related to compounds with antioxidant activity.[1]

RESULTS AND DISCUSSION

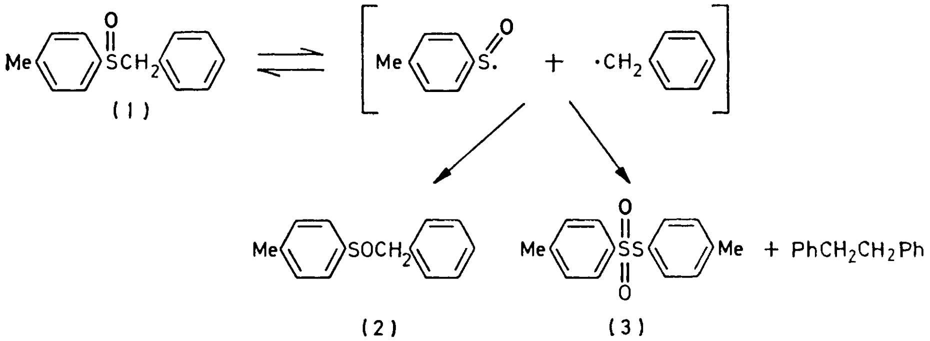
Radicals detected from Sulphoxides.—(a) *On photolysis.* When a solution of diphenyl sulphoxide in methylbenzene was photolysed in the cavity of an e.s.r. spectrometer at low temperature (*ca.* 220 K), an e.s.r. spectrum was detected with a(3H) 0.239, a(2H) 0.07 mT, and g 2.009 1. This is attributed to the benzenesulphinyl radical, $C_6H_5SO\cdot$. Radicals of this type have been detected [14] during the oxidation of disulphides and thiols with ·OH and also in the low-temperature photolysis of sulphinyl chlorides, and the structural assignment has been justified previously.



$$Me_3C\overset{O}{S}CMe_3 \xrightarrow{\Delta} CH_2{=}CMe_2 + Me_3CSOH \xrightarrow{-O} Me_3C\overset{O}{S}SCMe_3$$

(1)

(2)



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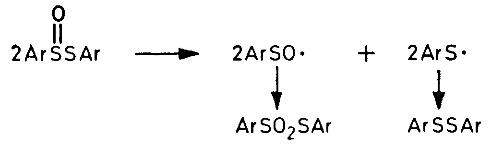


$$2Ar\overset{O}{S}SAr \longrightarrow 2ArSO\cdot + 2ArS\cdot$$

$$2ArSO\cdot \longrightarrow ArSO_2SAr \qquad 2ArS\cdot \longrightarrow ArSSAr$$

(4)

The generality of this behaviour was confirmed when signals from the appropriate arenesulphinyl radicals (5) were detected under similar conditions during the photolysis of a number of diaryl sulphoxides (4), including the antioxidant (4, $R^1 = R^2 = CMe_3$, $X = OH$). The results are shown in Table 1, which also includes spectroscopic parameters for analogous radicals from thiolsulphonates (see later). The splittings are assigned on the basis [14] that the 2- and 4-protons, where present, give rise to the larger splittings and that methyl-group protons have approximately the same splittings as a ring proton at that position, as expected for π-type radicals. Photolysis of bis-(4-nitrophenyl) sulphoxide and bis-(4-methoxyphenyl) sulphoxide gave weak signals with *g ca.* 2.009 1, but hyperfine splittings could not be satisfactorily resolved. [In contrast photolysis of bis-(4-nitrophenyl) sulphoxide in tetrahydrofuran at 207 K led to the

TABLE 1

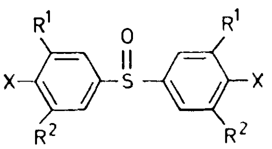
E.s.r. data for sulphinyl radicals (ArSO·)

Radical	T/K	Method of generation [a]	Hyperfine splittings (mT) [b] a(2,6-H)	a(3,5-H)	a(4-H)	$a(CH_3)$	g [c]	Other methods for generation [d]
(5; $R^1 = R^2 = X = H$)	216	A	0.239	0.070	0.239		2.0091	B
(5; $R^1 = R^2 = H$, $X = Me$)	199	A	0.250	0.050		0.250	2.0091	B
(5; $R^1 = R^2 = H$, $X = Br$)	213	B	0.252	*e*			2.0104	A, D
(5; $R^1 = R^2 = H$, $X = NO_2$)	193	B	0.227	*e*			2.0092	A, D
(5; $R^1 = R^2 = H$, $X = OMe$)	*ca.* 210	A	*e*	*e*			2.0091	
(5; $R^1 = R^2 = H$, $X = Cl$)	213	B	0.25 [g]	0.075 [f]			2.0095	
(5; $R^1 = R^2 = CMe_3$, $X = OH$)	255	A	0.227				2.0091	B—D
(5; $R^1 = CMe_3$, $R^2 = Me$, $X = OH$)	255	A	0.20 [g]			0.075	2.0092	C
[$PhCH_2SO\cdot$	203	A	a (2 H)	1.083			2.0107	B]

[a] A, Photolysis of corresponding sulphoxide. B, Photolysis of corresponding thiolsulphonate. C, Thermolysis of sulphoxide. D, Thermolysis of thiolsulphonate. [b] ±0.005 mT. [c] ±0.0001. [d] Method led to less well resolved signals than method specified in Table. [e] Not resolved. [f] And a(Cl) *ca.* 0.045 mT. [g] ±0.01 mT.

detection of a strong signal with a(N) 1.32, a(2H) 0.315, a(2H) 0.10 mT, g 2.004 9; this is assigned to an alkoxy-nitroxide resulting from addition of the radical formed by α-hydrogen abstraction from tetrahydrofuran to an oxygen atom of the nitro-group in the substrate (see, *e.g.* ref. 15); this reaction was not studied further.] The sulphinyl radical (6), with a(2H) 1.083 mT, g 2.010 7, was detected during the photolysis of bis(phenylmethyl) sulphoxide.

In most cases, the spectra could be observed only during photolysis at low temperature, but the more highly substituted aromatic sulphinyl radicals could be readily detected at room temperature. The sulphinyl radicals appear to be formed in the primary photolysis process; thus their concentration did not build up with time after the commencement of photolysis and was found to be proportional to the square root of the incident light intensity (as expected for a primary species which decays bimolecularly).



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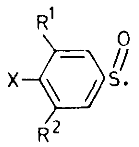

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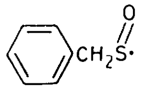

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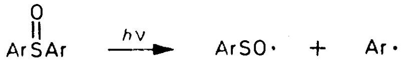
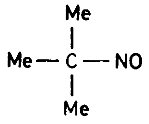
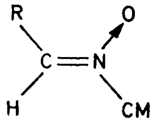


$$\mathrm{Ar\overset{O}{\overset{\|}{S}}Ar} \xrightarrow{h\nu} \mathrm{ArSO\cdot} + \mathrm{Ar\cdot} \qquad (5)$$

The direct detection of sulphinyl radicals on photolysis of diaryl sulphoxides and bis(phenylmethyl) sulphoxide suggests that carbon–sulphur bond cleavage [*e.g.* reaction (5)] has occurred. In an attempt to characterize other radicals which may be formed but which were not detected, we have carried out the photolysis in the presence of the spin traps[16] 2-methyl-2-nitrosopropane (7) and the nitrones (8; R = Ph) and (8; R = H).



