Electron Spin Resonance Studies. Part 57.[1] Alkane- and Arene-sulphinate Esters: an Investigation of their Photochemical Decomposition and Reactions with the t-Butoxyl Radical

By **Chryssostomos Chatgilialoglu, Bruce C. Gilbert,* Christopher M. Kirk,** and **Richard O. C. Norman,**
Department of Chemistry, The University of York, Heslington, York YO1 5DD

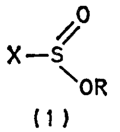
E.s.r. evidence is described for three modes of photolytic decomposition of sulphinate esters [XS(O)OR]. For some alkyl arenesulphinates (X = *p*-tolyl, R = alkyl) the arenesulphinyl radical (XSO·) is detected, evidently as a result of S–O bond fission; for some alkyl alkanesulphinates, photolysis apparently cleaves the O–R bond and alkanesulphonyl radicals (XSO_2·) are formed; for methyl phenylmethanesulphinate (X = $PhCH_2$, R = Me) the detection of the benzyl radical and MeOSO· suggests that the C–S bond has been broken.

It is suggested that the reaction between Bu^tO· (from di-t-butyl peroxide) and sulphinates usually involves attack at sulphur to give an intermediate sulphuranyloxyl radical $X\dot{S}(O)(OR)OBu^t$. Evidence that this can undergo dealkylation derives from the detection of the benzyl radical in the reaction of $PhCH_2S(O)OMe$. On the other hand, the production of sulphonyl radicals (XSO_2·; X = alkyl, aryl) from this intermediate may involve dealkoxylation and further reaction of the resulting t-butyl sulphinate ester.

Line-width variation in the e.s.r. spectrum of $MeSO_2$· at low temperature is attributed to the occurrence of restricted rotation about the C–S bond in a radical of pyramidal type.

RECENT e.s.r. studies on a variety of sulphur-containing compounds have enabled several novel types of radical to be characterised. For example, photolysis of sulphenates or of disulphide–peroxide mixtures led to the detection [2] of spectra from sulphuranyl radicals $R^1\dot{S}(OR^2)_2$, and photolysis of dialkyl sulphites both in the absence and in the presence of di-t-butyl peroxide gave the previously uncharacterised radicals [3] ROSO· and [4] $(RO)_2\dot{S}(O)OBu^t$, respectively. Other sulphur-centred radicals such as sulphinyl [5] (RSO·) and sulphonyl [6] (RSO_2·) species have also been generated recently under photolytic conditions and their e.s.r. parameters are now well established. These studies have also enabled mechanistic conclusions to be drawn about the radical chemistry of a variety of sulphur-containing compounds.

Product studies have indicated [7] that in the photolysis of some alkyl toluene-*p*-sulphinates [$4\text{-}CH_3C_6H_4S(O)OR$] the predominant reaction involves the cleavage of the S–O bond, and a report of an e.s.r. study of the reactions of Bu^tO· with sulphoxides and with three alkyl alkanesulphinates has also appeared.[8] We now report the results of an e.s.r. investigation into the direct photolysis, and the photolysis in the presence of di-t-butyl peroxide, of a series of alkane- and arene-sulphinate esters (1; X = alkyl, *p*-tolyl, R = alkyl); we set out to gain information about the mechanisms of the reactions concerned (*e.g.*, which bonds are broken in photolysis, the possible role of sulphuranyloxyl species and their modes of fragmentation) and about the structure of the radicals detected.



