Electron Spin Resonance Studies. Part 51.[1] Aliphatic and Aromatic Sulphinyl Radicals

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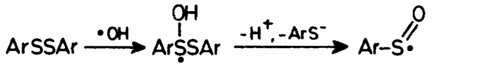
A variety of sulphinyl radicals (RSO·, ArSO·) have been prepared by the reaction between the hydroxyl radical and both thiols and disulphides and by the photolysis of sulphinyl chlorides. The e.s.r. parameters of the aromatic derivatives show that these are π-type species, with extensive delocalisation of the unpaired electron on to the aromatic ring. Typical aliphatic sulphinyl radicals have g *ca.* 2.011 and a(β-H) in the range 0.8—1.1 mT; some of these radicals show linewidth alternation associated with conformational interconversion, and a conformational analysis is presented.

E.S.R. spectroscopy has previously been employed to demonstrate that alkanesulphinyl radicals (RSO·) play an important role in the oxidation, under aqueous conditions, of some thiols,[2] disulphides,[2] and 1,4-bis-sulphoxides.[3] Radicals in this category (*e.g.* $HOCH_2CH_2SO\cdot$) have g *ca.* 2.010, splittings (*ca.* 1 mT) from the (β) protons attached to the carbon adjacent to the sulphur, and broad lines (typically 0.35 mT); a notable feature is that simple alkanesulphinyl radicals (*e.g.* MeSO·, EtSO·) were not detectable at room temperature in aqueous solution, despite evidence to suggest that these radicals were involved in the reactions studied. It was suggested [2] that these species might possess unusually large linewidths, on account of their small size and lack of hydrogen-bonding capacity and, hence, efficient spin-rotation relaxation.[4] Spectra attributed to MeSO· have, however, been reported; thus a signal with a(3H) 0.657 mT, g 2.009 65, ΔH 0.06 mT has been detected during the photolysis of t-butyl methanesulphenate (and of reaction mixtures which probably form this) in cyclopropane at —95 °C,[5] and γ-irradiation of a single crystal of dimethyl sulphoxide leads [6] to a radical with (at —100 °C) a(3H) 1.16 mT (isotropic), $A(^{33}S)$ —1.4, —2.1, 5.9 mT, g 2.023, 2.011, 2.003 (g_{iso} 2.012). These sets of data are surprisingly different if indeed each refers to MeSO·.

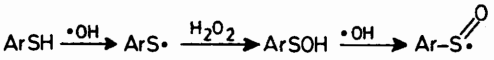
In view of the interest attached to the structure and reactions of sulphinyl radicals (for example, they are believed to play a vital role in the antioxidant activity of sulphenic acids,[7] in the thermal racemisation of certain sulphoxides,[8] and in the thermal decomposition of thiolsulphinates, thiolsulphonates, and sulphinyl sulphones [9]), and in view of the uncertainties concerning previous radical assignments, we have further investigated the formation of sulphinyl radicals and their characterisation by e.s.r. spectroscopy. We have extended the reactions studied and, in particular, have generated some aromatic sulphinyl radicals (ArSO·) with a view to establishing whether the radicals are of π-type (with the unpaired electron delocalised over the SO group and the ring) or of σ-type (*cf.* PhCO· [10]).

RESULTS AND DISCUSSION

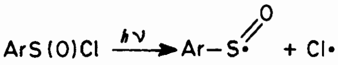
Aromatic Sulphinyl Radicals.—We have studied the oxidation by ·OH (from the Ti^{III}–H_2O_2 system) of some diaryl disulphides, arenethiols, and an alkyl aryl disulphide, under aqueous solution flow-system conditions described previously; [2] the requirement for significant water solubility limited the range of compounds available for study. For the substrates in this category listed in Table 1, the e.s.r. signals detected, although having low amplitude and relatively broad lines (*cf.* the sharper spectra detected using the photolysis method described below), could nevertheless be readily analysed. The spectra are assigned to aromatic sulphinyl radicals, ArSO·. Thus the g values (*ca.* 2.009 0) are in the range expected by comparison with the data [2,6] for aliphatic sulphinyl radicals (*ca.* 2.010); the slightly smaller value is consistent with there being delocalisation of the unpaired electron into the aromatic ring, as evidenced by the ring-proton splittings (see further later). Moreover, on the basis of previous studies [2] of the mechanism of oxidation of dialkyl disulphides and related substances, the formation of sulphinyl radicals would be expected. They should arise, from disulphides, *via* reaction (i); thiols react to form thiyl radicals, which can dimerise to disulphides [and thence react as in (i)] and also become oxidised to sulphenic acids, and hence sulphinyl radicals, *via* reaction (ii).