(7)



(8)

Evidence that aryl radicals are indeed produced derives from the detection of a signal with a(N) 1.18, a(3H) 0.225, a(2H) 0.09 mT, g 2.006 0 in the photolysis of diphenyl sulphoxide in methylbenzene at 200 K in the presence of (7); this is assigned to the adduct PhN(CMe_3)O·[17] {in this experiment, as with others in which Me_3CNO was employed, strong signals from $(Me_3C)_2NO\cdot$ [with a(N) 1.525 mT, g 2.006 0] were also detected}. Analogous signals were also detected during the photolysis of bis-(4-methylphenyl) sulphoxide and bis-(4-nitrophenyl) sulphoxide in the presence of (7) [unambiguous analysis was possible for the latter case; the aryl-radical adduct had a(N) 1.185, a(2H) 0.215, a(2H) 0.09 mT, g 2.006 1]. Aryl radical-adducts of (8; R = Ph), which would be expected[18] to have a(N) *ca.* 1.38 and a(1H) 0.21 mT were not detected, though any such signals may have been obscured by other nitroxides produced.

Photolysis of some of the sulphoxides studied in the presence of spin traps gave strong signals due to species which were clearly not those of aryl adducts; examples are listed in Table 2. Those radicals formed from (7) which have high a(N) values (*ca.* 1.8 mT) and g values (*ca.* 2.006 7) are assigned to arylthiyl radical-adducts ArSN(CMe_3)O·;[19] we have also generated these by photolysis of disulphides in the presence of (7) under similar conditions (see Table 2). Signals with a(N) 1.2 mT, g 2.006 0, which accompany the thiyl-adducts signals are assigned to arylsulphonyl radical-adducts $ArSO_2N(CMe_3)O\cdot$, both on the basis of previous literature assignments[20] and in view of their detection when sulphonyl chlorides were photolysed under similar conditions.

Further evidence for the formation of ArS· in these systems was provided by the detection of the appropriate adducts with (8; R = Ph), for which the low value of a(β-H) and the somewhat exalted g value of 2.006 7 are typical, and (8; R = H); for the latter adducts, the g value and low value of a(β-H), which indicates some degree of eclipsing of the orbital of the unpaired electron by the β-C–S bond, are also diagnostic. Again, the same types of adducts were detected during the photolysis of disulphides in the presence of the nitrone traps.*

One extra type of signal which was detected from various sulphoxides in the presence of (8; R = Ph) had a(N) *ca.* 1.3 mT with a low β-H splitting (*ca.* 0.15 mT) and characteristic g value of 2.006 3. These signals were also detected, along with a signal assigned to the chlorine-atom adduct in some cases,[21] on photolysis of some arenesulphonyl chlorides (see, *e.g.* Table 2).† It seems likely that S–Cl bond fission has taken place to give $ArSO_2\cdot$ (which is directly detectable if the trap is absent[22]) and that this has added directly to the nitrone, to give radical-adducts of the type $ArSO_2CHPhN(CMe_3)O\cdot$. Nitroxides of the related types $R^1SO_2CHR^2N(OR^3)O\cdot$[23] and also[24] $(ArSO_2CH_2)_2NO\cdot$ and $ArSO_2CH_2N(Ar)O\cdot$ have previously been characterized, so there is no reason for expecting β-sulphonyl substituted nitroxides to be thermally unstable (*e.g.* with respect to β-fission to regenerate sulphonyl species). Further, though the results are not strictly comparable because of structural variations, the species we detected and those previously reported have in common low values of a(β-H), indicative

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* On some occasions, use of (8; R = Ph) led to the detection of a signal with a(N) *ca.* 0.80 mT, g 2.0068, as has been previously noted.[16] This is evidently an acyl nitroxide formed from photolytic decomposition of the nitrone, and it will not be discussed further here.

† We were unable to confirm the previously reported finding (I. I. Kandrov, R. G. Gasanov, and R. Kh. Freidlina, *Tetrahedron Letters*, 1976, 1075) that photolysis of $PhSO_2Cl$ in the presence of (8; R = Ph) gives solely the spectrum from $Ph_2CHN(CMe_3)O\cdot$, with a(β-H) 0.21 mT (*i.e.* implying that C–S fission has taken place).

of structures in which the bond to the β-substituent eclipses the orbital of the unpaired electron (see *e.g.* ref. 23), a feature which supports our assignment.

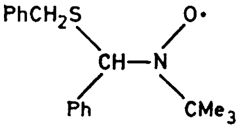
TABLE 2

Radical-adducts detected during the photolysis of some aromatic sulphur-containing compounds in the presence of spin traps [a]

Substrate	Trap	E.s.r. parameters for radical detected [b]				Radical
		a(N)	a(H)	a(other)	g	
Ph_2S_2	(7) [c]	1.675			2.0065	$PhSN(CMe_3)O\cdot$
	(8; R = Ph) [c]	1.40	0.16 (1 H)		2.0068	$PhSCHPhN(CMe_3)O\cdot$
$(4\text{-OH-3,5-Bu}^t_2C_6H_2)_2S_2$	(7) [c]	1.79			2.0067	$ArSN(CMe_3)O\cdot$ [e]
	(8; R = Ph) [c]	1.40	0.15 (1 H)		2.0067	$ArSCHPhN(CMe_3)O\cdot$ [e]
	(8; R = H) [d]	1.36	0.585 (2 H)		2.0064	$ArSCH_2N(CMe_3)O\cdot$ [e]
$PhSO_2Cl$	(7) [c]	1.23			2.0061	$PhSO_2N(CMe_3)O\cdot$
	(8; R = Ph) [c]	1.35	0.15 (1 H)		2.0062	$PhSO_2CHPhN(CMe_3)O\cdot$
		1.23	0.07 (1 H)	0.625(^{35}Cl) 0.52(^{37}Cl)	2.0070	$ClCHPhN(CMe_3)O\cdot$
$MeC_6H_4SO_2Cl$	(7) [c]	1.22			2.0061	$ArSO_2N(CMe_3)O\cdot$ [f]
	(8; R = Ph) [c,g]	1.36	0.15 (1 H)		2.0062	$ArSO_2CHPhN(CMe_3)O\cdot$
	(8; R = H) [d]	1.27	0.625 (2 H)		2.0062	$ArSO_2CH_2N(CMe_3)O\cdot$ [f]
(4; $R^1 = R^2 = X = H$)	(7) [c,h]	1.18	0.225 (3 H), 0.09 (2 H)		2.0060	$PhN(CMe_3)O\cdot$ [h]
	(8; R = Ph) [c]	1.335	0.13 (1 H)		2.0062	$PhSO_2CHPhN(CMe_3)O\cdot$
(4; $R^1 = R^2 = H$, X = OMe)	(7) [c]	1.79			2.0067	$ArSN(CMe_3)O\cdot$ [i]
		1.25			2.0061	$ArSO_2N(CMe_3)O\cdot$ [i]
	(8; R = Ph) [c]	1.385	0.13 (1 H)		2.0067	$ArSCHPhN(CMe_3)O\cdot$ [i]
(4; $R^1 = R^2 = CMe_3$, X = OH)	(7) [c]	1.81			2.0066	$ArSN(CMe_3)O\cdot$ [e]
		1.25			2.0060	$ArSO_2N(CMe_3)O\cdot$ [e]
	(8; R = Ph) [c]	1.335	0.13 (1 H)		2.0063	$ArSO_2CHPhN(CMe_3)O\cdot$ [e]
	(8; R = H) [d]	1.36	0.50 (2 H)		2.0064	$ArSCH_2N(CMe_3)O\cdot$ [e]
$(PhCH_2)_2SO$	(7) [c]	1.25			2.0060	$PhCH_2SO_2N(CMe_3)O\cdot$
		1.72			2.0067	$PhCH_2SN(CMe_3)O\cdot$
		1.505	0.750 (2 H)		2.0060	$PhCH_2N(CMe_3)O\cdot$
	(8; R = Ph) [c,j]	1.43	0.18 (1 H), 0.06 (1 H)		2.0068	$PhCH_2SCHPhN(CMe_3)O\cdot$
	(8; R = H) [d]	1.375	0.51 (2 H), 0.125 (2 H)		2.0064	$PhCH_2SCH_2N(CMe_3)O\cdot$