(1)

RESULTS AND DISCUSSION

Direct Photolysis.—The low temperature (*ca.* −100 °C) *in situ* photolysis of solutions of a variety of alkyl toluene-*p*-sulphinates (1; R = alkyl, benzyl, allyl, X = *p*-tolyl; see Table) in cyclopropane led to the detection solely of the toluene-*p*-sulphinyl radical ($4\text{-}CH_3C_6H_4SO$·) in each case; the e.s.r. parameters of this radical have been described previously.[5]

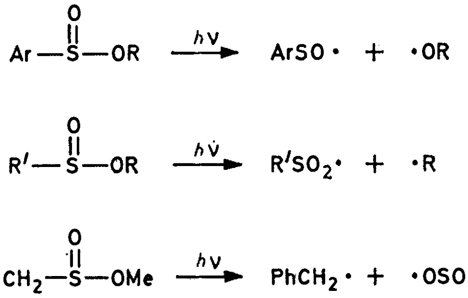
In contrast direct photolysis of solutions of some alkyl alkanesulphinate esters (1; X = Me, R = Me; X = Pr, R = Me; X = Me, R = Pr) in cyclopropane at low temperature (*ca.* −100 °C) gave detectable e.s.r. signals from the appropriate alkanesulphonyl species XSO_2· (with parameters essentially as described previously [6]). [An interesting feature was that the spectrum of $MeSO_2$· below *ca.* −110 °C showed broadening of the inner lines of the methyl-proton hyperfine splitting pattern. This radical was also generated in diethyl ether (by photolysis of $MeSO_2Cl$) and the broadening appeared to be even more pronounced; the effect then became noticeable as the temperature was lowered below −80 °C, and by about −120 °C the relative heights of the four lines were 1 : 0.8 : 0.8 : 1; this phenomenon is discussed in detail in a later section.] In these experiments, no signals were detected from alkanesulphinyl radicals (RSO·). Such radicals have previously been generated [5] under conditions similar to those employed here by the photolysis of the appropriate sulphinyl chlorides; although the e.s.r. spectrum from MeSO· shows pronounced broadening under these conditions (which would render detection difficult), there is no corresponding broadening for PrSO· and our failure to detect it here suggests that it is not formed to any considerable extent.

The e.s.r. signals of ArSO· and RSO_2· detected from alkyl arenesulphinates and alkyl alkanesulphinates, respectively, were present as soon as photolysis commenced and did not build up with time. This observation, coupled with the finding that for both sets of substrates the steady-state radical concentrations were proportional to the square root of the intensity of the light, suggests that these are radicals formed in primary processes (rather than *via* decomposition of photoproducts).

The methyl ester of phenylmethanesulphinic acid (1;

X = $PhCH_2$, R = Me) behaved differently from the other sulphinate esters studied: photolysis of a solution in cyclopropane at low temperature gave rise to the e.s.r. spectrum from[3] MeOSO· and in cyclopropane/oxiran under similar conditions the spectrum from this radical was accompanied by that from the benzyl radical.[9] The signals were weak and it was not possible to determine whether or not they derive from primary or secondary species. No evidence was obtained for the sulphonyl radical $PhCH_2SO_2\cdot$ [which, though it might be formed during the photolysis of $PhCH_2S(O)OMe$, might also be expected[10] to desulphonylate rapidly]. We attempted to generate this radical independently by photolysis of mixtures of $PhCH_2SO_2Cl$ and triethylsilane/di-t-butyl peroxide in cyclopropane at *ca.* −100 °C, but only a singlet, *g* 2.0045, was observed: this spectrum is assigned to $\cdot SO_2Cl$ (*cf.* ref. 6b). When a solution of $PhCH_2SO_2Cl$ in diethyl ether was photolysed, spectra from[3] HOSO· [a(1H) 0.93 mT, *g* 2.0053] and the benzyl radical were observed. There was no evidence for the formation of $PhCH_2SO\cdot$ from photolysis of (1; X = $PhCH_2$, R = Me) [though this radical, with a(2H) 1.083 mT, *g* 2.0107, is detectable when generated under similar conditions by the photolysis of dibenzyl sulphoxide[11]].

