An Electron Spin Resonance Study of Some Sulphonyl Radicals in Solution

By **Alwyn G. Davies** * and **Brian P. Roberts**, Christopher Ingold Laboratories, University College, 20 Gordon Street, London WC1H 0AJ
Brian R. Sanderson, Borax Consolidated Ltd., Research Centre, Cox Lane, Chessington, Surrey

The solution e.s.r. spectra of a series of alkane-, arene-, and alkoxy-sulphonyl radicals are reported. The magnitudes of the proton hyperfine splittings in the alkanesulphonyl radicals $-\overset{\gamma}{C}H-\overset{\beta}{C}H-\overset{\alpha}{C}H-\dot{S}O_2$ follow the unusual order $|a|(\beta\text{-H}) > |a|(\alpha\text{-H}) \simeq |a|(\gamma\text{-H})$. For the alkane- and arene-sulphonyl radicals evidence is found for the presence of hindered rotation about the C–S bond. t-Butoxyl radicals react with sulphur dioxide to form t-butoxysulphonyl radicals with a rate constant of *ca.* 10^7—10^8 l mol^{-1} s^{-1} at −40°.

THERE are few reports in the literature of the electron spin resonance spectra of sulphonyl radicals, $X\dot{S}O_2$ (X = R, Ar, or RO).[1-6] We report here the solution e.s.r. spectra of some alkane-, arene-, and alkoxy-sulphonyl radicals obtained by irradiation of appropriate mixtures with high intensity u.v. light whilst the sample was in the cavity of the spectrometer.[7]

RESULTS

(a) *Sulphonyl Radicals from Sulphonyl Halides.*—When triethylsilyl radicals, produced by photolysis of di-t-butyl peroxide in the presence of triethylsilane, react with alkyl halides the e.s.r. spectrum of the corresponding alkyl radical may be detected.[8] We have found that the triethylsilyl

$$Bu^tO\cdot + Et_3SiH \longrightarrow Et_3Si\cdot + Bu^tOH \qquad (1)$$

$$Et_3Si\cdot + RBr \longrightarrow Et_3SiBr + R\cdot \qquad (2)$$

radical will similarly abstract halogen from alkane- or arene-sulphonyl chlorides. When a mixture containing

$$Et_3Si\cdot + RSO_2Cl \longrightarrow Et_3SiCl + R\dot{S}O_2 \qquad (3)$$

$$R\dot{S}O_2 + Et_3SiH \longrightarrow RSO_2H + Et_3Si\cdot \qquad (4)$$

di-t-butyl peroxide, triethylsilane, and the sulphonyl chloride (usually with a hydrocarbon solvent) was irradiated at *ca.* −40°, the e.s.r. spectrum of the sulphonyl radical was apparent. Some typical spectra are shown in Figure 1. The signals were very intense and no trace of the silyl radical could be detected, indicating that reaction (3) is much faster than reaction (4). The spectroscopic parameters are summarised in Table 1. Where the assignment of coupling constants is not unique the most likely interpretation is given (see below).

The concentrations of the majority of the sulphonyl radicals were proportional to the square root of the incident light intensity and the radicals are probably being removed from the system by self-reaction to give disulphone.†

The appearance of the spectra of the primary alkanesulphonyl radicals was markedly temperature dependent. The hyperfine splitting from the α-hydrogen atoms increased as the temperature was decreased, whilst the β-hydrogen splittings remained virtually constant. These changes are shown in Table 2. The temperature dependence of the spectrum of the ethanesulphonyl radical was studied in most detail and three examples are given in Figure 2.