[a] For experimental details, see text: the temperature was in the range 265---298 K except where stated otherwise. [b] Splittings in mT, ±0.01; g ±0.0001. [c] In methylbenzene. [d] In diethyl ether. [e] Ar = 3,5-di-t-butyl-4-hydroxyphenyl. [f] Ar = 4-MeC_6H_4. [g] Signal from $ClCHPhN(CMe_3)O\cdot$ also detected. [h] At *ca.* 200 K. [i] Ar = 4-$MeOC_6H_4$. [j] In benzene.

Table 2 also includes details of the radicals detected from dibenzyl sulphoxide under photolytic conditions. Use of the nitroso-trap enabled adducts with $PhCH_2S\cdot$, $PhCH_2SO_2\cdot$, and $PhCH_2\cdot$ (*cf.* ref. 25) to be characterized (the benzyl radical could be formed by desulphonylation of $PhCH_2SO_2\cdot$ as well as in an initial cleavage). The use of the nitrone traps (8; R = Ph) and (8; R = H) led to the detection of signals assigned to the thiyl adducts (9) and (10), respectively. The data for both are characterized by long-range splittings across the β-substituent (probably aided by the interaction which causes the β-C–S bond to eclipse the orbital of the unpaired electron on nitrogen); in the former case, the detection of only a *single* benzyl-proton coupling presumably stems from the chirality of the carbon adjacent to the nitrogen (*cf.* ref. 26).



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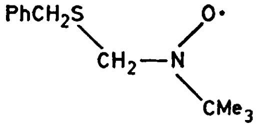


(10)

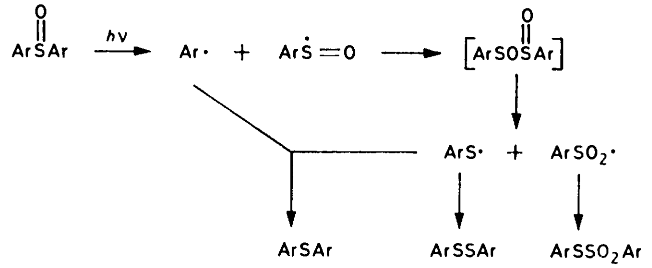
No evidence was obtained in any of our experiments for the trapping of a sulphinyl radical (ArSO· or RSO·), which is perhaps not surprising in view of the delocalization in these species (in contrast to $ArSO_2$; see *e.g.* ref. 22). Photolysis of 4-methylbenzenesulphinyl chloride at 259 K in the presence of (7) gave a spectrum with two weak triplets [a(N) 1.245 mT, g 2.006 1 and a(N) 1.725 mT, g 2.006 6] assigned to the appropriate sulphonyl- and thiyl-adducts respectively (though $4\text{-}MeC_6H_4SO\cdot$ is detected *directly* in the absence of the trap). Similarly, in the presence of (8; R = Ph) under similar conditions, a sulphonyl-adduct was detected [with a(N) 1.335, a(1H) 0.14 mT, g 2.006 2].

We recognize that care must be exercised when interpreting results from spin-trapping experiments (see *e.g.* ref. 27) but we believe that our results indicate that, when aromatic sulphoxides are photolysed, initial fission gives aryl and sulphinyl radicals [see reaction (5)], the latter of which undergo disproportionation to some extent [reaction (6)] to yield the appropriate sulphonyl and thiyl radicals which can both be trapped.

$$2\,ArSO\cdot \longrightarrow ArS\cdot + ArSO_2\cdot \qquad (6)$$

We have not attempted to isolate products from our reactions but we can gain some insight into the further reactions of these radicals by our observations concerning the direct photolysis of the antioxidant (4; $R^1 = R^2 =$

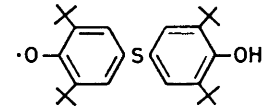
CMe$_3$, X = OH) in methylbenzene (typically at *ca.* 270 K). Thus the e.s.r. signal from the sulphinyl radical (5; R^1 = R^2 = CMe$_3$, X = OH) was accompanied by signals, which grew with time, from the phenoxyl radicals of the appropriate sulphide [(11), *a*(2H), 0.125 mT, *g* 2.005 5] and disulphide[28] [(12), *a*(2H), 0.15 mT, *g* 2.005 2]. Similarly, photolysis of (4; R^1 = Me, R^2 = CMe$_3$, X = OH) under similar conditions led to the development of a spectrum with *a*(3H) 0.54, *a*(2H) 0.10 mT, *g* 2.005 5, from the phenoxyl radical of the appropriate sulphide,[28] to join that from the sulphinyl radical (5; R^1 = Me, R^2 = CMe$_3$, X = OH). Scheme 1 outlines a mechanism for the formation of the sulphides and disulphides which is also consistent with our detection of sulphinyl radicals and our evidence from spin-trapping that these disproportionate to thiyl and sulphonyl radicals (*cf.* refs. 8 and 9 and evidence for production of thiolsulphonates from $RSO\cdot$).



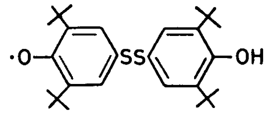
SCHEME 1

(b) *On thermolysis.* Thermolysis of a solution of (4; R^1 = R^2 = CMe$_3$, X = OH) in naphthalene at 393 K gave a spectrum from the appropriate sulphinyl radical (see Table 1), though the signal was weaker, and had a larger line-width, than that detected during photolysis. Thermolysis of (4; R^1 = Me, R^2 = CMe$_3$, X = OH) under similar conditions also gave a weak, broadened signal with *g* 2.009 2, presumably from the appropriate sulphinyl radical, but no signals were detected directly during thermolysis of a range of other diaryl sulphoxides and bis(phenylmethyl) sulphoxide.