Modes of Photolytic Cleavage.—The assertion[7] on the basis of product studies that photolysis of arenesulphinate esters leads to the cleavage of the S–O bond is supported by our direct detection of the appropriate arenesulphinyl radicals ArSO· [reaction (1)]. On the other hand, spectra due to alkanesulphinyl radicals were not detected during the photolysis of alkanesulphinate esters and our results indicate that, in contrast, O–R bond cleavage to give alkanesulphonyl radicals [reaction (2)] has taken place. We believe that the explanation for this difference is that the S–O bond strength is weaker for the arene- than the alkane-sulphinate esters because of extra stability conferred upon arenesulphinyl species by delocalisation of the unpaired electron around the aromatic π-system,[5] and that this effect offsets the normal preference for cleavage of O–C rather than S–O (we note here that extra stability of this type should not be available for arenesulphonyl σ-radicals,[6] $ArSO_2\cdot$, in which the unpaired electron is not delocalised into the aromatic π-system).*



$$Ar{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OR \xrightarrow{h\nu} ArSO\cdot + \cdot OR \qquad (1)$$

$$R'{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OR \xrightarrow{h\nu} R'SO_2\cdot + \cdot R \qquad (2)$$

$$PhCH_2{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OMe \xrightarrow{h\nu} PhCH_2\cdot + \cdot OSOMe \qquad (3)$$

The formation of MeOSO· and benzyl during the direct photolysis of the methyl ester of phenylmethanesulphinic acid suggests that for this substrate direct C–S fission [reaction (3)] may have taken place, presumably on account of the resonance stabilisation in the benzyl radical produced.

Photolysis in the Presence of Di-t-butyl Peroxide.—Experiments which were carried out on solutions of alkyl arenesulphinates (1; R = alkyl, X = *p*-tolyl) which also contained di-t-butyl peroxide (see Table) led in general to the detection of the signal from the sulphinyl radical $4\text{-}CH_3C_6H_4SO\cdot$ along with that of the corresponding sulphonyl radical ($4\text{-}CH_3C_6H_4SO_2\cdot$); the splittings and *g*-value of the latter radical have been reported previously.[6] The signals from these radicals appeared as soon as the light was switched on, and the sulphonyl radical was generally present in higher concentrations than the sulphinyl radical (especially when the peroxide was present in excess); it seems likely that the sulphinyl radical derives from direct photolysis (as described earlier) whereas the sulphonyl radical derives from reaction of the sulphinate ester with $Bu^tO\cdot$. In the reaction of (1; R = Et, X = *p*-tolyl) a signal slowly developed which had a(3H) 2.25, a(1H) 1.53, a(1H) 0.15 mT, *g* 2.0033 (at −80 °C). This is attributed to $\cdot CH(CH_3)OH$,[12] evidently formed from reaction of $Bu^tO\cdot$ with ethanol, generated during the reaction.

TABLE

Radicals detected by e.s.r. during photolysis of some arene- and alkane-sulphinate esters [XS(O)OR] [a]

Substrate [b]		Direct photolysis [b]	Photolysis in the presence of $(Bu^tO)_2$ [b]
X	R		
Ar	Me	ArSO·	
Ar	Et	ArSO·	ArSO·, $ArSO_2\cdot$
Ar	Pr^i	ArSO·	ArSO·, $ArSO_2\cdot$
Ar	CH_2Bu^t	ArSO·	ArSO·, $ArSO_2\cdot$
Ar	CH_2Ph	ArSO·	ArSO·
Ar	$CH_2CH{=}CH_2$	ArSO·	$ArSO_2\cdot$, (2)
Me	Me	$MeSO_2\cdot$	$MeSO_2\cdot$, Me·
Me [c]	Me [c]		$MeSO_2\cdot$
Me	Pr	$MeSO_2\cdot$	$MeSO_2\cdot$
Pr	Me	$PrSO_2\cdot$	$PrSO_2\cdot$
$PhCH_2$	Me	MeOSO·	$PhCH_2\cdot$, MeOSO·
$PhCH_2$ [c]	Me [c]	$PhCH_2\cdot$, MeOSO·	$PhCH_2\cdot$, MeOSO·

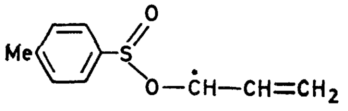
[a] In cyclopropane solution unless otherwise indicated. [b] Ar = *p*-tolyl. [c] Solution also contained oxiran as co-solvent.

