

## A Kinetic-Electron Spin Resonance Study of the Self-reactions of Some Aromatic and Aliphatic Sulphonyl Radicals and Aromatic Sulphinyl Radicals

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A variety of aromatic and aliphatic sulphonyl radicals ( $\text{RSO}_2\cdot$ ) have been found to undergo diffusion-controlled self-reaction in solution (with  $2k_t$  typically *ca.*  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ); reaction proceeds somewhat slower for some sterically hindered arenesulphonyl radicals ( $\text{ArSO}_2\cdot$ ) and for some arenesulphinyl analogues ( $\text{ArSO}\cdot$ ). The observation of curved Arrhenius plots for some  $\text{ArSO}_2\cdot$  radicals, as well as the detection of  $\text{ArSO}\cdot$  from sulphonyl precursors under steady-state conditions, is attributed to the thermal decomposition of an unstable intermediate formed by dimerisation (sulphur-to-oxygen) of  $\text{ArSO}_2\cdot$ . A thermodynamic and kinetic analysis is presented.

It is well established that a wide range of sulphur-containing compounds (*e.g.*, thiols, thioethers, and disulphides) can inhibit the autoxidation of hydrocarbons, but the detailed mechanisms of action are not completely understood. For example, a major part of the antioxidant activity has been attributed to subsequent oxidation products, such as sulphoxides, sulphones, sulphenic acids, and sulphur dioxide.<sup>1-6</sup>

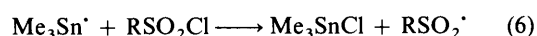
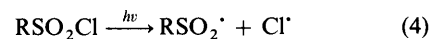
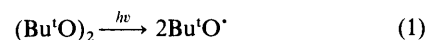
Sulphinyl ( $\text{RSO}\cdot$ ) and sulphonyl ( $\text{RSO}_2\cdot$ ) radicals have recently been identified as important intermediates in the oxidation reactions, as well as the thermolysis and photolysis, of a variety of organo-sulphur compounds (see *e.g.* refs. 7 and 8); analysis of electron spin resonance (e.s.r.) spectra indicates that sulphinyl radicals are *p*-type species<sup>9</sup> (with the unpaired electron in a  $\pi$ -molecular orbital on sulphur and oxygen) in contrast to the  $\sigma$ -nature of sulphonyl radicals (with the unpaired electron in  $\text{ArSO}_2\cdot$  largely based in an in-plane  $\sigma$ -orbital on sulphur<sup>10</sup>). Kinetic data on the reactions of these radicals are sparse, being confined mainly to measurements at a single temperature (223 K).<sup>11</sup> Self-reaction appears to be a diffusion-controlled process (with  $2k_t$ , *ca.*  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  as determined by e.s.r. spectroscopy), though flash-photolysis results<sup>12</sup> suggest that certain sulphonyl radicals have  $2k_t$  well below this value ( $1-5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

In this paper we report measurements of the rate constants for the self-reactions of some arene-sulphinyl and -sulphonyl radicals, as well as some alkanesulphonyl radicals, over a large temperature range.

### Results

**E.S.R. Results: Radical Identification and Kinetics of Formation and Decay.**—Sulphonyl radicals were normally generated in the cavity of an e.s.r. spectrometer by the *in situ* photolysis (with a 1 kW mercury-xenon lamp) of mixtures of di-*t*-butyl peroxide, triethylsilane,<sup>13</sup> and the appropriate sulphonyl chloride [reactions (1)–(3)] in methylbenzene; spectra were recorded over a range of temperature, from a lower limit of *ca.* 180 K to an upper limit which varied from *ca.* 220–370 K with the nature of the substrate. Alternative methods involved either the direct photolysis of the sulphonyl chloride [reaction (4)] or the photolysis of hexamethylditin in the presence of the sulphonyl chloride<sup>14</sup> [reactions (5) and (6)]. Sulphinyl radicals were generated from the appropriate

sulphinyl chlorides. The spectra of the sulphonyl and sulphinyl<sup>9,10</sup> radicals have been reported previously.



In experiments involving the continuous irradiation of sulphonyl chlorides (during which the complete spectra were recorded with the normal field scan), it was observed that for some substrates signals from the corresponding *sulphinyl* radicals grew over a period of several minutes to accompany those from the sulphonyl species (see *e.g.* Figure 1). In general, the steady-state proportion of the sulphinyl radicals was small at low temperatures and increased with temperature (see Figure 2). The proportion at a given temperature varied somewhat with the structure of the aryl group. With most radicals studied [ $\text{ArSO}\cdot$ ] grew to be *ca.* 20–30% of the total radical signal, though for the 2,5-dichloro and 3,5-bis(trifluoromethyl) substituents this value approached 60%. No sulphinyl radicals were detected from the two hindered arene derivatives studied or from the aliphatic substrates.