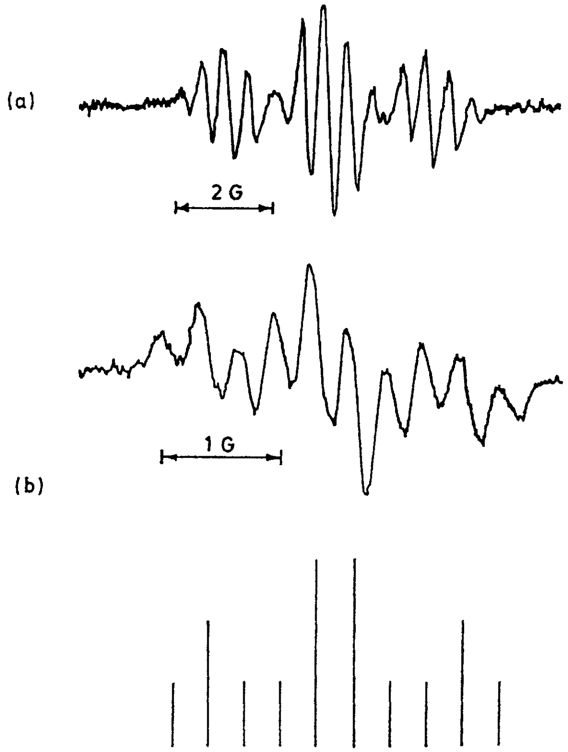

FIGURE 1 E.s.r. spectra of (a) $Bu^n\dot{S}O_2$ from Bu^nSO_2Cl at −40° in toluene and (b) *p*-chlorobenzenesulphonyl radical from *p*-chlorobenzenesulphonyl chloride at −40° in toluene, with stick diagram

Apart from the change in α-hydrogen splitting, there was a pronounced broadening of the central line of the triplet arising from coupling with these nuclei [lines which have $M_I(\alpha\text{-H}) = 0$]. Attempts to obtain spectra in the slow exchange region by using cyclopropane as solvent failed because the same spectral changes that had occurred in toluene took place in cyclopropane some 30° lower in

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† Measurements of these absolute rate constants are in progress.

[1] P. B. Ayscough, J. H. O'Donnell, and K. J. Ivin, *Trans. Faraday Soc.*, 1965, **61**, 1110.

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[6] B. D. Flockhart, K. J. Ivin, R. C. Pink, and B. D. Sharma, *Chem. Comm.*, 1971, 339.

[7] See *e.g.* A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

[8] A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323.

temperature. Similar line broadening effects were observed with the n-propanesulphonyl radical.

(b) *Sulphonyl Radicals from Sulphinic Acids.*—U.v. irradiation of a solution of an alkanesulphinic acid and di-t-butyl peroxide in carbon tetrachloride gave rise to a strong spectrum of the alkanesulphonyl radical. A typical spectrum is shown in Figure 3 and the results are listed in Table 3.

TABLE 1

Alkane- and arene-sulphonyl radicals obtained from sulphonyl chlorides at −40°

Sulphonyl chloride [a]	Hyperfine splitting constants (G)
$MeSO_2Cl$	(α-H) 0·58 g 2·0049 [b]
$EtSO_2Cl$	(α-H) 0·90 (β-H) 1·74
Pr^nSO_2Cl [c]	(α-H) 0·70 (β-H) 2·12 (γ-H) 0·70
Bu^nSO_2Cl	(α-H) 0·47 (β-H) 2·09 (γ-H) 0·47
n-$C_{16}H_{33}SO_2Cl$	(α-H) 0·50 (β-H) 1·89 (γ-H) 0·50
Pr^iSO_2Cl	(α-H) 0·40 (β-H) 1·90
Bu^tSO_2Cl	(β-H) 2·08
$PhSO_2Cl$	(*o*-H) 1·06; (*m*-H) 0·33; (*p*-H) 0·50 g 2·0046
p-$FC_6H_4SO_2Cl$	(*o*-H_1) 0·30; (*o*-H_2) 1·75; (*m*-H) 0·30; (*p*-F) 1·75
p-$ClC_6H_4SO_2Cl$ [d]	(*o*-H_1) 0·90; (*o*-H_2) 1·20; (*m*-H) 0·30
p-$BrC_6H_4SO_2Cl$	(*o*-H) 0·95; (*m*-H) 0·31
$C_6F_5SO_2Cl$	(*o*-F_1) 0·85; (*o*-F_2) 1·67; (*m*-F) 0·30; (*p*-F) 0·85
p-$MeOC_6H_4SO_2Cl$	(*o*-H) 0·78; (*m*-H) 0·16; (*p*-MeO) 0·16
p-$MeC_6H_4SO_2Cl$	(*o*-H) 1·18; (*m*-H) 0·30; (*p*-Me) 0·63
2,3,4-$Cl_3C_6H_2SO_2Cl$	(*o*-H) 1·63; (*m*-H) 0·53
3,4-$Cl_2C_6H_3SO_2Cl$ [e]	(*o*-H_1) 1·08; (*o*-H_2) 0·52; (*m*-H) 0·52