No sulphonyl radical was detected during the photolysis of the benzyl ester (1; R = benzyl, X = *p*-tolyl). Photolysis of the corresponding allyl ester at temperatures above *ca.* −70 °C led to the detection of the expected sulphonyl radical; at temperatures below this another spectrum was observed which, although it could not be analysed in detail, clearly corresponds to a radical of allyl type [with three splittings of *ca.* 1.38 mT (from ' terminal ' hydrogens), and one splitting of 0.28 mT, evidently from the ' central ' hydrogen; *cf.* ref. 3]. It is assigned to the species (2) formed by hydrogen-atom abstraction (a radical of analogous type has been detected during the reaction of $Bu^tO\cdot$ with diallyl sulphite[3]).

---

* The opposite conclusion, that $ArSO_2\cdot$ possesses greater resonance stabilisation than ArSO·, is reached on the basis of thermodynamic arguments by S. W. Benson (*Chem. Rev.*, 1978, **78**, 23).

When solutions of sulphinate esters (1; X = Me, R = Me; X = Pr, R = Me; X = Me, R = Pr) in cyclopropane were photolysed sulphonyl radicals ($RSO_2\cdot$) were again detected, their signal intensities being significantly enhanced compared with the signals of the same radicals produced in the direct photolysis. The signals appeared to be present as soon as photolysis commenced and they did not build up with time.



(2)

Photolysis of MeS(O)OMe in cyclopropane in the presence of di-t-butyl peroxide led to the detection of the methyl radical, as well as $MeSO_2\cdot$ (see also ref. 8). The ratio of [Me·] to [$MeSO_2\cdot$] varied from experiment to experiment in non-reproducible fashion which may be a result of the limited solubility of the sulphinate in cyclopropane: as the solution cooled to the low temperature employed, the sulphinate gradually came out of solution. Accordingly, experiments were carried out with oxiran added as a co-solvent; the only signal detected was that due to $MeSO_2\cdot$. No spectra attributed to alkyl radicals could be detected during experiments with MeS(O)OPr and PrS(O)OMe.

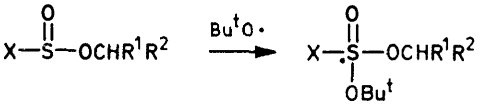
Signals from benzyl and MeOSO· were detected during photolysis of (1; X = $PhCH_2$, R = Me) in the presence of di-t-butyl peroxide in both cyclopropane and cyclopropane/oxiran, the signal from benzyl being more prominent under these conditions than in the direct photolyses. In the experiments with peroxide, traces of other signals were also detected; these were also observed more clearly when oxiran was omitted from the solvent. One weak signal, detected at −80 °C, appeared to be a quintet [a(4H) 0.17 mT, g 2.0064]; the other, prominent at −120 °C, had g 2.0073, a(1H) 0.37, a(1H) 0.19 mT. It seems possible that the former is the ‘ dimer ’ radical-cation $[PhCH_2S(O)OMe]_2^{+\cdot}$ [*cf.* the analogous species[13] $Me_2S(O)\text{–}S(O)Me_2^{+\cdot}$] and the second may be the first-formed sulphuranyloxyl radical $PhCH_2\dot{S}(O)(OMe)OBu^t$; however, these assignments must remain tentative at this stage (and it may in any case be significant that in these experiments the limited solubility of the substrate caused this to come out of solution at low temperatures).