In a series of kinetic-e.s.r. experiments the growth and decay of the signals of  $\text{RSO}_2\cdot$  ( $\text{R} = \text{aryl, alkyl}$ ) and  $\text{RSO}\cdot$  (generated from the parent chlorides) were monitored during intermittent illumination (achieved either with a rotating sector or shutter—see Experimental section).

A typical trace is shown in Figure 3. Good second-order plots were generally obtained for the decays of the sulphonyl and sulphinyl radicals; data for  $2k_t(\text{obs})$  at 203 K (except where indicated otherwise) are given in Table 1. The upper temperature limits for the kinetic measurements were determined by the signal-to-noise ratio for the decay curve and varied considerably from radical to radical; for example, the decays of the two aliphatic radicals could only be measured over a very limited temperature range.

The Arrhenius plots for the radicals are given in Figure 4. Most plots are reasonably linear, but those for the 2,4-dichloro-

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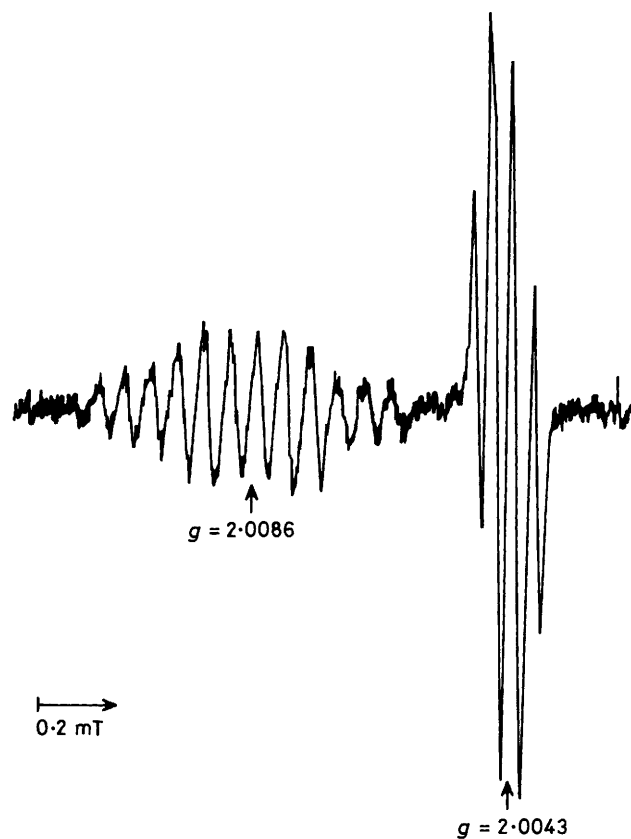


Figure 1. E.s.r. spectra of sulphonyl ( $\text{RSO}_2^\bullet$   $g$  2.0043) and sulphinyl ( $\text{RSO}^\bullet$   $g$  2.0086) radicals [ $\text{R} = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$ ] obtained during the photolysis of a solution of 3,5-bis(trifluoromethyl)-benzenesulphonyl chloride in methylbenzene at 213 K

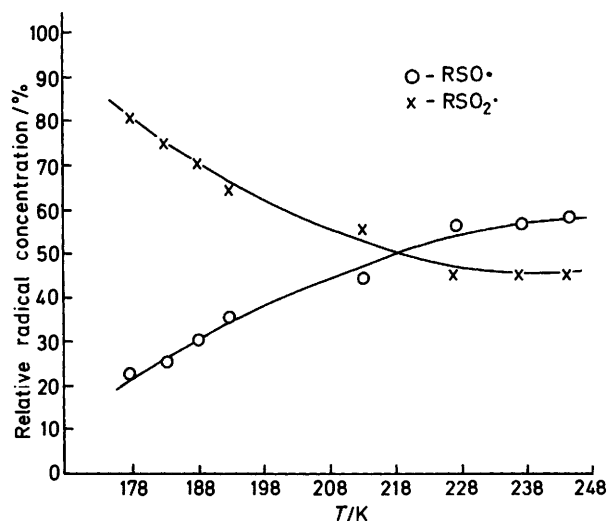


Figure 2. Variation with temperature in the steady-state concentrations (expressed as percentages of the total detected radical concentration) for  $\text{RSO}_2^\bullet$  and  $\text{RSO}^\bullet$  [ $\text{R} = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$ ] during the photolysis of a solution of 3,5-bis(trifluoromethyl)benzenesulphonyl chloride in methylbenzene