[a] Samples were composed of the sulphonyl chloride (10% w/w) in a mixture of di-t-butyl peroxide, triethylsilane, and toluene (1·5 : 1 : 1 v/v). [b] The parameters reported[3] for $Me\dot{S}O_2$ in aqueous solution at room temperature are a(H) 0·95 G, g 2·00499. The difference in proton hyperfine splitting from that reported here is probably a solvent effect. [c] By varying the temperature it was not possible to obtain spectra in which any difference between a(α-H) and a(γ-H) was resolved. [d] An identical spectrum was obtained when *p*-chlorobenzenesulphonyl bromide was used in place of the sulphonyl chloride. [e] Coupling constants were assigned by comparison with the spectra of the other arenesulphonyl radicals.

TABLE 2

Temperature dependence of the coupling constants in alkanesulphonyl radicals

Radical	Temp. (°C)	a(α-H) (G)	a(β-H) (G)
$Me\dot{S}O_2$ [a]	−20	0·56	
	−90	0·67	
$Et\dot{S}O_2$ [a]	−10	0·71	1·74
	−20	0·80	1·73
	−30	0·84	1·74
	−40	0·90	1·74
	−50	0·96	1·73
	−70	1·10	1·73
	−90	1·25	1·71
$Et\dot{S}O_2$ [b]	−50	0·75	1·73
	−65	0·86	1·73
	−80	0·90	1·73
	−120	1·15	1·72

[a] The sulphonyl chloride (10% w/w) in a mixture of di-t-butyl peroxide, triethylsilane, and toluene (1·5 : 1 : 1 v/v). [b] Ethanesulphonyl chloride, triethylsilane, and di-t-butyl peroxide each 6% v/v in cyclopropane.

At −40° the concentrations of the ethane- and 1,1-dimethylethane-sulphonyl radicals were proportional to the square root of the incident light intensity.

TABLE 3

Alkanesulphonyl radicals obtained from alkanesulphinic acids in carbon tetrachloride at −40°

Sulphinic acid [a]	Hyperfine splitting constants (G)
$EtSO_2H$	(α-H) 0·85 (β-H) 1·74
Bu^nSO_2H [b]	(α-H)0·45 (β-H) 2·15 (γ-H) 0·45
Bu^tSO_2H	(β-H) 2·10 g 2·0054

[a] Sulphinic acid (10% w/w) in a mixture of carbon tetrachloride and di-t-butyl peroxide (1 : 2 v/v). [b] At −12° although the signal was weaker it was possible to resolve a(α-H) and a(γ-H); the spectrum consisted of a triplet (2·1 G) of triplets (0·5 G) of triplets (0·3 G).