Thermolysis of the sulphoxides in the presence of the nitroso-trap (7) generally gave only the strong signal from $(CMe_3)_2NO\cdot$, though some observations are worthy of mention. For example, in the presence of (7), the signal from (5; R^1 = R^2 = CMe$_3$, X = OH) from the appropriate sulphoxide was not removed (reinforcing our belief that, at least under these conditions, sulphinyl radicals do not add to the nitroso-group) but actually increased significantly in intensity; it was also accompanied by the signal from the phenoxyl radical (11). It seems likely that the thermal decomposition resembles fairly closely the photochemical decomposition described earlier; the role of the trap here may simply be to remove reactive radicals which otherwise serve to reduce the concentration of (11) and (5; R^1 = R^2 = CMe$_3$, X = OH). Thermolysis of bis-(4-nitrophenyl) sulphoxide at 454 K in the presence of (7) gave a signal with *a*(N) 1.20, *a*(2H) 0.19, *a*(2H) 0.09 mT, *g* 2.006 1, which is assigned to the 4-nitrophenyl adduct. Thermolysis of $(PhCH_2)_2SO$ led to the detection initially of a signal with *a*(N) 1.56, *a*(2H) 0.81 mT, *g* 2.006 1, assigned to the phenylmethyl adduct $PhCH_2N(CMe_3)O\cdot$; continued thermolysis led to the appearance of a second radical, with *a*(N) 1.49, *a*(1H) 0.28 mT, *g* 2.006 1, assigned to the adduct $PhCH_2CHPhN(CMe_3)O\cdot$ formed from $PhCH_2\cdot$ and the nitrone $PhCH = N(CMe_3)O$ which is evidently generated *in situ* from an initial adduct. Confirmation for the assignment comes from the detection of the same species in the thermolysis of $(PhCH_2)_2SO$ in the presence of (8; R = Ph). No signals were detected from other sulphoxides in the presence of this nitrone trap.



(11)

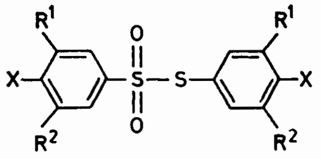


(12)

Although our observations for certain sulphoxides, notably those with both alkyl and hydroxyl substituents, indicates that for these substrates at least, C–S homolysis has occurred, the use of spin-traps has not enabled thiyl and sulphonyl species to be characterised. It seemed possible that the nitroxides from these might themselves be thermally unstable under the conditions employed; however, this explanation can be ruled out in the case of arylsulphonyl radical-adducts of (7), since an example proved detectable when it was generated from the thermolysis of 4-methylbenzenesulphonyl iodide at 393 K [$4\text{-}MeC_6H_4SO_2N(CMe_3)O\cdot$ had *a*(N) 1.285 mT, *g* 2.006 1]. It appears then that in the thermolytic reactions of sulphoxides any sulphonyl radicals formed are not generated sufficiently rapidly for a detectable steady-state concentration of adducts to be built up.

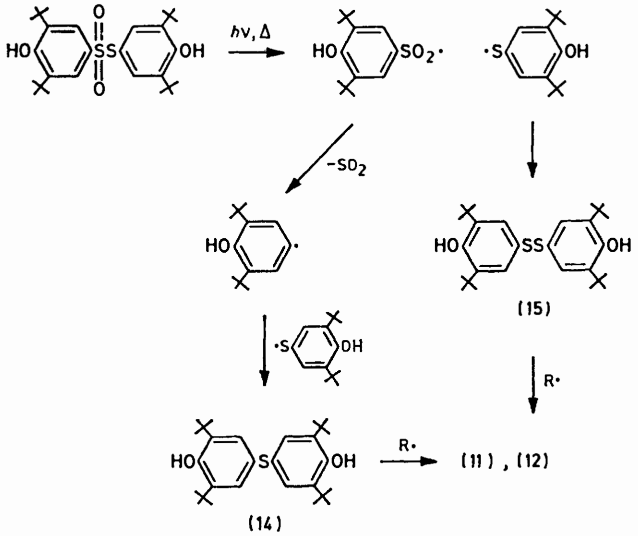
Radicals detected from Thiolsulphonates.—(a) *On photolysis.* Photolysis of solutions in methylbenzene of some 4,4-disubstituted aryl arenethiolsulphonates (13; R^1 = R^2 = H), in the range 190—250 K gave rise to two clearly separated signals; one, with *g* in the range 2.009 0—2.010 is the appropriate sulphinyl radical ($ArSO\cdot$; see Table 1) and the other, with *g* typically 2.004 7, has the parameters diagnostic of the corresponding sulphonyl radical ($ArSO_2$; data for these have been previously reported[22]). For these substrates (see Table 3) the sulphonyl radical was the dominant species (being *ca.* 60% of the total detectable radical concentration); an increase in the prominence of the sulphinyl radical signals at the lower end of the temperature range (behaviour which was reversed as the temperature was raised) is attributed to the reduction in line-widths of the signals from these radicals with temperature.[14] The intensities of the two signals did not increase significantly as a function of time, but both decayed immediately when the light was cut off. The mechanism of the formation of sulphinyl radicals is discussed in detail in the next section.

Photolysis of (13; R^1 = R^2 = CMe$_3$, X = OH) led also to the detection of the triplet characteristic of the sulphinyl radical (5; $R^1 = R^2 = CMe_3$, X = OH) as well as to the triplets from phenoxyl radicals from the appropriate sulphide and disulphide, (11) and (12), as also observed for the corresponding sulphoxide [the presence of the expected sulphonyl radical could not be ascertained, because of the strong signals at the appropriate *g* value from (11) and (12), though analogy with other thiolsulphonates leads us to suppose that it is indeed formed]. The formation of radicals (11) and (12) may be rationalised in terms of the mechanism outlined in Scheme 2; evidence for a corresponding decomposition on thermolysis of the same compound derives from the characterization [1] of the products of this reaction [SO_2, (14), (15), and the biaryl Ar_2, Ar = 4-hydroxy-3,5-di-t-butylphenyl].



(13)

Photolysis of the thiolsulphonate $PhCH_2SO_2SCH_2Ph$ led to the detection of $PhCH_2SO\cdot$ (see Table 1) in addition to a doublet (with *a* 0.88 mT, *g* 2.005 4) assigned to the radical [29] HOSO· (which is also detected during the photolysis [30a] of dialkyl sulphites as well as during the photolytic reactions of SO_2 in ethereal solvents [30b]) and a singlet with *g* 2.004 9. The latter cannot be $PhCH_2SO_2\cdot$ (which has a significant proton splitting [31]) but may be $PhCH_2O\dot{S}O$ (the *g* value is appropriate and the methylene proton splittings would be expected to be hardly, if at all, resolvable [30a]). The origin of these radicals and the mechanism of the photolytic decomposition of the particular thiolsulphonate will not be discussed further here.



SCHEME 2

The radical-adducts detected on photolysis of thiolsulphonates in the presence of spin-traps are summarized in Table 3. In the presence of the nitroso-trap (7), a strong signal [with *a*(N) *ca.* 1.2 mT, *g* 2.006 1] assigned to the appropriate sulphonyl adduct was generally detected. In several cases, an additional small splitting of *ca.* 0.02 mT arising from an odd number of equivalent protons (at least seven, but probably nine) could be resolved; this is evidently due to the equivalent protons of the Me_3C group [*n.b.* resolvable splittings with a similar origin have been reported [32] for sulphonamidyl radicals ($RSO_2\dot{N}CMe_3$) though not previously for the corresponding nitroxides]. Sulphonyl adducts of the nitrone (8; R = Ph) were also characterized. The generation of thiyl radicals from the thiolsulphonates was also confirmed, *via* the detection of adducts with each of the traps (though adducts with the nitroso-trap were only rarely observed, and it seems likely that alkyl arylthiyl nitroxides are relatively unstable). The sulphinyl and phenoxyl radicals obtained during the photolysis of (13; $R^1 = R^2 = CMe_3$, X = OH) were not scavenged in the presence of the traps.