(i)

$$ArSSAr \xrightarrow{\cdot OH} ArS\overset{OH}{\underset{\cdot}{S}}Ar \xrightarrow{-H^+,\,-ArS^-} Ar{-}\dot{S}{=}O \qquad (i)$$


(ii)

$$ArSH \xrightarrow{\cdot OH} ArS\cdot \xrightarrow{H_2O_2} ArSOH \xrightarrow{\cdot OH} Ar{-}\dot{S}{=}O \qquad (ii)$$


(iii)

$$ArS(O)Cl \xrightarrow{h\nu} Ar{-}\dot{S}{=}O + Cl\cdot \qquad (iii)$$

Further support for our assignment comes from the finding that radicals of the same type were detected during the low-temperature photolysis of aromatic sulphinyl chlorides in diethyl ether [reaction (iii)]. The spectra were much better resolved than those

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[1] Part 50, B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin II*, 1976, 1047.

[2] B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 892.

[3] P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 1245.

[4] J. R. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 2064.

[5] T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Letters*, 1972, 4075.

[6] K. Nishikida and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 4781.

[7] P. Koelewijn and H. Berger, *Rec. Trav. chim.*, 1972, **91**, 1275.

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

[9] J. L. Kice, in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 2, p. 715.

[10] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, 1970, **92**, 722.

obtained using the flow method. Radicals were studied over a range of temperatures, typically −50 to −110 °C, and the spectra showed little dependence on temperature other than a slight line broadening at both upper and lower ends of this range; in the middle of this range ΔH was typically *ca.* 0.04 mT. Table 1 contains details of spectrum analysis and assignment, and Figure 1 shows the spectrum from PhSO· at −75 °C.

TABLE 1

E.s.r. spectra of some aromatic sulphinyl (ArSO·) radicals

Substrate	Method of generation [a,b]	Radical	Hyperfine splittings (mT) [c,d] a(2-H)	a(3-H)	a(4-H)	a(H-CH_3)	g[f]
$PhSSCH_2CH_2OH$ PhSH	·OH	PhSO·	0.26(2)	*e*	0.26		2.008 4
PhS(O)Cl	*hν*, −75 °C	PhSO·	0.240(2)	0.070(2)	0.240		2.009 0
$(2\text{-}CO_2HC_6H_4S)_2$ $2\text{-}CO_2HC_6H_4SH$	·OH	$2\text{-}CO_2HC_6H_4SO\cdot$	0.26(1)	0.07(2)	0.26		2.008 8
$(4\text{-}\overset{+}{N}H_3C_6H_4S)_2$	·OH	$4\text{-}\overset{+}{N}H_3C_6H_4SO\cdot$	0.325(2)	*e*			2.008 5
$4\text{-}MeC_6H_4S(O)Cl$	*hν*, −80 °C	$4\text{-}MeC_6H_4SO\cdot$	0.230(2)	0.075(2)		0.285	2.008 9
$3\text{-}MeC_6H_4S(O)Cl$	*hν*, −90 °C	$3\text{-}MeC_6H_4SO\cdot$	0.240(2)	0.075(1)	0.240	0.075	2.009 0
$2\text{-}MeC_6H_4S(O)Cl$	*hν*, −97 °C	$2\text{-}MeC_6H_4SO\cdot$	0.250(1) [g]	0.075(2)	0.250 [g]	0.125 [g]	2.009 2
$4\text{-}ClC_6H_4S(O)Cl$	*hν*, −69 °C	$4\text{-}ClC_6H_4SO\cdot$	0.250(2)	*h*			2.009 2