2,4-dichloro-5-methyl-, and 3,5-bis(trifluoromethyl)-benzenesulphonyl radicals are noticeably curved. The reasons for the curvature, which is outside experimental error, will be discussed in the next section. The values of the Arrhenius constants are

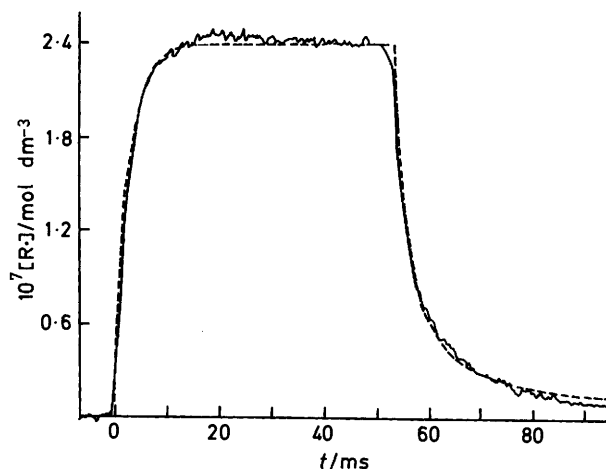


Figure 3. Growth and decay curve of the 2,4-dichloro-5-methylbenzenesulphonyl radical, formed by the photolysis of 2,4-dichloro-5-methylbenzenesulphonyl chloride in methylbenzene at 198 K, together with a kinetic simulation (for parameters employed, see text)

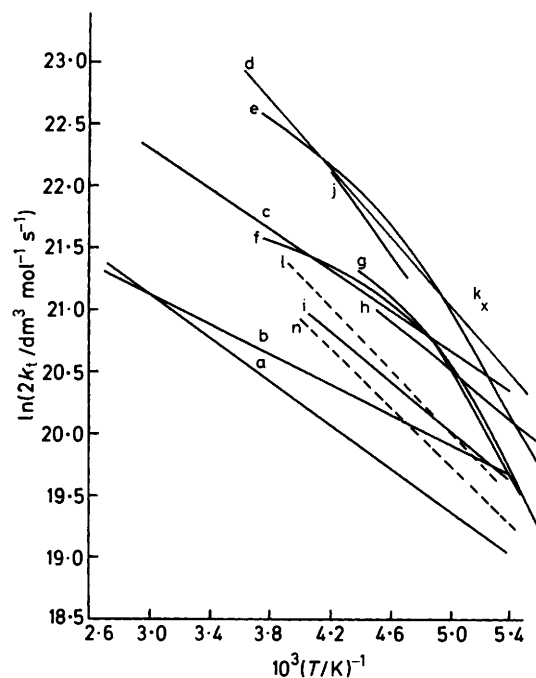


Figure 4. Dependence on temperature of the observed rate constant for bimolecular termination of sulphonyl and sulphinyl radicals: variation of  $\ln 2k_t$  with  $T^{-1}$ . (a)–(j)  $\text{C}_6\text{H}_5\text{-}_n\text{X}_m\text{SO}_2^\bullet$ : (a) 2,3,4,5,6-Me; (b) 2,3,5,6-Me; (c) 2,5-Cl; (d) 4-Me; (e) 2,4-Cl-5-Me; (f) 3,5-( $\text{CF}_3$ ); (g) 2,4-Cl; (h) 4-Cl; (i) 2,4,5-Cl; (j)  $\text{CF}_3\text{CH}_2\text{SO}_2^\bullet$ ; (k)  $\text{PrSO}_2^\bullet$ ; (l) 4-Cl- $\text{C}_6\text{H}_4\text{SO}^\bullet$ ; (n) 2,5- $\text{Cl}_2\text{-C}_6\text{H}_3\text{SO}^\bullet$

given in Table 1; for the curved plots the portion at higher temperatures was used to determine  $E_t$  and  $A_t$ .

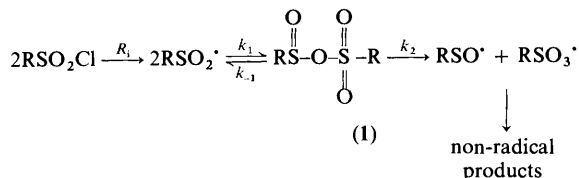
For some sulphonyl radicals the growth curves following the onset of photolysis were also recorded; curve-fitting procedures (discussed in the next section) showed that the growth curves were not always typical of a simple reaction mechanism in which radical generation is followed by irreversible self-termination.