(b) *On thermolysis.* Thermolysis of (13; $R^1 = R^2 = CMe_3$, X = OH) at temperatures >360 K gave a signal from the sulphinyl radical (5; $R^1 = R^2 = CMe_3$, X = OH) which was rapidly joined by a triplet due to the phenoxyl radical (12). Weak signals attributed to the appropriate sulphinyl radicals on the basis of their *g* values (see Table 1) were also observed on thermolysis of (13; $R^1 = R^2 = H$, X = Br) and (13; $R^1 = R^2 = H$, X = NO_2); the line-widths were larger than those observed on photolysis, and no fine-structure could be resolved. A singlet with *g ca.* 2.003 5 detected on thermolysis of (13; $R^1 = R^2 = H$, X = Me) and (13; $R^1 = R^2 = H$, X = Cl) above 450 K is tentatively assigned to $SO_3^{-\cdot}$ or a structural analogue ($HOSO_2\cdot$ or $ROSO_2\cdot$; *cf.* ref. 33). No signals from arenesulphonyl radicals could be detected in these experiments.

Thermolysis of aryl arenethiolsulphonates at 400 K in the presence of the nitrone (8; R = Ph) did, however, provide evidence for the mediation of sulphonyl radicals (see Table 3 for details of the adducts) though the spectra were weak and transient. Under the same conditions, thermolysis of $PhCH_2SO_2SCH_2Ph$ led to the trapping of $PhCH_2\cdot$. In the presence of the nitroso-trap (7), thermolysis of aryl arenethiolsulphonates led to the production of complex spectra dominated by signals from the sulphonyl radical-adducts (see Table 3). Also present were signals from secondary radicals including those assigned to acyl nitroxides [*a*(N) 0.7 mT, *g* 2.007 0, *cf.* ref. 34] and those with *a*(N) *ca.* 3.0 mT, *g* 2.004, which may be of iminoxyl [35] type; their origin will not be discussed. Thermolysis of $PhCH_2SO_2SCH_2Ph$ in the presence of (7) led, as with the thermolysis of the sulphoxide $PhCH_2S(O)CH_2Ph$ under similar conditions, to the detection of $PhCH_2CHPhN(CMe_3)O\cdot$.

(c) *Mechanism of the formation of sulphinyl radicals in homolytic reactions of thiolsulphonates.* Our e.s.r. results indicate that photolysis and, in some cases, thermolysis of aryl arenethiolsulphonates leads to the formation of sulphinyl radicals. At the same time, the spin-trapping results, although complicated by the appearance of radicals arising from secondary reactions, suggest that the primary decomposition step of these compounds on both thermolysis and photolysis involves homolysis of the sulphur–sulphur bond to generate sulphonyl and thiyl radicals (in contrast, it has previously been suggested [10b] that, at least for some alkyl alkanethiolsulphonates and alkyl arenethiolsulphonates, thermolysis is ionic in character, and that aryl arenethiolsulphonates do not decompose at *ca.* 100 °C [10a]).

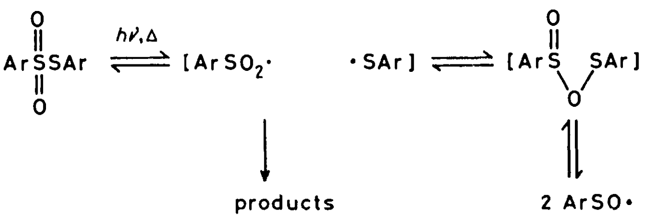
Table 3

Radicals characterized during the photolysis and thermolysis of arenethiolsulphonates

Substrate ($ArSO_2SAr$)	In the absence of a trap		In the presence of a trap		Hyperfine splittings (mT) [d]			
	Method [a]	Radical [b]	Trap	Method [a,c]	a(N)	a(H)	g [e]	Radical added
Ar = 4-ClC_6H_4	$h\nu$	4-$ClC_6H_4SO\cdot$	(7)	$h\nu$,	1.22 [f]		2.0061	$ArSO_2\cdot$
		4-$ClC_6H_4SO_2\cdot$		Δ	1.285		2.0061	
			(8; R = Ph)	$h\nu$	1.32	0.15 (1 H)	2.0061	$ArSO_2\cdot$
Ar = 4-BrC_6H_4	$h\nu$, Δ	4-$BrC_6H_4SO\cdot$	(7)	$h\nu$,	1.23 [f]		2.0061	$ArSO_2\cdot$
				Δ	1.285		2.0061	
	$h\nu$	4-$BrC_6H_4SO_2\cdot$	(8; R = Ph)	$h\nu$	1.40	0.15 (1 H)	2.0067	$ArS\cdot$
Ar = 4-$NO_2C_6H_4$	$h\nu$, Δ	4-$NO_2C_6H_4SO\cdot$	(7)	$h\nu$,	1.20		2.0059	$ArSO_2\cdot$
				Δ	1.27		2.0060	
	$h\nu$	4-$NO_2C_6H_4SO_2\cdot$	(8; R = Ph)	$h\nu$	1.40	0.20 (1 H)	2.0067	$ArS\cdot$
Ar = 4-MeC_6H_4	$h\nu$	4-$MeC_6H_4SO\cdot$	(7)	$h\nu$,	1.725		2.0068	$ArS\cdot$
					1.21 [f]		2.0061	$ArSO_2\cdot$
				Δ	1.31		2.0061	
		4-$MeC_6H_4SO_2\cdot$	(8; R = Ph)	$h\nu$	1.41	0.14 (1 H)	2.0068	$ArS\cdot$
					1.335	0.14 (1 H)	2.0062	$ArSO_2\cdot$
Ar = 4-OH-3,5-$Bu^t_2C_6H_2$	$h\nu$, Δ	(5; $R^1 = R^2 = CMe_3$, X = OH)	(7)	$h\nu$	1.25 [f]		2.0061	$ArSO_2\cdot$
					1.30		2.0061	
	$h\nu$	(11)	(8; R = Ph)	$h\nu$	1.34	0.14 (1 H), 0.04 (2 H)	2.0062	$ArSO_2\cdot$
	$h\nu$, Δ	(12)	(8; R = H)	$h\nu$	1.27	0.625 (2 H)	2.0064	$ArSO_2\cdot$
$PhCH_2SO_2SCH_2Ph$	$h\nu$	(6)	(7)	$h\nu$	1.26		2.0061	$PhCH_2SO_2\cdot$
		HOSO [g]			1.49	0.86 (2 H)	2.0061	$PhCH_2\cdot$
			(8; R = Ph)	$h\nu$	1.435	0.23 (1 H), 0.05 (1 H)	2.0067	$PhCH_2S\cdot$
				Δ	1.49	0.28 (1 H)	2.0061	$PhCH_2\cdot$
			(8; R = H)	$h\nu$	1.375	0.55 (2 H), 0.125 (2 H)	2.0064	$PhCH_2S\cdot$

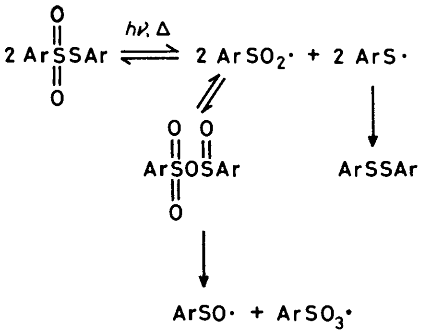
[a] For details of method, temperature, *etc.*, see text. [b] Data for sulphinyl radicals ($ArSO\cdot$) are given in Table 1; signals were generally broader under thermolytic conditions; e.s.r. data for sulphonyl radicals ($ArSO_2\cdot$) are in agreement with those reported in ref. 22 though complete resolution was often not possible. [c] Other radicals detected in some cases included $(Me_3C)_2NO\cdot$ from (7), acyl nitroxides from (8; R = Ph) and, on occasions, other uncharacterized signals (see text). [d] ±0.01 mT. [e] ±0.0001. [f] Indication of extra fine structure, see text. [g] See text.