We also attempted to employ e.s.r. in a study of the reactions of $Et_3Si\cdot$ and of $PhCO_2\cdot$ (from dibenzoyl peroxide) with sulphinates. Reaction of $Et_3Si\cdot$ with a sulphinate might be expected to take place *via* addition at oxygen (S=O) to give a sulphuranyl species of the type $X\dot{S}(OSiEt_3)OR$ [*cf.* reaction of the triethylsilyl radical with ketones and esters[14]]; however, no such radicals could be detected in our experiments. When a solution of ethyl toluene-*p*-sulphinate in methylbenzene containing dibenzoyl peroxide was photolysed (at *ca.* −80 °C) only the spectrum of $4\text{-}CH_3C_6H_4SO\cdot$ could be detected.

Mechanisms of Reaction with $Bu^tO\cdot$.—When the mixtures of sulphinate esters and di-t-butyl peroxide to be photolysed also contained an excess of cyclopentane, signals from the cyclopentyl radical,[15] but not sulphonyl radicals, were detected. From this we conclude that the production of sulphonyl radicals in the absence of cyclopentane is a reaction initiated by $Bu^tO\cdot$ (rather than *via* energy transfer from photo-excited peroxide). t-Butoxyl radicals would be expected to react with sulphinate esters either by hydrogen-atom abstraction [reaction (4)] or by addition at sulphur [reaction (5)] or both (*cf.* reactions of $Bu^tO\cdot$ with sulphides,[2] sulphites,[3] and sulphoxides[8]). Reaction (4) presumably occurs to some extent for (1; X = *p*-tolyl, R = allyl), since the appropriate radical (2) was directly detected (evidently as a consequence of the extra delocalisation available in this radical). Radicals of the type (3) without such delocalisation would probably fragment to give a carbonyl compound and a sulphinyl radical [reaction (6)] (*cf.* the behaviour of the analogous radicals from sulphites[3]), and it is notable that aromatic sulphinyl radicals were detected in some cases, although we cannot distinguish between this pathway and direct photolysis.

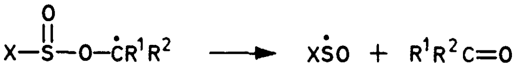
$$\mathrm{X{-}\overset{\overset{O}{\|}}{S}{-}OCHR^1R^2 \xrightarrow{Bu^tO\cdot} X{-}\overset{\overset{O}{\|}}{S}{-}O\dot{C}R^1R^2} \qquad (4)$$

(3)



$$\mathrm{X{-}\overset{\overset{O}{\|}}{S}{-}OCHR^1R^2 \xrightarrow{Bu^tO\cdot} X{-}\underset{\underset{OBu^t}{|}}{\overset{\overset{O}{\|}}{\dot{S}}}{-}OCHR^1R^2} \qquad (5)$$

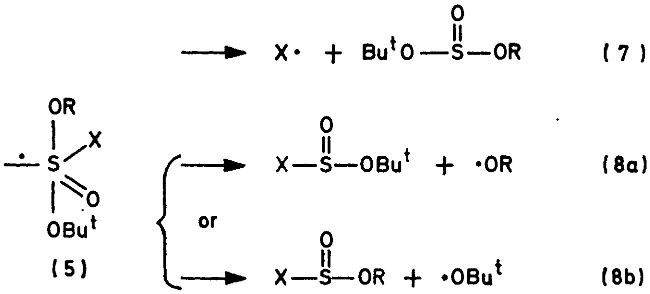
(4)



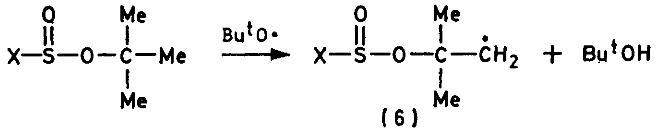
$$\mathrm{X{-}\overset{\overset{O}{\|}}{S}{-}O{-}\dot{C}R^1R^2 \longrightarrow X\dot{S}O + R^1R^2C{=}O} \qquad (6)$$