*Kinetic and Mechanistic Analysis.*—We have previously presented evidence to support the conclusion that formation of

**Table 1.** Kinetic parameters for the self-reaction of some sulphinyl and sulphonyl radicals

Radical		$10^{-9} \times 2k_1(\text{obs})^a / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Arrhenius parameters <sup>b</sup>	
Type	Phenyl substituent		$2A_i / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$E_i / \text{kJ mol}^{-1}$
ArSO <sub>2</sub> ·	4-Me	1.5	$4.8 \times 10^{11}$	9.6
	4-Cl	0.97	$4.7 \times 10^{10}$	8.1
	2,4-Cl	0.93	$8.2 \times 10^{10}$	7.3 <sup>c</sup>
			$(1.6 \times 10^{11})$	(9.2)
	2,5-Cl	0.98	$7.9 \times 10^{10}$	7.3
	2,4-Cl-5-Me	1.5	$2.6 \times 10^{11}$	8.3 <sup>d</sup>
			$(7.3 \times 10^{10})$	(7.2)
	2,4,5-Cl	0.5	$6.6 \times 10^{10}$	8.1
	3,5-CF <sub>3</sub>	1.3	$2.4 \times 10^{10}$	5.0 <sup>c</sup>
			$(8.3 \times 10^{10})$	(7.2)
ArSO·	2,3,5,6-Me	0.45	$8.8 \times 10^9$	5.0
	2,3,4,5,6-Me	0.23	$2.0 \times 10^{10}$	7.2
MeSO <sub>2</sub> ·	4-Cl	0.44	$3.2 \times 10^{10}$	7.4
	2,5-Cl	0.52	$2.4 \times 10^{10}$	10.3
CF <sub>3</sub> CH <sub>2</sub> SO <sub>2</sub> ·		0.93 <sup>d</sup>		
PrSO <sub>2</sub> ·		1.7	$6.0 \times 10^{12}$	14.6
		1.4 <sup>e</sup>		

<sup>a</sup> At 203 K unless stated otherwise. Estimated accuracy  $\pm 20\%$ . <sup>b</sup> Obtained from decay curves (values in parentheses obtained by analysis of growth curves (see text). Estimated errors in  $A_i$  and  $E_i \pm 20\%$ . <sup>c</sup> Curved Arrhenius plots; values from high-temperature portion of the graphs. <sup>d</sup> 217 K. <sup>e</sup> 213 K.

**Scheme 1.**

sulphinyl radicals from sulphonyl precursors involves the generation of an unstable sulphinylsulphonate (1) (Scheme 1).<sup>8</sup> We suggest below that the formation of such an intermediate can also explain the curvature of some of the Arrhenius plots. It should be noted at this stage that oxygen-centred radicals of the type  $\text{RSO}_3\cdot$  would, like alkoxy and thiyl ( $\text{RS}\cdot$ ) radicals, be undetected by e.s.r. spectroscopy in fluid solution.<sup>15</sup>

The kinetic results show that the observed rate constants for the self-reactions of the aromatic sulphonyl radicals lie close to the diffusion-controlled limit, with values in the range  $10^9$ – $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at room temperature; these values will include a contribution from cross-termination with other radicals (e.g.  $\text{RSO}\cdot$ ,  $\text{RSO}_3\cdot$ ) generated during reaction (see later). The activation energies ( $E_i$   $8 \pm 4 \text{ kJ mol}^{-1}$ ) are identical within experimental error and are comparable to the activation energy for solvent reorganization (as measured by the temperature dependence of the solvent viscosity<sup>16</sup>). There appears to be little correlation between the observed rate constants and the structures of the radicals, except that the two radicals with methyl substituents in both *ortho* positions have the lowest rate constants. This lack of dependence on ring substituents (except for those radicals with marked steric hindrance) is not unexpected since the  $\sigma$ -orbital containing the unpaired electron will not be influenced strongly by the aromatic ring system. The limited measurements on the alkanesulphonyl radicals show that their rate constants lie at the upper end of the range observed for their aryl counterparts and that the activation energies are comparable; these results agree well with those reported recently by Chatgililoglu and

co-workers<sup>11</sup> but are significantly higher than those measured earlier by optical techniques.<sup>12</sup>

The rate constants for termination of the delocalized sulphinyl ( $\pi$ )-radicals are also close to the diffusion-controlled limit, with activation energies similar to those for  $\text{ArSO}_2\cdot$ . For the radical  $\text{Bu}\cdot\text{SO}\cdot$ , a value for  $2k_t$  of  $6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 173 K has been reported.<sup>17</sup>