[a] ·OH; aqueous solution, room temperature. [b] *hν*; photolysis of the appropriate sulphinyl chloride in diethyl ether. [c] For ·OH oxidations, ±0.02 mT; for photolyses, ±0.005 mT. [d] Linewidth 0.04 mT unless indicated otherwise. [e] Proton splittings not resolved; ΔH *ca.* 0.15 mT. [f] For ·OH oxidations, ±0.000 4; for photolyses ±0.000 1. [g] Tentative assignment; see text. [h] Further proton splittings not resolved; a(4-Cl) *ca.* 0.045 mT.

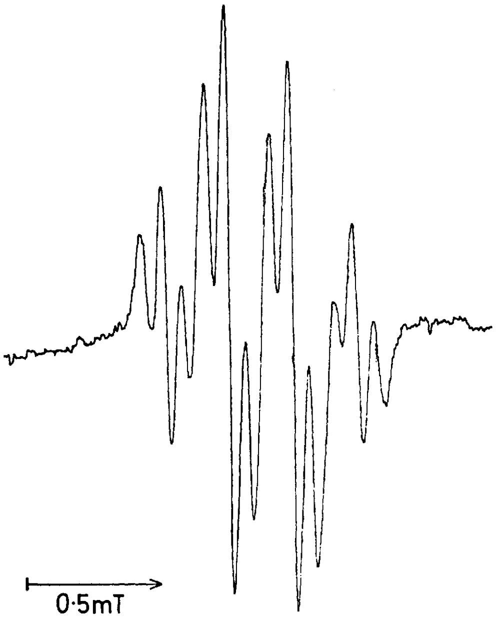

FIGURE 1 E.s.r. spectrum of $C_6H_5SO\cdot$ at −75 °C

The sets of splitting constants observed for the benzenesulphinyl radical and its 3- and 4-methyl-substituted derivatives can only be satisfactorily rationalised on the basis that, first, the methyl protons have approximately the same splitting constant as the ring proton at the same position, and, secondly, the splittings from the protons at the 2- and 4-positions are much larger than that from the protons at C-3. These are characteristics of π-radicals (as MeSO· has been suggested to be on the basis of its anisotropic parameters [6]) and not of σ-radicals. The spectra of 2- and 4-substituted radicals generated using the flow method add confirmatory evidence for the assignments of splittings. Structurally, then, the radicals resemble the π-type species,[11] $PhNO^{-\cdot}$.

The spectrum of the 2-methylbenzenesulphinyl radical could not be unambiguously analysed and assigned; thus it appears that there is a splitting of 0.125 mT in addition to those typical of 2- and 4-protons (*ca.* 0.25 mT) and of the 3-protons (0.07 mT), although some doubt remains as to the number of protons associated with each of the larger splittings. Our tentative assignment (Table 1) associates the 0.125 mT splitting with the 2-methyl group protons; it does not seem likely that twisting about the C–SO bond is responsible for this behaviour [since the ring-proton splittings, and particularly a(4-H), would then be affected [12,13]] and the explanation may involve some novel mode of spin transmission to the protons of the 2-methyl group adjacent to the radical centre, of opposite sign to that associated with the π-delocalisation mechanism.

It is significant that an uncharacterised e.s.r. signal has been detected [8] during the thermolysis of benzyl toluene-*p*-sulphenate ($PhCH_2OSC_6H_4CH_3$) in naphthalene at 160 °C; we have repeated this experiment and have found that the broad singlet has g *ca.* 2.008 5. We suggest that this is the 4-methylbenzenesulphinyl radical (formed, presumably, by homolysis of the *O*-benzyl bond in the sulphenate); the large linewidth, which precludes observation of the expected proton splittings, is as anticipated from our results which suggest that linewidths in sulphinyl radicals increase with increasing temperature.

Aliphatic Sulphinyl Radicals.—We have also photolysed solutions of some aliphatic sulphinyl chlorides, RS(O)Cl, in diethyl ether and have found that e.s.r.

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[11] G. A. Russell and E. J. Geels, *J. Amer. Chem. Soc.*, 1965, **87**, 122.