Of the various possible mechanisms for the formation of sulphinyl radicals in these reactions, the following two, in particular, deserve further consideration. The first mechanism involves the recombination of the first-formed sulphonyl and thiyl radicals to form an intermediate with an O–S bond, and its subsequent homolysis (see Scheme 3); this intermediate is that which we believe to be involved in the reverse of this process, namely the formation of thiosulphonates (*via* sulphonyl and thiyl radicals) from sulphinyl radicals generated by the photolysis of sulphoxides (see earlier) and the peroxidation of thiolsulphinates.[9] The second mechanism involves the reaction of first-formed arylsulphonyl radicals, without the mediation of thiyl radicals, *via* an intermediate sulphinyl sulphonyl 'anhydride' (see Scheme 4), decomposition of which under either thermal or photochemical conditions might be expected to yield sulphinyl radicals ($ArSO\cdot$) and oxygen-centred radicals $ArSO_3\cdot$ (which would not be expected to be directly detectable using e.s.r.). A mechanism of this type has been proposed [36] to account for the products derived from the thermolysis of sulphonyl iodides (these include sulphonic anhydrides and aryl arenethiolsulphonates).



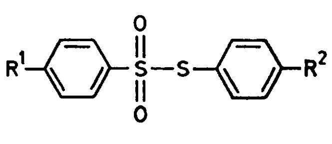
Scheme 3

If Scheme 4 is the major route for the formation of sulphinyl radicals from thiolsulphonates, then it would be expected that any method which generates a large concentration of sulphonyl radicals should also give rise to sulphinyl radicals. That this route is likely to contribute significantly is suggested by our previous finding [22] that when sulphonyl radicals are generated by direct photolysis of sulphonyl chlorides or abstraction of chlorine from sulphonyl chlorides with $Et_3Si\cdot$ (from Et_3SiH and $Me_3CO\cdot$) signals from sulphinyl radicals (albeit relatively weak) accompany those from sulphonyl radicals for some substrates. We have now confirmed that these include sulphonyl radicals typical of those studied here; for example, photolysis of 4-chlorobenzenesulphonyl chloride in methylbenzene at *ca.* 220 K led to the detection of 4-ClC$_6$H$_4$SO· (see Table 1) as well as to the stronger signal expected from 4-ClC$_6$H$_4$SO$_2$· (*cf.* ref. 22). 4-Bromobenzenesulphonyl chloride and both 4-methylbenzenesulphonyl chloride and iodide behaved similarly. In these and other examples the ratio of [ArSO·] to [ArSO$_2$·] was similar to that noted in the photochemical experiments with aryl arenethiolsulphonates under comparable conditions (*i.e.* with the former *ca.* 40% of the mixture of radicals).



SCHEME 4

We also sought evidence for a contribution of Scheme 3 to the formation of sulphinyl radicals by a study of some 'mixed' thiolsulphonates, namely (16; R^1 = H, R^2 = Cl), (16; R^1 = Cl, R^2 = H), and (16; R^1 = H, R^2 = Br). These were chosen as substrates since if sulphinyl radicals were to be obtained from both moieties of the molecule (as would be required on the basis of the operation of Scheme 3) their separate signals would be resolvable, to some extent at least [mixtures of most pairs of aromatic sulphinyl radicals would give almost exactly overlapping spectra at *g ca.* 2.009 1, but the *g* values for C$_6$H$_5$SO·, 4-ClC$_6$H$_4$SO· and 4-BrC$_6$H$_4$SO· are noticeably different (see Table 1)].



(16)

Photolysis of these thiolsulphonates in methylbenzene in the range 220—260 K led in each case to the detection of signals which were largely (up to *ca.* 70% at least) those of R^{1}C$_6$H$_4$SO$_2$· and R^{1}C$_6$H$_4$SO·, with no clear evidence for the formation of the corresponding R^2-substituted radicals (it may be notable, however, that the signals from the sulphinyl radicals detected were somewhat broader, with slight asymmetry, than those obtained from the appropriate substrates described earlier, and this lack of resolution may result from the presence of a low concentration of the other sulphinyl radical R^{2}C$_6$H$_4$SO·). We conclude that, for the photolytic decomposition of examples of aryl arenethiolsulphonates such as these, Scheme 3 makes only a minor contribution, at most, to the production of ArSO· [though the proposed intermediate ArSOS(O)Ar is, apparently, effectively formed *from* ArSO·, see earlier].

Conclusions.—Our e.s.r. results demonstrate that free-radical pathways contribute to both the thermolytic and photolytic decomposition of a variety of diaryl sulphoxides and aryl arenethiolsulphonates. Sulphinyl radicals (which are relatively delocalised and unreactive π-radicals) have been identified as the primary species formed on photolysis (and in some cases thermolysis) of diaryl sulphoxides, the corresponding aryl radicals being identified by their spin-adducts (see *e.g.* Scheme 1). Sulphinyl radicals were also detected on both thermolysis and photolysis of the aryl arenethiolsulphonates; evidently initial S–S bond cleavage (to yield sulphonyl and thiyl radicals, which can be intercepted by spin traps), is followed by two possible modes of reaction. Though both Schemes 3 and 4 provide realistic pathways for this process, it seems likely that Scheme 4 (involving the dimerization of ArSO$_2$·) represents the predominant mode of reaction. Our results suggest that both π-type sulphinyl and σ-type sulphonyl radicals can react at either sulphur or oxygen. The disproportionation of sulphinyl radicals is consistent with the products identified on thermolysis of aryl alkyl sulphoxides [5] and [8] aryl arenethiosulphinates [*e.g.*[8] PhS(O)SPh gives PhSO$_2$SPh and PhSSPh], and is in accord with the finding that thermolysis of both (4; R^1 = R^2 = CMe$_3$, X = OH) and (13; R^1 = R^2 = CMe$_3$, X = OH) leads to the formation of the same set of products [SO$_2$, (14), (15), and Ar$_2$ (Ar = 4-hydroxy-3,5-di-t-butylphenyl)], as is also suggested by our detection of the phenoxyl radicals from (14) and (15) in both cases.

On the basis of our findings it may be suggested that an important contribution to the production of sulphur dioxide (the important antioxidant) from a variety of aromatic sulphoxides and thiolsulphonates (and also from their precursor sulphides and disulphides in hydroperoxide-containing media), is *via* the desulphonylation of arenesulphonyl radicals. These σ-type species do not possess any delocalization of the unpaired electron from the sulphonyl group to the ring, and may undergo ready fragmentation [*cf.* the equilibria [37] between alkanesulphonyl radicals (RSO$_2$·) and R· and SO$_2$], especially at the high temperatures employed.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E-104 X-band spectrometer employing 100-kHz modulation. The field scan was calibrated using Fremy's salt [38] [*a*(N) 1.309 1 ± 0.000 4 mT], and *g* values were measured by comparison with the signal associated with radiation damage in the sample tube (this *g* value was determined, relative to that of αα'-diphenyl-β-picrylhydrazyl,[39] as 2.000 6 ± 0.000 1).