Curved Arrhenius plots at sub-ambient temperatures have been observed previously for some secondary-alkylperoxy radicals.<sup>18</sup> This curvature may be explained in terms of the involvement of an unstable intermediate (either a dialkyl trioxide<sup>19</sup> or dialkyl tetraoxide<sup>18,20</sup>) in the reaction sequence. Following the treatment given in reference 20 it can be shown that, for the mechanism outlined in Scheme 1 (in which cross-termination reactions are neglected):

$$\frac{d[\text{RSO}_2\cdot]}{dt} = \frac{R_i - 2k_2[\text{RSO}_2\cdot]^2/K}{(1 + 4[\text{RSO}_2\cdot]/K)} \quad (7)$$

where  $K = k_{-1}/k_1$  and  $R_i$  is the rate of initiation and where the equilibrium is established rapidly compared with the irreversible decay of the complex. A closely related kinetic treatment has also been presented<sup>21</sup> for the observed decay characteristics of some iminoxyl radicals ( $\text{R}_2\text{C}=\text{NO}\cdot$ ), where establishment of an equilibrium involving an unstable dimer has been proposed.

When  $K/[\text{RSO}_2\cdot] \gg 1$ , this expression reduces to the normal second-order equation, with an observed decay rate constant ( $2k_{\text{obs}}$ ) of  $2k_2/K$ . Thus, the Arrhenius plot should show linear behaviour at the higher temperatures. Further, irrespective of the value of  $K$ , the steady-state concentration of sulphonyl radicals should be given by

$$R_i = \frac{2k_2}{K} [\text{RSO}_2\cdot]_{\text{ss}}^2 = 2k_{\text{obs}} [\text{RSO}_2\cdot]_{\text{ss}}^2 \quad (8)$$

The rate of initiation can be determined from the initial stage of the growth curve (see e.g. Figure 3) and together with  $[\text{RSO}_2\cdot]_{\text{ss}}$  gives an independent value of  $2k_{\text{obs}}$  which is not affected by the formation of an unstable intermediate. The

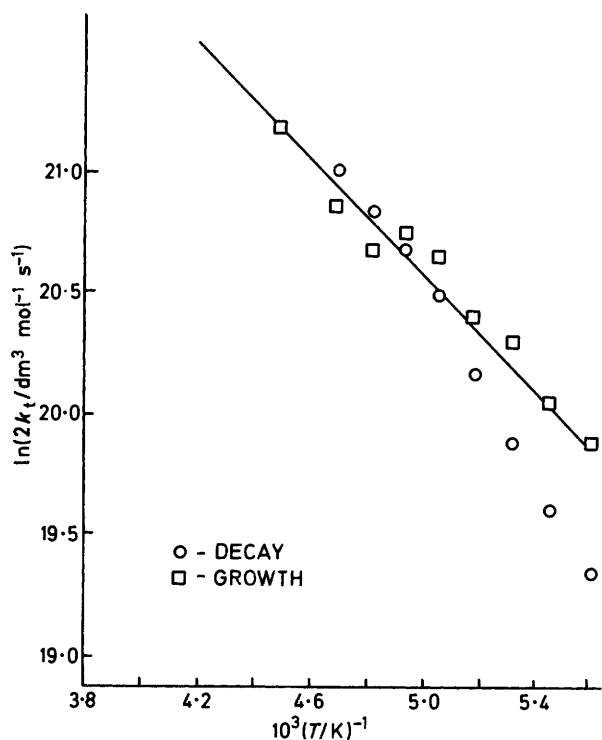


Figure 5. Arrhenius plots of  $2k_1$  for the 2,4-dichlorobenzesulphonyl radical, determined from analysis of decay (○) and growth (□) characteristics of the e.s.r. signal

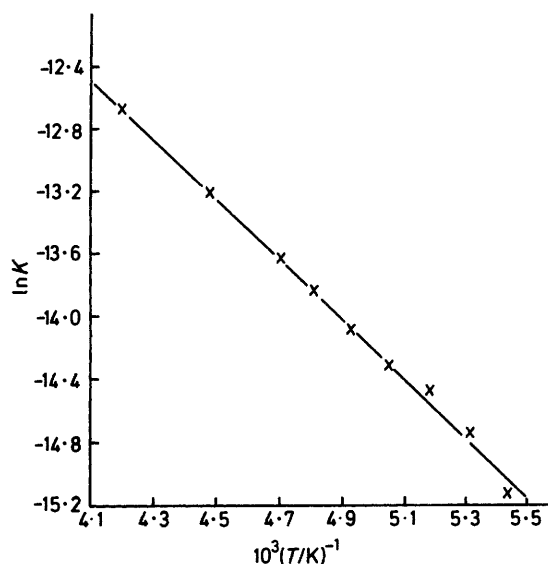


Figure 6. Variation of  $\ln K$  (the equilibrium constant for complex formation) with  $T^{-1}$  for the 2,4-dichloro-5-methylbenzenesulphonyl radical in methylbenzene

values of  $2k_{\text{obs}}$  calculated by this method for the 2,4-dichlorobenzesulphonyl radical are shown in Figure 5. As predicted, the values of  $2k_{\text{obs}}$  calculated from  $R_1$  and  $[\text{RSO}_2^*]_{\text{ss}}$  do not fall off at lower temperatures and confirm that the Arrhenius plot at higher temperatures gives the true values of the Arrhenius constants.