[12] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

[13] D. Clarke, B. C. Gilbert, and P. Hanson, *J.C.S. Perkin II*, 1975, 1078.

spectra are detectable at low temperatures. The results in Table 2 refer, in general, to the temperatures at which optimum spectra were obtained; the linewidths increased both as the temperature was raised and also at very low temperatures where solvent viscosity was significantly increased. The g values and splittings are entirely as expected on the basis of data for radicals, assigned the structure RSO•, formed from •OH and disulphides[2] (*cf.* also Bu^{t}SO•, g 2.010 6, generated[14] from reaction of Bu^{t}O• with Bu^{t}SOH at low temperature), and we infer that photolysis of the S–Cl bond has occurred. In one case, $HOCH_2CH_2SO•$, the same radical was generated by both flow (aqueous solution) and photolytic methods, and the spectral parameters under the two conditions are in excellent agreement (see Table 2); in general, the photolytic method provides a means for preparing a range of simple alkanesulphinyl radicals whose spectra proved undetectable in aqueous solution at room temperature.[2]

TABLE 2

E.s.r. spectra of aliphatic sulphinyl radicals (RSO•) [a]

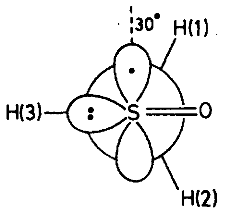
R	T/°C	a(H)/mT [b]		g [c]	ΔH/mT
Me	−113	1.15 (3 H)	(±0.05)	2.010 0	1.10
$MeCH_2$	−116	0.91 (2 H)		2.011 0	0.10
$HOCH_2CH_2$	−65	0.86 (2 H)		2.011 0	0.12
	(r.t.[d])	(0.95)		(2.010 9)	
$MeCH_2CH_2$	−105	0.89 (2 H)		2.011 1	0.12
$MeCH_2CH_2CH_2$	−92	0.91 (2 H)		2.011 1	0.12
Me_2CHCH_2	−98	0.79 (2 H)		2.010 5	0.10
Me_2CH	−110	1.00 (1 H)		2.011 0	0.10
$MeCH_2CH(Me)$	−112	0.76 (1 H)		2.011 0	0.17
	−61	0.86 (1 H)		2.011 0	0.10

[a] Generated by photolysis of the corresponding sulphinyl chlorides in diethyl ether. [b] ±0.01 mT, unless otherwise stated. [c] ±0.000 1. [d] Flow experiment; see ref. 2.

Our data for MeSO• [g 2.010, a(3H) 1.15 (±0.05) mT] are in excellent agreement with the analysis presented for the species assigned this structure which is formed in irradiated dimethyl sulphoxide. The large linewidth for MeSO• in solution is notable (ΔH 1.1 mT at −113 °C); this increased as the temperature was raised and it is clear that this species would be undetectable at, and around, room temperature.

It is apparent that the radical to which we assign the structure MeSO• is not the same as that derived[5] from the photolysis of t-butyl methanesulphenate at low temperature and also assigned this structure. The latter, and those in the same family derived by photolysis[5] of mixtures of, for example, alkyl disulphides and di-t-butyl peroxide, evidently belong to a class of radical different from those whose parameters appear in Table 2, and which have lower g-values and splittings and narrower lines. We have also examined the photolysis of t-butyl methanesulphenate (in diethyl ether at low temperatures) and detect the radical reported by Kawamura *et al.*,[5] confirming their spectral analysis; our suggestions for reassignment are presented at the end of this paper.