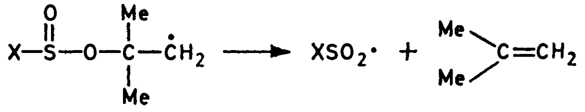
Addition of t-butoxyl at sulphur would lead to the sulphuranyloxyl species (4); if we assume that, as with phosphoranyl radicals, the apicophilicities of the ligands in (4) follow the order of the group electronegativities,[16] then the structure of this intermediate should be (5) (as suggested by Gara and Roberts[8]). No intermediate of this type could be directly detected, but it seems likely that these species are involved. One possible mode of cleavage for (5) is dealkylation [reaction (7)], which is probably the route by which methyl is formed in the reaction between $Bu^tO\cdot$ and MeS(O)OMe and by which the prominent benzyl signal largely arises in the corresponding reaction of $PhCH_2S(O)OMe$. An alternative mode of decomposition is the loss of the apical ligands $Bu^tO\cdot$ or RO· [t-butoxydealkoxylation, reactions (8a) and (8b)]; loss of the latter would lead to the formation of a t-butyl sulphinate ester and ·OR. The detection of $\cdot CH_2[CH_2]_3OH$, evidently formed *via* ·OBu, from the reaction between $Bu^tO\cdot$ and MeS(O)OBu,[8] lends support to this interpretation, as does the detection of $\cdot CH(CH_3)\text{-}OH$ (evidently from ethanol formed *via* EtO·) in the reactions of (1; R = Et, X = *p*-tolyl).

The formation of (5), its breakdown to give $XS(O)OBu^t$, and the subsequent reaction of this could account for the observation that sulphonyl radicals are detected from photolysis of most sulphinates in the presence of di-t-butyl peroxide. Thus, direct cleavage of the t-butyl esters would yield sulphonyl radicals; further, reaction of Bu^{t}O· with the t-butyl sulphinates XS(O)OBu^t would take place preferentially at sulphur, to give a sulphuranyloxyl species, but also possibly by hydrogen-atom abstraction [reaction (9)] as well. Radical (6) formed in the latter reaction would be expected to fragment as in reaction (10) [*cf.* fragmentation reactions of radicals of the types[17] ·C–C–S(O)R]. In an attempt to obtain evidence that radicals of this type would undergo ready fragmentation, we generated the radical ·CH$_2$CH$_2$OS(O)Me by reaction of BrCH$_2$CH$_2$OS(O)Me with triethylsilyl radicals (from photolysis of di-t-butyl peroxide/triethylsilane in oxiran/cyclopropane); this radical itself was not detected, but a strong signal from MeSO$_2$· was observed, consistent with the occurrence of reaction (11).



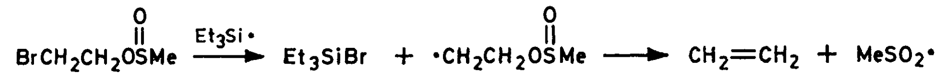
$$\mathrm{X{-}\overset{O}{\overset{\|}{S}}{-}O{-}\underset{Me}{\overset{Me}{C}}{-}Me \xrightarrow{Bu^tO\cdot} X{-}\overset{O}{\overset{\|}{S}}{-}O{-}\underset{Me}{\overset{Me}{C}}{-}\dot{C}H_2 + Bu^tOH}$$


(6) (9)



$$\mathrm{X{-}\overset{O}{\overset{\|}{S}}{-}O{-}\underset{Me}{\overset{Me}{C}}{-}\dot{C}H_2 \longrightarrow XSO_2\cdot + Me_2C{=}CH_2}$$

(10)



$$\mathrm{BrCH_2CH_2O\overset{O}{\overset{\|}{S}}Me \xrightarrow{Et_3Si\cdot} Et_3SiBr + \cdot CH_2CH_2O\overset{O}{\overset{\|}{S}}Me \longrightarrow CH_2{=}CH_2 + MeSO_2\cdot}$$