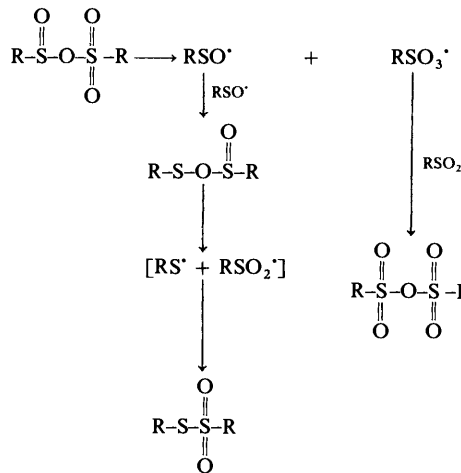
An alternative approach to the kinetic analysis is to use computer simulations to fit both the experimental growth and decay curves using the integrated forms of equation (7). Values

of the equilibrium constant  $K$  and the rate constant  $k_2$  can be determined by this method and from measurements over a range of temperature it is in principle possible to determine the heat of dissociation,  $\Delta H^\circ$ , for the intermediate and Arrhenius parameters for its irreversible decomposition.

This procedure was followed for the growth and decay curves of the 2,4-dichloro-5-methylbenzenesulphonyl radical in methylbenzene over a wide temperature range. Optimum matching between observed and simulated behaviour was obtained when values of  $K$  in the range  $(3\text{--}30) \times 10^{-7} \text{ mol dm}^{-3}$  (for the temperature range 183–238 K) were employed; Figure 3 shows the best-fit for the growth and decay curves at 198 K, for which  $K$  is calculated to be  $6.0 \times 10^{-7} \text{ mol dm}^{-3}$  and  $k_2 6.60 \times 10^2 \text{ s}^{-1}$ .\* A plot of the temperature dependence of the optimum values of  $K$  is shown in Figure 6, which leads to a value of  $-16 \pm 2 \text{ kJ mol}^{-1}$  for  $\Delta H^\circ$ . The appropriate Arrhenius parameters for  $k_2$  are  $E_2 27 \text{ kJ mol}^{-1}$  and  $A_2 2 \times 10^{10} \text{ s}^{-1}$ .

A similar analysis for the 2,4-dichlorobenzesulphonyl radical over a more restricted range of temperature (178–193 K) gave values of  $K$  in the range  $(4\text{--}7) \times 10^{-6} \text{ mol dm}^{-3}$  with  $\Delta H^\circ -11 \pm 2 \text{ kJ mol}^{-1}$ ,  $k_2 \text{ ca. } 10^2 \text{ s}^{-1}$ ,  $E_2 25 \text{ kJ mol}^{-1}$ , and  $A_2 2.5 \times 10^9 \text{ s}^{-1}$ .

**Thermochemical Calculations.**—The enthalpy changes,  $\Delta H^\circ$  associated with dimerization of two sulphonyl radicals to give a disulphone (S–S coupling), sulphinyl sulphonate (S–O coupling), or a bis(sulphinyl) peroxide (O–O coupling) have been estimated using the group additivity approach.<sup>22–24</sup> Using accepted values for contributions to  $\Delta H_f^\circ$  of different atoms and groups,<sup>22</sup> we calculated heats of formation  $\Delta H_f^\circ$  at 298 K for a variety of sulphur-containing species (see Table



Scheme 2.

\* It follows from the mechanism outlined in Scheme 1 that if  $2k_1$  is diffusion-controlled (ca.  $5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) then  $k_{-1} \sim 1500 \text{ s}^{-1}$ . Thus, the rate of fission of (1) to give  $2 \times \text{RSO}_2^*$  is ca. 2.5 times faster than that to give  $\text{RSO}^* + \text{RSO}_3^*$ . Under these circumstances our original assumption that equilibrium is established rapidly is not entirely rigorous. However, a full computer simulation of Scheme 1 (for the case shown in Figure 3) shows that the error involved lies well within the experimental accuracy. When the cross-termination reactions including  $\text{RSO}_2^*$ ,  $\text{RSO}^*$ , and  $\text{RSO}_3^*$  are also included, each with  $2k_1 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , then optimum matching of simulated and experimental curves for build-up and decay was obtained with values of  $k_2$  and  $K$  ca. 25% less and 25% more, respectively than those obtained via the simplified treatment.