Several interesting structural features are revealed by the e.s.r. spectra of the aliphatic sulphinyl radicals. For example, the central lines of the quartet from MeSO• were broader than the outside lines in the temperature range −120 to −130 °C, although the large intrinsic linewidth of this radical rendered quantitative study impossible. This behaviour is indicative of interconversion (presumably *via* rotation about the C–S bond) of conformations involving non-equivalent hydrogen splittings, as noted previously by Nishikida and Williams.[6] These authors found that for this radical in a rigid matrix at −185 °C only two proton splittings (a 1.73 mT) are detected, and they suggested that these splittings typify a fixed conformation with one proton in the nodal plane of the orbital of the unpaired electron [*i.e.* (1) or (2)]. The magnitude of a(β-H) for H(1) and H(2) (which make a dihedral angle of 30° with the orbital of the unpaired electron) and the lack of a splitting for H(3) (dihedral angle 90°) are then understandable in relation to a(β-H) at higher temperatures (1.16 mT) (where the methyl group is freely-rotating and $\langle \cos^2\theta \rangle = 1/2$), if a(β-H) is proportional to $\cos^2\theta_H$.[6]



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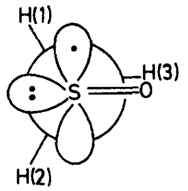

(2)

In the spectra of some of the primary aliphatic sulphinyl radicals $RCH_2SO•$ (R = $HOCH_2$, $MeCH_2$, $MeCH_2CH_2$, or Me_2CHCH_2), the central line of the 1 : 2 : 1 pattern showed a marked broadening as the temperature was lowered, a phenomenon which again indicates the operation of conformational interconversion, at intermediate rates, involving structures with non-equivalent β-hydrogen splittings. Figure 2 shows the spectrum from $MeCH_2CH_2SO•$ as a function of temperature. For the radicals $RCH_2SO•$ (R = $MeCH_2$,

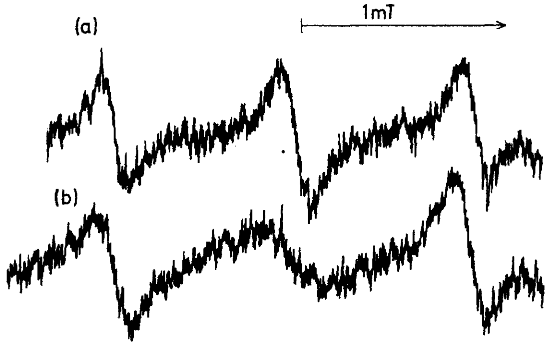

FIGURE 2 E.s.r. spectrum of $CH_3CH_2CH_2SO•$: (a) at −79 °C; (b) at −118 °C

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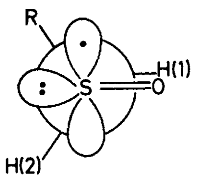
[14] J. A. Howard and E. Furimsky, *Canad. J. Chem.*, 1974, **52**, 555.

$MeCH_2CH_2$, or Me_2CHCH_2) the central line had completely collapsed by *ca.* −120 °C; as the temperature was lowered further (the lower limit achieved was −130 °C) no further change took place and the ' missing ' lines did not reappear. For $HOCH_2CH_2SO\cdot$, which showed complete broadening of the central line by −80 °C, no extra lines could be resolved at lower temperatures (down to −120 °C) and the spectrum appeared as a doublet (*a ca.* 1.7 mT). No alternating linewidth effect was detected for $CH_3CH_2SO\cdot$ down to −120 °C.

It is perhaps significant that radicals of the type $RCH_2SO\cdot$ have $a(CH_2)$ *ca.* 0.85 mT at the lowest temperatures employed and that there is little temperature dependence for a(H) in this region [*e.g.* for $MeCH_2CH_2SO\cdot$ a(H) is 0.89 at −79 and 0.88 mT at −118 °C]. This suggests that by *ca.* −120 °C the preferred conformations of these radicals have achieved complete, or near complete, weighting, and also that the preferred conformations for the different radicals are similar. Further, if we assume that a(β-H) for these radicals can indeed be expressed[6] as $\rho_S B \cos^2\theta_H$ (with $\rho_S B$ 2.3 mT, from our splitting for MeSO·), then some conclusions about conformational preferences are possible. We know the average β-H splittings for $RCH_2SO\cdot$ (*ca.* 0.85 mT) and, since the dihedral angle between the two C–H bonds should be *ca.* 120°, an estimate of the two individual dihedral angles (θ_H) can be obtained. Angles of *ca.* 90 and 30° lead to predicted β-H splittings for the individual protons of 0 and 2.3 $\cos^2 30°$, *i.e.* 1.725 mT, with an average, as observed, of 0.86 mT.* The appropriate conformations are (3), and the equivalent conformation (4), or (5) and the equivalent conformation (6).