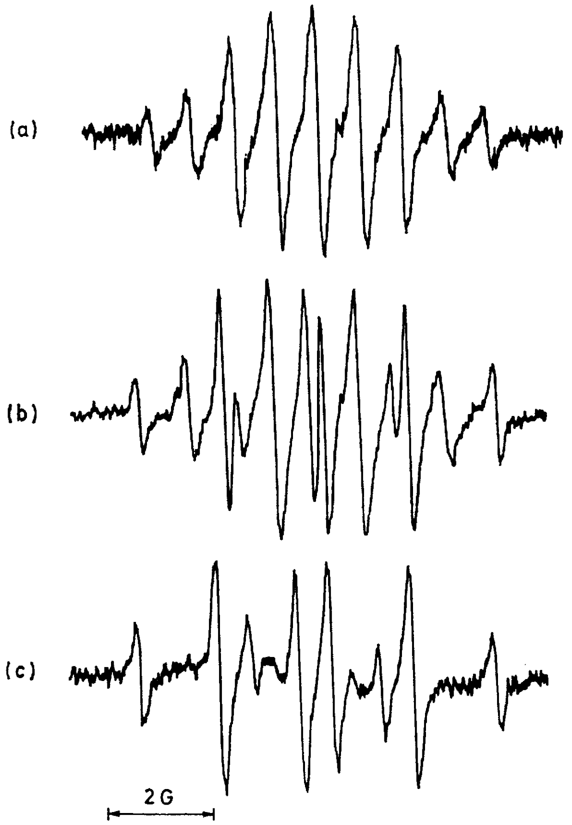

FIGURE 2 E.s.r. spectra of $Et\dot{S}O_2$ in toluene at (a) −40°, (b) −60°, and (c) −90° showing linewidth effects

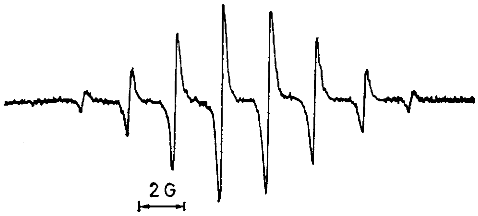

FIGURE 3 E.s.r. spectrum of $Bu^t\dot{S}O_2$ from Bu^tSO_2H in toluene–CCl_4 at −40°

(c) *Alkoxysulphonyl Radicals.*—U.v. irradiation at −40° of di-t-butyl peroxide which had been saturated with sulphur dioxide at 0° gave rise to an intense e.s.r. signal (see Figure 4) assigned to the t-butoxysulphonyl radical. A similar spectrum was obtained by irradiation of a

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad (5)$$

$$Bu^tO\cdot + SO_2 \longrightarrow Bu^tO\dot{S}O_2 \qquad (6)$$

solution of di-t-butyl hyponitrite in 1,1,2-trichloro-1,2,2-trifluoroethane (CF_2ClCCl_2F) saturated with sulphur dioxide.

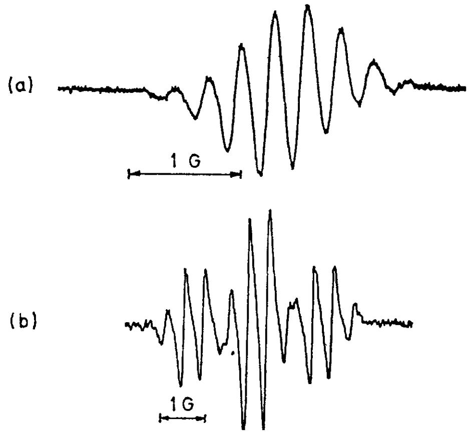

FIGURE 4 E.s.r. spectra of (a) $Bu^tO\dot{S}O_2$ from photolysis of Bu^tOOBu^t in the presence of SO_2 at −22° and (b) $EtO\dot{S}O_2$ from photolysis of EtOOEt in the presence of SO_2 in hexane at −25°

When tri-n-butylborane (0·5—1M) was added to the peroxide–sulphur dioxide system at −40° both t-butoxysulphonyl and n-butanesulphonyl radicals were detected. If it is assumed * that sulphonyl radicals react only slowly with tributylborane at −40° and that the rate constants describing the removal of the two sulphonyl radicals are similar, then we may estimate the rate of reaction (6).