**Table 2.** Heats of formation of some thiyl, sulphinyl, and sulphonyl-containing species calculated using the group additivity approach

Molecule	$\Delta H_f^\circ$ /kJ mol <sup>-1</sup>
Ph-S-S-Ph	+243
Ph-SO-SO-Ph	-31
Ph-SO <sub>2</sub> -S-Ph	-92
Ph-SO-O-Ph	-11
Ph-SO <sub>2</sub> -SO <sub>2</sub> -Ph	-483
Ph-SO-O-SO <sub>2</sub> -Ph	-331
Ph-SO-O-O-SO-Ph	-78
Ph-SO <sub>2</sub> -O-SO <sub>2</sub> -Ph	-541
Ph-SO-OH	-255
Ph-SO <sub>2</sub> -OH	-836
PhSO	53
PhSO <sub>2</sub> <sup>•</sup>	-155
PhSO <sub>3</sub> <sup>•</sup>	-736

2). Given the calculated value for the disulphone and the measurement<sup>25</sup> of  $\Delta H^\circ$  for dissociation of bis-(4-methylphenyl) disulphone as 171 kJ mol<sup>-1</sup>, we estimate the heat of formation of PhSO<sub>2</sub><sup>•</sup> as -155 kJ mol<sup>-1</sup>. It follows that estimated values of  $\Delta H^\circ$  for the formation of S-S, S-O, and O-O coupled dimers are thus, respectively, -171, (*i.e.*, as measured experimentally<sup>25</sup>), -21, and +232 kJ mol<sup>-1</sup>.

Now disulphones are thermally stable (in the temperature range studied) and have been isolated as minor products (<20%) from reactions involving sulphonyl radicals;<sup>26</sup> these are not believed to be the unstable intermediates suggested on the basis of the kinetic analysis. The high positive values of  $\Delta H^\circ$  for the peroxide suggests that this very unstable species is unlikely to be formed in the dimerization step. On the other hand, within the accuracies of the experimental and theoretical results, the values of  $\Delta H^\circ$  of the proposed sulphinyl sulphonate are in reasonable agreement ( $\Delta H_{\text{exp}}^\circ - 16$  kJ mol<sup>-1</sup> for the 2,4-dichloro-5-methylbenzenesulphonyl radical,  $\Delta H_{\text{calc}}^\circ - 21$  kJ mol<sup>-1</sup>). Furthermore, dissociation of the sulphinyl sulphonate to give sulphinyl and sulphonyloxyl radicals (Scheme 2) is calculated to be energetically favourable ( $\Delta H^\circ$  *ca.* -350 kJ mol<sup>-1</sup>);\* subsequent reactions of these two radicals can lead to the thiosulphonate and sulphonic anhydride, which have been found as major products (up to *ca.* 50%) of the reactions of sulphonyl radicals.<sup>26</sup>

## Conclusions

Our results establish that both the  $\sigma$ -type sulphonyl radicals and the delocalized (resonance-stabilized) sulphinyl ( $\pi$ ) radicals undergo self-termination at rates approaching the diffusion-controlled limit; for arenosulphonyl radicals di-*ortho* substitution appears to provide a small degree of steric retardation.

Evidence that aromatic sulphonyl radicals (ArSO<sub>2</sub><sup>•</sup>) may undergo S-O dimerization derives from the detection of the associated sulphinyl species (ArSO<sup>•</sup>) during the production of the former *via* steady-state illumination. Observation of several curved Arrhenius plots for the rate constants  $2k_1(\text{obs})$  derived

\*  $\Delta H_f^\circ$  for PhSO<sup>•</sup> was obtained as 53 kJ mol<sup>-1</sup> from data given above and the value of 115.5 kJ mol<sup>-1</sup> for  $\Delta H^\circ$  for the thermal decomposition of PhS(O)S(O)<sub>2</sub>Ph into PhSO<sup>•</sup> and PhSO<sub>2</sub><sup>•</sup>.<sup>27</sup> From the enthalpies of hydrolysis of PhS(O)<sub>2</sub>S(O)<sub>2</sub>Ph and PhS(O)S(O)<sub>2</sub>Ph of -67.8 and -6.3 kJ mol<sup>-1</sup> respectively<sup>28</sup> we calculate values of  $\Delta H_f^\circ$  for PhSO<sub>2</sub>H and PhSO<sub>3</sub>H of -255 and -836 kJ mol<sup>-1</sup> respectively. In order to make an estimate of  $\Delta H_f^\circ$  for PhSO<sub>3</sub><sup>•</sup> of -736 kJ mol<sup>-1</sup> we have assumed that removal of a hydrogen atom from PhSO<sub>3</sub>H requires *ca.* 100 kJ mol<sup>-1</sup> (*cf.*  $\Delta H^\circ$  for the conversion of PhSO<sub>2</sub>H into PhSO<sub>2</sub><sup>•</sup>).