Splittings were measured to ±0.01 mT, and *g* values to ±0.000 1. Splittings were checked using a spectrum-simulation program (incorporating routines for second-order effects and exchange processes) executed on the DEC KL10 computer at the University of York.

For the photolytic experiments, samples in the cavity of the spectrometer were exposed to the unfiltered radiation of an Hanovia 977B-1 1-kW mercury–xenon compact arc. The temperature of the sample (as also in the thermolysis experiments) was controlled with a Varian variable temperature accessory and monitored using a Comark 3015 Cr–Al digital thermometer; temperatures quoted are believed to be accurate to within ±2 K. Samples to be photolysed were prepared by dissolving the substrate (typically 0.1 g) in methylbenzene (*ca.* 2 cm^3) which had been deoxygenated with a nitrogen purge. In the case of less soluble compounds, a saturated solution of the substrate in methylbenzene was used, although in some cases, notably bis-(3-methyl-4-hydroxy-5-t-butylphenyl) sulphoxide, it was found necessary to use deoxygenated tetrahydrofuran as the solvent for photolysis experiments. Nitrogen was passed through the tubes before samples of these solutions were added. Direct photolysis experiments were performed at a number of temperatures between 190 and 298 K; the temperatures stated in the text are those at which optimum signals were obtained. Experiments in the presence of the spin traps were performed at temperatures between 265 and 298 K unless otherwise stated. The samples for the spin-trapping experiments were prepared as above, with *ca.* 5×10^{-3} g of the solid traps (7) or (8; R = Ph) added before photolysis. Where the substrate studied included a 4-methylphenyl group or a phenylmethyl group, the spin-trapping experiments were repeated using benzene as the solvent, in an attempt to ensure that any phenylmethyl radicals detected were not derived from the solvent. The trap (8; R = H) was prepared as a solution in diethyl ether; samples for experiments with this trap contained *ca.* 0.1 g of the substrate in *ca.* 2 cm^3 of the ethereal solution containing the trap.

Thermolysis experiments were also carried out directly in the cavity of the e.s.r. spectrometer. Nitrogen was passed through the cavity as in the photolysis experiments but in this case the coils of the variable temperature accessory were at room temperature, not immersed in liquid nitrogen. Thermolysis experiments were typically carried out at *ca.* 393 K unless otherwise indicated. Samples were prepared by mixing the substrate (typically *ca.* 0.06 g) with naphthalene (0.6 g) in the sample tube. Samples for experiments in the presence of spin traps were prepared by first mixing *ca.* 5×10^{-3} g of the solid trap with the substrate.

Bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphoxide, bis-(3-methyl-4-hydroxy-5-t-butylphenyl) sulphide, 4-hydroxy-3,5-di-t-butylphenyl 4-hydroxy-3,5-di-t-butylbenzenethiolsulphonate, 4-methylphenyl 4-methylbenzenethiolsulphonate, phenylmethyl phenylmethanethiolsulphonate, and bis-(4-hydroxy-3,5-di-t-butylphenyl) disulphide were kindly supplied by Esso Chemical Ltd. 4-Chlorophenyl benzenethiolsulphate, phenyl 4-chlorobenzenethiolsulphonate and 4-bromophenyl benzenethiosulphonate were kindly supplied by Dr. R. Leardini, and methylbenzenesulphinyl chloride was a gift from Dr. C. M. Kirk. Diphenyl sulphoxide (R. N. Emanuel), bis(phenylmethyl) sulphoxide (Aldrich), bis-(4-methylphenyl) sulphoxide (Aldrich), diphenyl sulphide (Aldrich, >99.9%), bis(phenylmethyl) sulphide (Eastman), dialkyl disulphides (Aldrich), diphenyl disulphide (Eastman), 4-methylbenzenesulphonyl chloride (Fisons), and benzenesulphonyl chloride (Aldrich) were commercial samples and used as supplied.

Bis-(1-methyl-4-hydroxy-5-t-butylphenyl) sulphoxide,[40] bis-(4-hydroxyphenyl) sulphoxide,[41] bis-(4-nitrophenyl) sulphoxide, bis-(4-bromophenyl) sulphoxide, and bis-(4-methoxyphenyl) sulphoxide [42] were prepared by oxidation of the corresponding monosulphides with 3-chloroperbenzoic acid according to the procedure of Johnson and McCants.[43] Bis-(4-bromophenyl) sulphide,[42] bis-(4-hydroxyphenyl) sulphide,[44] and bis-(4-nitrophenyl sulphide) [45] were prepared following literature procedures; attempts to prepare bis-(4-methoxyphenyl) sulphide by the method of Ariyan and Wiles [46] resulted in the deposition of elemental sulphur, but the compound was successfully prepared following the method of ref. 47. The aryl arenethiolsulphonates $ArSO_2SAr$ (Ar = C_6H_5, 4-MeC_6H_4, 4-$NO_2C_6H_4$, and 4-ClC_6H_4,[48] and 4-BrC_6H_4 [49]) were prepared by the oxidation [50] of the corresponding disulphides with 3-chloroperbenzoic acid. Bis-(4-bromophenyl) disulphide [51] was prepared *via* phenylthioethanoic acid [52] and 4-bromophenylthioethanoic acid,[53] followed by oxidation of the latter with hydrogen peroxide.[53] Bis-(4-chlorophenyl) disulphide [54] and bis-(4-methylphenyl) disulphide [55] were prepared by oxidation of the appropriate thiols,[55] bis-(4-nitrophenyl) disulphide [56] was prepared similarly from 4-nitrobenzenethiol.[57] 4-Chlorobenzene- and 4-bromobenzene-sulphonyl chlorides were prepared as described previously.[22] 4-Methylbenzenesulphonyl iodide and phenylmethanesulphonyl chloride were prepared according to the appropriate methods described by Truce *et al.*[58] Satisfactory analytical data (m.p. or b.p., i.r., and n.m.r. spectra) were obtained for all compounds prepared.

Samples of the spin traps 2-methyl-2-nitrosopropane (7) and *N*-benzylidene-t-butylamine *N*-oxide (α-phenyl-*N*-t-butylnitrone) (8; R = Ph) were obtained from Aldrich and were used without further purification. The trap *N*-methylene-t-butylamine *N*-oxide (8; R = H) was prepared from 2-methyl-2-nitrosopropane and diazomethane [59] using a modification of the method of Baldwin *et al.*[60] A distillation apparatus was arranged with the receiver in an ice-bath. In the distillation flask were placed diethylene glycol monoethyl ether (12 cm^3), diethyl ether (3 cm^3) and a solution of potassium hydroxide (2 g) in water (3 cm^3). The receiver contained sufficient ether that the inlet tube dropped below the surface of the liquid. The distillation flask was heated to 343 K and a solution of *N*-methyl-*N*-nitroso-4-methylphenylsulphonamide (7 g) in diethyl ether (45 cm^3) was added over 20 min. Occasional shaking of the flask ensured thorough mixing of the reactants. During the addition, diazomethane was liberated and trapped in the ether in the receiver. The solution of diazomethane was added to 2-methyl-2-nitrosopropane (1.0 g) in diethyl ether (10 cm^3). The resulting colourless solution of *N*-methylene-t-butylamine *N*-oxide was stored at 273 K under nitrogen and in the absence of light; at this temperature it was stable for *ca.* two weeks.