$$Bu^tO\cdot + Bu^n{}_3B \longrightarrow Bu^tOBBu^n{}_2 + Bu^n\cdot \quad (7)$$

$$Bu^n\cdot + SO_2 \longrightarrow Bu^n\dot{S}O_2 \quad (8)$$

Reaction (8) is fast and irreversible at low temperatures[10] and with the above assumptions it may be shown that equation (9) holds. If the concentration of sulphur

$$k_6/k_7 = [Bu^tO\dot{S}O_2][Bu^n{}_3B]/[Bu^n\dot{S}O_2][SO_2] \quad (9)$$

dioxide is *ca.* 0·5M in saturated hydrocarbon solution at 0°,[11] and k_7 is taken [12] as 3×10^7 l mol^{-1} s^{-1} then k_6 must be between 10^7 and 10^8 l mol^{-1} s^{-1} at −40°.

Photolysis of a hexane solution of diethyl peroxide in the presence of sulphur dioxide gave rise to the e.s.r. spectrum of the ethoxysulphonyl radical. The results are summarised in Table 4.

TABLE 4
Alkoxysulphonyl radicals from photolytic generation of alkoxyl radicals in the presence of sulphur dioxide

Alkoxysulphonyl radical	Source of alkoxyl radical	Solvent	Temp. (°C)	Hyperfine splittings (G)	*g*
$Bu^tO\dot{S}O_2$	Bu^tOOBu^t	Bu^tOOBu^t	−40	$Me_3CO\dot{S}O_2$ 0·28	2·0036
$Bu^tO\dot{S}O_2$	$Bu^tON{=}NOBu^t$	CF_2ClCCl_2F	−20	$Me_3CO\dot{S}O_2$ 0·29	
$EtO\dot{S}O_2$	EtOOEt	Hexane	−40	CH_3–$CH_2O\dot{S}O_2$ 0·43 1·43	

DISCUSSION

The production of alkane- and arene-sulphonyl radicals for e.s.r. study by photolysis of mixtures of di-t-butyl peroxide, triethylsilane, and the sulphonyl halides requires little comment. The method is a straightforward extension of that used for the generation of carbon-centred radicals.[8] However, the ready availability of the sulphonyl chlorides and the high rate of reaction (3) even at very low temperatures makes this a particularly useful route to these little-studied radicals. Abstraction of halogen from suitable molecules (*e.g.* R·SO·Cl) by trialkylsilyl radicals should prove a general route to radicals in which the unpaired electron is centred on an atom other than carbon.

Alkanesulphonyl radicals are produced in relatively high concentrations when di-t-butyl peroxide is photolysed in the presence of an alkanesulphinic acid at low temperatures. Sulphinic acids have the structure RS(O)OH rather than $RS(O)_2H$ with an S–H bond,[13] and it has been suggested [14] that the O–H bond dissociation energy is similar to that in a carboxylic acid at *ca.* 111 kcal mol^{-1}. Provided the sulphonyl radicals are not produced by hydrogen abstraction from a small equilibrium concentration of the S–H tautomer which may be present, our results indicate that reaction (10)

$$Bu^tO\cdot + RS(O)OH \longrightarrow Bu^tOH + R\dot{S}O_2 \quad (10)$$

must be at least thermoneutral and probably quite exothermic. Since *D*(O–H) in t-butyl alcohol is *ca.* 104 kcal mol^{-1} [15] the O–H bond energy in an alkanesulphinic acid is probably appreciably less than this figure.

The e.s.r. spectrum of the t-butoxysulphonyl radical has been observed previously during the reaction of sulphur dioxide and t-butyl hydroperoxide in a flow system at room temperature.[6] However, the spectrum was complicated by the presence of $HO\dot{S}O_2$ and $Me\dot{S}O_2$ radicals.

$$Bu^tOOH + SO_2 \longrightarrow Bu^tO\cdot + HO\dot{S}O_2 \quad (11)$$

$$Bu^tO\cdot + SO_2 \longrightarrow Bu^tO\dot{S}O_2 \quad (6)$$

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* Alkane- and arene-sulphonyl halides do not react with trialkylboranes at low temperatures in the presence of a source of free radicals.[9]

[9] B. R. Sanderson, unpublished results.