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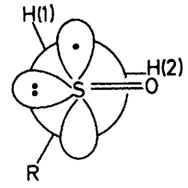

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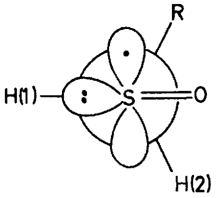

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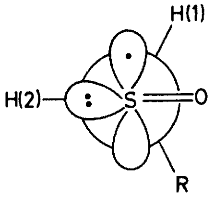

(6)

It is interesting that one C–H bond is evidently located in, or close to, the nodal plane of the orbital of the unpaired electron (as with MeSO·). In view of the expected greater steric requirement of the oxygen compared with the lone-pair of electrons, conformations (5) and (6) appear to be most likely to be preferred.

A conformational analysis involving interconversion of (3) and (4) or (5) and (6) has the advantage not only that the observed average β-proton splitting is correctly predicted but also that the separate hydrogen atoms would then have significantly different splittings in the individual conformations; this would account for the marked line-broadening effect referred to above and for our failure to observe two splittings in the low-temperature limit (at *slow* interconversion rates, the spectra would simply show a doublet pattern with no inner lines). On this basis, assuming individual splittings of 1.77 mT and zero [*e.g.* for H(2) and H(1), respectively, in (3) or (5)], we have simulated the effect of rapid exchange for the radical $MeCH_2CH_2SO\cdot$ with a simulation programme which incorporates two-jump exchange using a Bloch equation model; interconversion rates at different temperatures have been obtained (*e.g.* 8.0×10^9 at −79, 4.7×10^8 s^{-1} at −118 °C) from which we estimate that the barrier to rotation about the C–S bond is 18 (±2) kJ mol^{-1}.

Results for $CH_3CH_2SO\cdot$ suggest that here the energy barrier for motion about C–S is relatively low, whereas for $HOCH_2CH_2SO\cdot$ it is evidently greater. In the latter example, intramolecular hydrogen-bonding between the hydroxy-hydrogen atom and the sulphinyl oxygen atom [in (5) and (6)] may be implicated.

For the radical $Me_2CHSO\cdot$ the temperature dependence of a(β-H) was small, like those for radicals of the type $RCH_2SO\cdot$. This suggests that in $Me_2CHSO\cdot$ the preferred conformation is again significantly weighted. The magnitude of the splitting is, however, quite surprising and suggests that the favoured conformation has θ_H *ca.* 50° [*i.e.* of the type (7) or (8)]. This is in contrast to that expected by comparison with many other radicals in which a 1-methylethyl group is attached to the radical centre (ref. 15 describes many examples of this type), for which low values of a(β-H) indicate the favoured conformations to be those in which the β-C–H bond lies in the nodal plane of the unpaired electron [*e.g.* (9)]. We suggest that conformation (7) is preferred, on steric grounds, to (8). The reasons for the preference of (7) or (8) over the symmetrical conformations (9) or (10) is not clear but we note that the preferred conformation may, as has been suggested[16] for, *e.g.*, $\cdot CH_2CHMe_2$, represent a balance between minimisation of steric repulsion and the maximisation of C–H hyperconjugation.

The radical $MeCH_2CH(Me)SO\cdot$ showed a marked temperature dependence (see Table 2); although it appears that conformational motion has not been frozen out, the significant value for a(β-H) indicates that, as with $Me_2CHSO\cdot$, the single C–H bond does not prefer to eclipse the SO bond or the lone-pair orbital.

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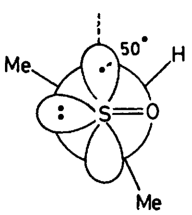
* Although the average splittings vary around 0.86, from 0.79 to 0.91 mT, these limiting values are accommodated using small (*ca.* 5°) deviations from 90 and 30° (85 and 35°, and 85 and 25°, respectively).

[15] D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125.

[16] P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, 1971, **74**, 3438.