Naphthalene (Fisons) was the grade employed for molecular-weight determinations; it was finely ground then stored under nitrogen. All other materials were commercially available materials (AnalaR grade where possible) and, as with other commercial materials referred to above, were used without further purification.

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REFERENCES

[1] A. J. Bridgewater and M. D. Sexton, *J.C.S. Perkin II*, 1978, 530.

[2] (*a*) W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. and Ind.*, 1966, 342; (*b*) C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810.

[3] D. H. R. Barton, *Pure Appl. Chem.*, 1973, **33**, 1.

[4] T. Colclough and J. I. Cunneen, *Chem. and Ind.*, 1960, 626.

[5] E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4861.

[6] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.

[7] E. Block, *J. Amer. Chem. Soc.*, 1972, **94**, 642, 644; E. Block and J. O'Connor, *ibid.*, 1974, **96**, 3921, 3929.

[8] D. Barnard, *J. Chem. Soc.*, 1957, 4675; E. Block and S. W. Weidman, *J. Amer. Chem. Soc.*, 1973, **95**, 5046.

[9] B. C. Gilbert, B. Gill, and M. J. Ramsden, *Chem. and Ind.*, 1979, 283.

[10] J. L. Kice in (*a*) 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, p. 717; (*b*) 'The Chemistry of Organic Sulphur Compounds,' eds. N. Kharasch and C. Y. Meyers, Pergamon Press, Oxford, 1966, vol. 2, p. 129.

[11] B. C. Gilbert, B. Gill, and M. D. Sexton, *J.C.S. Chem. Comm.*, 1978, 78.

[12] J. R. Shelton and K. E. Davis, *Internat. J. Sulphur Chem.*, 1973, **8**, 217 (see also K. A. Muszkat, K. Praefcke, I. Khait, and R. Lüdersdorf, *J.C.S. Chem. Comm.*, 1979, 898).

[13] W. B. Gara and B. P. Roberts, *J.C.S. Perkin II*, 1977, 1708.

[14] B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J.C.S. Perkin II*, 1977, 497.

[15] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590; N. H. Anderson, M. McMillan, and R. O. C. Norman, *ibid.*, 1970, 1075.

[16] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31.

[17] G. Barbarella and A. Rassat, *Bull. Soc. chim. France*, 1969, 2378; J. Goldman, T. E. Petersen, K. Torssell, and J. Becher, *Tetrahedron*, 1973, **29**, 3833.

[18] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1968, **90**, 5909; 1969, **91**, 4481.

[19] I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669.

[20] M. Kobayashi, E. Akiyama, H. Minato, and N. Kito, *Bull. Chem. Soc. Japan*, 1974, **47**, 1504; M. Kobayashi, M. Gotoh, and H. Minato, *J. Org. Chem.*, 1975, **40**, 140; Th. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 696.

[21] E. G. Janzen, B. R. Knauer, L. T. Williams, and W. B. Harrison, *J. Phys. Chem.*, 1970, **74**, 3025.

[22] C. Chatgilialoglu, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1979, 770.

[23] J. J. Zeilstra and J. B. F. N. Engberts, *J. Amer. Chem. Soc.*, 1975, **97**, 7091.

[24] G. Rawson and J. B. F. N. Engberts, *Tetrahedron*, 1970, **26**, 5653; see also H. G. Aurich, K. Hahn, and K. Stork, *Angew. Chem. Internat. Edn.*, 1975, **14**, 551.

[25] A. Mackor, Th. A. J. Wajer, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1966, 2115.

[26] B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1973, 1834.

[27] A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 701.

[28] B. C. Gilbert and B. Gill, *J.C.S. Perkin II*, 1979, 776.

[29] C. Chatgilialoglu, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J.C.S. Perkin II*, 1979, 1084.

[30] (*a*) B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, (2) 173, (M) 1974; (*b*) C. Chatgilialoglu and B. C. Gilbert, unpublished observations.

[31] M. Geoffroy and E. A. C. Lucken, *J. Chem. Phys.*, 1971, **55**, 2719.

[32] G. Zomer and J. B. F. N. Engberts, *Tetrahedron Letters*, 1977, 3901.

[33] R. O. C. Norman and P. M. Storey, *J. Chem. Soc.* (*B*), 1971, 1009.

[34] A. L. Bluhm and J. Weinstein, *J. Amer. Chem. Soc.*, 1970, **92**, 1444; A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 1968, **24**, 1623.

[35] B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 3290.

[36] C. M. M. da Silva Corrêa and W. A. Waters, *J. Chem. Soc.* (*C*), 1968, 1874; see also C. M. M. da Silva Corrêa, *J.C.S. Perkin I*, 1979, 1519.

[37] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 308.

[38] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[39] J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance,' McGraw-Hill, New York, 1972, p. 465.

[40] G. Brunton, B. C. Gilbert, and R. J. Mawby, *J.C.S. Perkin II*, 1976, 1267.

[41] Beilsteins 'Handbuch der Organischen Chemie,' 4th Auflage, 3rd Ergänzungswert, Band 6 p. 860.

[42] H. Rheinsbolt and E. Giesbrecht, *J. Amer. Chem. Soc.*, 1946, **68**, 973.

[43] C. R. Johnson and D. McCants, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 1109.

[44] A. J. Neale, P. J. S. Bain, and T. J. Rawlings, *Tetrahedron*, 1969, **25**, 4583.

[45] C. C. Price and G. W. Stacy, *Org. Synth.*, 1955, Coll. Vol. 3, 667.

[46] Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 4709.

[47] T. Fujisawa, N. Ohtsuka, T. Kobori, and G. Tsuchihashi, *Tetrahedron Letters*, 1968, 4533.

[48] L. Field and T. F. Parsons, *J. Org. Chem.*, 1965, **30**, 657.

[49] T. W. Gibson and P. Strassburger, *J. Org. Chem.*, 1976, **41**, 791.

[50] A. K. Bhattacharya and A. G. Hortmann, *J. Org. Chem.*, 1978, **43**, 2728.

[51] C. W. Schimelpfenig and J. J. Spurlock, *J. Org. Chem.*, 1960, **25**, 1251.

[52] G. Kresze, W. Schramm, and G. Cleve, *Chem. Ber.*, 1961, **94**, 2060 (*Chem. Abs.*, 1961, **55**, 25829e).

[53] D. Walker and J. Leib, *J. Org. Chem.*, 1962, **27**, 4455.

[54] Beilsteins 'Handbuch der Organishchen Chemie,' 4th Auflage, 2nd Ergänszungswert, Band 6, p. 400.

[55] J. P. Danehy and M. Y. Oester, *J. Org. Chem.*, 1967, **32**, 1941.

[56] C. C. Price and G. W. Stacy, *J. Amer. Chem. Soc.*, 1946, **68**, 498.

[57] H. Baganz and H. Peissker, *Arch. Pharm.*, 1956, **289**, 262 (*Chem. Abs.*, 1957, **51**, 1064).

[58] W. E. Truce, D. L. Heuring, and G. C. Wolf, *J. Org. Chem.*, 1974, **39**, 238.

[59] Th. J. de Boer and H. J. Backer, *Rec. Trav. chim.*, 1954, **73**, 229.

[60] J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc.* (*C*), 1969, 1073.