[10] A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2708, 2720.

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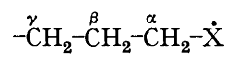
[14] C. C. Badcock, H. W. Sidebottom, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *J. Amer. Chem. Soc.*, 1971, **93**, 3115.

[15] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

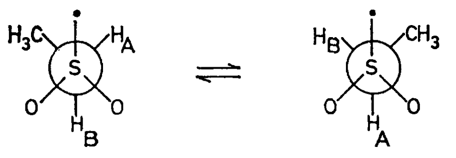
The reaction of alkyl radicals with sulphur dioxide to form alkanesulphonyl radicals is a very rapid process.[10,14] Our results show that alkoxyl radicals add to sulphur dioxide in a similarly rapid reaction which must have a very low activation energy.

The e.s.r. parameters of the alkane- and arenesulphonyl radicals are of particular interest. In these radicals the unpaired electron is centred mainly on sulphur in an orbital partaking predominantly of $3p$ character (in $PhCH_2\dot{S}O_2$ the orbital populations are calculated [5] as 8% $3s$ and 42% $3p$).[5] These sulphonyl radicals are pyramidal with respect to the sulphur atom.[2,5] Inspection of Tables 1—3 reveals the surprising result that in the alkanesulphonyl radicals the β-hydrogens exhibit a larger coupling constant than those attached to the carbon adjacent to sulphur. This is shown most clearly by comparison of the splittings in the methane- and 1,1-dimethylethane-sulphonyl radicals and by analysis of the spectrum of the ethanesulphonyl radical. When γ-hydrogens are present their hyperfine splitting constants are similar to those of the α-hydrogen atoms. Clearly the mechanism by which spin density arrives on the α- and β-hydrogens is not the same. Molecular models indicate that the proximity of the β- and γ-hydrogens to the oxygen atoms in certain conformations may be responsible for the relatively large coupling constants of these hydrogen atoms. There appears to be no other example in the literature of an acyclic radical of the type (I), in which the unpaired electron is centred mainly on a heteroatom, and which shows a β-hydrogen splitting greater than that for the α-hydrogens.



$$-\overset{\gamma}{C}H_2-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-\dot{X} \qquad (I)$$

The hyperfine splitting from the α-hydrogens in the primary alkanesulphonyl radicals was particularly temperature dependent. This is probably a result of incomplete averaging of the environment of these hydrogens by rotation about the C_α–S bond. The line-width effects in the spectra of the ethane- and propanesulphonyl radicals probably have a similar origin. If the two most stable rotamers of the ethanesulphonyl radical are (II) and (III), broadening of the hyperfine lines for which $M_I(\alpha\text{-H}) = 0$ would result as interconversion of (II) and (III) became slower. Exchange involving the symmetrical rotamer, which is probably less stable for steric reasons, would be expected to broaden all the lines in the spectrum. Complete non-equivalence of H_A and H_B in the slow exchange limit was not observed because of practical difficulties.

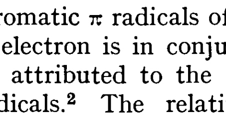


(II) (III) (12)

Although the coupling constants for the benzenesulphonyl radical differ somewhat from those reported in aqueous solution [2] the observation that $a(o\text{-H})$ is greater than $a(p\text{-H})$ is confirmed.* Such an order is unusual for aromatic π radicals of the type $Ph\dot{X}$ where the unpaired electron is in conjugation with the ring, and has been attributed to the σ character of arenesulphonyl radicals.[2] The relatively large value of $a(m\text{-H})$ in the radicals which we have detected is also consistent with this argument. The total unpaired electron density on the aromatic ring in the arenesulphonyl radicals is little affected by the presence of different substituents in the ring.