Conclusions.—The evidence presented in this paper characterises a wide range of sulphinyl radicals, RSO· and ArSO·, and shows that these are π-electron species.



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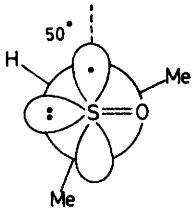

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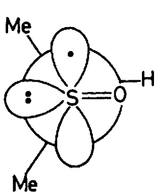

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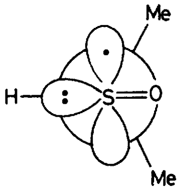


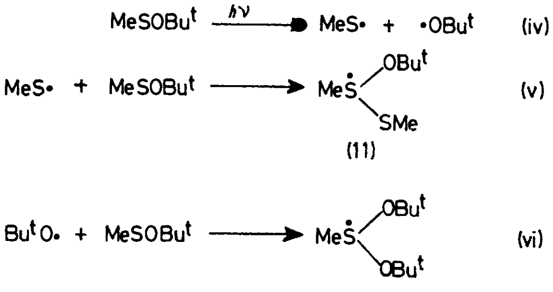
(10)

Results are entirely consistent with other assignments of spectra from $Bu^tSO\cdot$ [14] and MeSO·.[6] It is clear that these radicals are important intermediates in the oxidation of disulphides, thiols, and sulphenic acids and in the radiolysis and photolysis of S=O containing compounds (*e.g.* sulphoxides, sulphinyl chlorides).

Finally we return to the assignments to RSO· (erroneous, we suggest) of signals detected during the low temperature photolysis of t-butyl methanesulphenate and of mixtures of, for example, dialkyl disulphides and di-t-butyl peroxide.[5] In the case of t-butyl methanesulphenate, it seems likely that photolysis will break the S–O bond [reaction (iv)]; the next step in the reaction may well involve attack on more sulphenate by either MeS· [reaction (v)] or $Bu^tO\cdot$ [reaction (vi)]. The sulphur atom in the sulphenate should be the site of attack, as judged by the readiness with which ·OH attacks the sulphur atoms in, for example, thiols and disulphides,[2] and sulphoxides;[3] attack of RS· at sulphur in thiols is also known to be rapid.[2] Adducts with structures related to (11) and (12) have been proposed as intermediates in the radical reactions of, for example, sulphides (*e.g.* $R_2\dot{S}OH$ [17]) and disulphides [$RS\dot{S}(H)R$,[18,19] $RS\dot{S}(OH)R$ [2,20]].

When the disulphide–peroxide or thiol–peroxide mixtures are photolysed,[5] t-butyl alkenesulphenates may be formed *in situ* (from RS· and Bu^tOOBu^t or from $Bu^tO\cdot$ and RSSR) and subsequently decomposed as in reaction (iv). An alternative route to radicals of type (11) would involve direct addition of $Bu^tO\cdot$ to disulphides.

Although we cannot at this stage make an unambiguous structural assignment to the anomalous radical-type detected, we tentatively suggest that these are novel radicals formed by an addition reaction at sulphur [*cf.* tetraco-ordinate phosphoranyl radicals formed from P^{III} species [21]].



EXPERIMENTAL

The e.s.r. spectrometer, flow system design and operation, spectrum measurement, calibration, and simulation,[2] and photochemical arrangement [22] have been described previously.

Thiols and disulphides were commercial samples except for 2-hydroxyethyl phenyl disulphide, which was prepared from *N*-(phenylthio)succinimide and 2-hydroxyethanethiol by the method of Boustany and Sullivan;[23] these substrates were oxidised by ·OH (from the Ti^{III}–H_2O_2 system) as described previously.[2]

Benzenesulphinyl chloride and 4-methylbenzenesulphinyl chloride were prepared from the sodium salts of the corresponding sulphinic acids;[24] other aromatic sulphinyl chlorides were prepared from the corresponding thiols by the method of Douglass and Norton.[25] All aliphatic sulphinyl chlorides were prepared by chlorination of the appropriate thiol or disulphide.[25] All sulphinyl chlorides were purified by distillation.

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