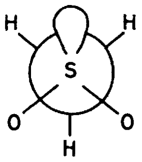
(11)

We also considered the possibility that the sulphonyl radicals arise by the decomposition of other sulphur-containing compounds produced during reactions of the types outlined here [*e.g.* from sulphonate esters, which would be formed by loss of ·R or ·Bu^t from the first-formed sulphuranyloxyl species (5), or from sulphites, which might be produced during reaction (8)]. However, we were unable to detect any radicals during the photolysis of MeS(O)$_2$OPr; nor are sulphites[3] sources of sulphonyl radicals on direct photolysis or on reaction with Bu^{t}O· [though MeOSO· from C$_6$H$_5$CH$_2$S(O)OMe may arise from a sulphite formed *in situ*, *cf.* reaction (7)]. We note that an e.s.r. signal from Bu^{t}SO$_2$· detected[8] during the photolysis of bistrimethylsilyl peroxide in the presence of di-t-butyl sulphoxide is thought to derive from hydrogen-atom abstraction from the corresponding sulphinic acid (Bu^{t}SO$_2$H) formed during the reaction. However, we excluded the possibility that traces of sulphinic acids are responsible for the detection of ArSO$_2$· and RSO$_2$· in the reactions of arene- and alkane-sulphinate esters with Bu^{t}O· by repeating our experiments with sulphinate esters in the presence of small quantities of BuSO$_2$H and, in separate experiments, 4-MeC$_6$H$_4$SO$_2$H. The signals were unaffected and no trace of the sulphonyl radicals from the added sulphinic acids could be detected.

Lastly, we showed that the sulphonyl radicals do not arise from oxidation of sulphinyl radicals produced, *e.g.*, by direct photolysis; when 4-CH$_3$C$_6$H$_5$SO· was generated by photolysis of toluene-*p*-sulphinyl chloride in the presence of di-t-butyl peroxide, its e.s.r. signal remained unaltered.

We conclude therefore that the sulphonyl radicals detected during the reactions of a variety of sulphinate esters with Bu^{t}O· probably derive from the radical decomposition of the t-butyl ester produced by an initial t-butoxydealkylation reaction.

Line-broadening in the Spectra of MeSO$_2$· *and* CF$_3$SO$_2$·.—The observation of selective line-broadening of the inner lines of the methyl-protons' 1 : 3 : 3 : 1 hyperfine pattern in the spectrum of MeSO$_2$· is clearly indicative of the occurrence, at rates intermediate between those for 'slow-exchange' and 'fast-exchange,' of a motional process which modulates individual proton splittings. Similar effects have been observed in the low-temperature e.s.r. spectra of certain other radicals with a methyl group attached to the radical centre, *e.g.* ·CF$_2$Me[18] and ·CMe(OMe)$_2$.[19] These two radicals have in common the fact that the radical centre is markedly bent, and there is, consequently, a significant barrier to rotation about the ·C–CH$_3$ bond (*e.g.* 9 kJ mol^{-1} for ·CF$_2$Me[18]). It seems likely that a similar explanation applies here; thus evidence has previously been presented[6] for the occurrence of pyramidal geometry at sulphur in sulphonyl radicals (*viz.* the relative magnitude of 2-, 3-, and 4-H splittings in C$_6$H$_5$SO$_2$·,[6b] and the low magnitude of the splitting from protons on the carbon attached to sulphur in alkanesulphonyl radicals). The radical $MeSO_2\cdot$ can thus best be represented as (7), in which two protons have a splitting different from that of the third. At very low temperatures, in the slow-exchange limit, the spectrum should be a doublet of triplets [*cf.* the behaviour [19b] of $\cdot CMe(OMe)_2$ at −196 °C]. However, this limit could not be achieved in our experiments on $MeSO_2\cdot$, so that we could not determine the individual values of the proton splittings. We have therefore been unable to simulate the line-broadening and hence derive rate constants for the rate of rotation about $S-CH_3$ at different temperatures. Since the radical centre is bent, it is unlikely that the β-proton splitting follows a $B\cos^2\theta$ dependence, so a calculational approach of this type to an estimate of the a(H) values is invalid here.