Perhaps the most interesting feature of the e.s.r. spectra of the arenesulphonyl radicals is the non-equivalence of the *ortho*-hydrogen atoms in the *p*-chloro- and *p*-fluoro-substituted species [see Figure 1(b)]. No evidence was found for the *ortho*-hydrogens becoming equivalent as the temperature was increased. Such non-equivalence does not show itself in the n.m.r. spectra of the corresponding sulphonyl halides or sulphones.[16]

A relatively high barrier must exist to rotation about the C–S bond in these arenesulphonyl radicals and the equilibrium conformation must have non-equivalent *ortho*-hydrogen atoms as in (IV).



(IV)

In contrast diaryl- and alkylaryl-sulphones possess preferred conformations in which the two oxygen atoms are symmetrically disposed with respect to the *ortho*-hydrogens.[17] Although equal splittings were assigned to the *ortho*-hydrogens in the *p*-bromobenzenesulphonyl radical the lines were broad ($\Delta H_{\text{peak-peak}}$ 0·3 G). Since the difference in the *ortho*-hydrogen splittings decreases on passing from a *p*-fluoro- to a *p*-chloro-substituent, it is possible that in the *p*-bromo-analogue the splittings are unequal but the difference is masked by the line width. In fact, it is not clear whether the *p*-chloro-, and *p*-fluoro-substituents increase the barrier to rotation about the C–S bond causing the *ortho*-hydrogens to be non-equivalent on the e.s.r. time scale or whether their presence serves to produce unequal splittings from the *ortho*-hydrogens which are magnetically non-equivalent in all arenesulphonyl radicals. The spectra of arenesulphonyl radicals obtained from ceric ion oxidation of

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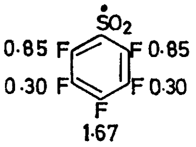
* The coupling constants given in Table 1 refer to a toluene solution at −40°. On decreasing the temperature the appearance of the spectrum and the coupling constants were unchanged even at −120° in cyclopropane solution.

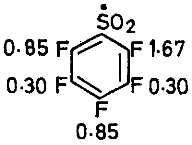
[16] N. F. Chamberlain and J. J. R. Reed, 'Nuclear Magnetic Resonance of Sulphur Compounds,' in 'The Analytical Chemistry of Sulphur and its Compounds,' ed. J. H. Karchmer, Wiley–Interscience, New York, 1971.

[17] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7; G. Jeminet, C. Pigenet, and H. Lumbroso, *Bull. Soc. chim. France*, 1966, 3631; E. Keller and R. G. Hayes, *J. Phys. Chem.*, 1969, **73**, 3901.

the corresponding sulphinic acids in an aqueous flow system do not show non-equivalence of the *ortho*-hydrogen atoms,[2] particularly in the *p*-fluorobenzenesulphonyl radical. This may be a solvent effect on the polar sulphonyl group perhaps coupled with the fact that the spectra appear to have been more poorly resolved than ours.



(V)



(VI)

It should be noted that we cannot, at present, distinguish between assignments (V) and (VI) for the pentafluorobenzenesulphonyl radical spectrum, but we favour (VI) (the splittings shown are in gauss).

EXPERIMENTAL

The e.s.r. spectrometer, irradiation apparatus, and experimental procedures have been described previously.[7] The reagents used in this work were either commercial products purified before use or were prepared by standard methods. The alkanesulphinic acids were prepared by the reaction of sulphur dioxide with the appropriate Grignard reagents following the method of Allen.[18] *p*-Chlorobenzenesulphonyl bromide, m.p. 55° (lit.,[19] 56°), was prepared from the commercially available sulphonyl chloride.[19] 1-Methylethanesulphonyl chloride, b.p. 69° at 12 mmHg (lit.,[20] 74° at 16 mmHg), was prepared by chlorination of di-isopropyl disulphide.[21]

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[2/2111 *Received*, *7th September*, 1972]

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