(7)

We have also generated the radical $CF_3SO_2\cdot$ (from photolysis of mixtures of CF_3SO_2Cl, $Bu^t_2O_2$, and Et_3SiH in cyclopropane) in an attempt to determine whether this radical also exhibits the restricted rotation typical of $MeSO_2\cdot$ [*cf.* also evidence for restricted rotation about the $S-CF_3$ bond in $CF_3\dot{S}(OBu^t)_2$]. This radical has g 2.0052 and a(3F) 1.55 mT at −100 °C. The inner lines of the 1 : 3 : 3 : 1 pattern from the ^{19}F-splittings were slightly broadened compared with the outer lines but the effect was not marked, even at the lowest temperatures employed.

EXPERIMENTAL

The e.s.r. spectra were recorded on a Varian E-104 spectrometer; details of spectrum measurement and calibration, sample preparation, and the photolytic apparatus have been described previously.[20] Solutions to be photolysed directly typically contained substrate and solvent in the volume ratio *ca.* 1 : 10; for reaction in the presence of peroxide, the concentrations were typically substrate : peroxide : solvent, 1 : 3 : 5.

The toluene-*p*-sulphinate esters [21] were prepared by addition of the appropriate alcohol to the sulphinyl chloride.[22] The alkyl alkanesulphinates were prepared by the method of Douglass [23] except that the superior method [24] for preparing the sulphinyl chlorides was employed. Propyl methanesulphonate was prepared [25] from the sulphonyl chloride. Other reagents were commercially available and were used without further purification.

We thank the S.R.C. for support and Dr. B. P. Roberts for communicating to us his results prior to publication and also for helpful suggestions.

[8/1614 *Received, 8th September,* 1978]

REFERENCES

[1] Part 56, B. Ashworth, B. C. Gilbert, R. G. G. Holmes, and R. O. C. Norman, *J.C.S. Perkin II*, 1978, 951.

[2] W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, (*S*) 152; (*M*) 1748.

[3] B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Research*, 1977, (*S*) 173; (*M*) 1974.

[4] W. B. Gara, B. P. Roberts, C. M. Kirk, B. C. Gilbert, and R. O. C. Norman, *J. Magnetic Resonance*, 1977, **27**, 509.

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

[6] (*a*) A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626; (*b*) C. Chatgilialoglu, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1979, 770.

[7] M. Kobayashi, H. Minato, Y. Miyaji, T. Yoshioka, K. Tanaka, and K. Honda, *Bull. Chem. Soc. Japan*, 1972, **45**, 2817.

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

[9] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4857.

[10] G. E. Robinson and J. M. Vernon, *J.C.S. Perkin II*, 1977, 1682.

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

[12] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

[13] M. C. R. Symons, *J.C.S. Perkin II*, 1976, 908.

[14] A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323; A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc.* (*B*), 1971, 1947.

[15] A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1823.

[16] J. W. Cooper and B. P. Roberts, *J.C.S. Perkin II*, 1976, 808; J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.

[17] 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.

[18] K. S. Chen and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 794.

[19] (*a*) C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 1161; (*b*) C. Gaze, B. C. Gilbert, and M. C. R. Symons, *J.C.S. Perkin II*, 1978, 235.

[20] C. Gaze and B. C. Gilbert, *J.C.S. Perkin II*, 1977, 116.

[21] H. F. Herbrandson, R. T. Dickerson, jun., and J. Weinstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2576.

[22] *Org. Synth.*, 1963, Coll. Vol. IV, p. 937.

[23] I. B. Douglass, *J. Org. Chem.*, 1965, **30**, 633.

[24] I. B. Douglass and R. V. Norton, *J. Org. Chem.*, 1968, **33**, 2104.

[25] H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 2984.