by direct analysis for some ArSO<sub>2</sub><sup>•</sup>—as well as simulation of growth and decay curves for these species—suggests that S-O dimerization leads to the formation of an unstable intermediate (exothermic by *ca.* 20 kJ mol<sup>-1</sup>, as suggested both *via* thermodynamic analysis of simulated curves and by thermochemical calculations). This intermediate can either regenerate ArSO<sub>2</sub><sup>•</sup> or give ArSO<sup>•</sup> (as detected) and ArSO<sub>3</sub><sup>•</sup>, with rate constants in the range 10<sup>2</sup>–10<sup>3</sup> s<sup>-1</sup>.

The greatest deviation from linear Arrhenius plots occurs for some (but not all) moderately hindered radicals ArSO<sub>2</sub><sup>•</sup> (containing a single *ortho* chlorine substituent) along with the unhindered radical 3,5-bis(trifluoromethyl)benzenesulphonyl; this suggests that both steric and electronic effects play a part in governing the observed behaviour, which may reflect a delicate balance between electronic effects on the relative polarity (and spin-density) at sulphur and oxygen centres† as well as steric effects which might both hinder the appropriate coupling and accelerate the decomposition of the intermediate. We believe that further speculation is unjustified.

## Experimental

E.s.r. spectra were recorded on a Varian E104 spectrometer fitted with a standard Varian variable-temperature system. Temperatures were measured with a copper-constantan thermocouple (Comark 5000). The radicals were generated by photolysis *in situ* in the sample cavity of the spectrometer by the radiation from an Hanovia 1 kW mercury-xenon lamp (977B-1).

The light was passed through a water heat-filter and then focussed by a silica lens and passed through either a programmable rotating sector (Rofin) or electronically operated camera shutter (Compur Electronic-m). The light beam was then refocused on the sample by a second silica lens; care was taken to obtain reasonably uniform illumination across the sample.

The growth and/or decay curves of radical concentration were collected in a Datalab Signal Averager (DL 4000), fitted with a DL417 microprocessor unit. Typically 1 024–4 096 separate curves were averaged to obtain a reasonable signal-to-noise ratio. Analysis of the curves was carried out in the DL 417 microprocessor. Substrate concentrations of typically 0.1 mol dm<sup>-3</sup> were employed (sufficient to give an e.s.r. signal whose magnitude was independent of the substrate concentration) normally together with [Et<sub>3</sub>SiH] = [(Bu<sup>•</sup>O)<sub>2</sub>] 0.3 mol dm<sup>-3</sup> (or [Me<sub>3</sub>SnSnMe<sub>3</sub>] 0.01 mol dm<sup>-3</sup>). Radical concentrations were measured by comparing the intensity of the steady-state signal with that of a standard sample of DPPH ( $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazyl) in methylbenzene; double integrations of both sets of spectra were carried out with the DL 417 microprocessor.

The majority of the chemicals were obtained commercially (at the highest purity available) and were used without further purification. The tetra- and penta-methylbenzenesulphonyl chlorides were gifts from Dr. C. Chatgililoglu. The arenosulphinyl chlorides were prepared from the corresponding disulphides using the method of Douglass and Norton.<sup>30</sup>

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† Approximately 50% of the unpaired electron density resides on the sulphur atom in sulphonyl radicals;<sup>29</sup> in ArSO<sub>2</sub><sup>•</sup> there is effectively no delocalization into the  $\pi$ -orbitals of the ring, so we can estimate that each oxygen has  $\rho_0$  *ca.* 25%.

## References

- 1 L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1955, 1596.
- 2 L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 1962, 3570.
- 3 P. Koelwijin and H. Berger, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1275; *ibid.*, 1974, **93**, 63.
- 4 W. J. M. van Tilborg and P. S. Smael, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 38, 133.
- 5 J. R. Shelton, *Rubber Chem. Technol.*, 1974, **47**, 949.
- 6 A. J. Bridgewater and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1978, 530.
- 7 B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 892.
- 8 C. Chatgililoglu, B. C. Gilbert, B. Gill, and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1141.
- 9 B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J. Chem. Soc., Perkin Trans. 2*, 1977, 497.
- 10 C. Chatgililoglu, B. C. Gilbert, and R. O. C. Norman, (a) *J. Chem. Soc., Perkin Trans. 2*, 1979, 770; (b) *ibid.*, 1980, 1429.
- 11 C. Chatgililoglu, L. Lunazzi, and K. U. Ingold, *J. Org. Chem.*, 1983, **48**, 3588.
- 12 H. H. Thoi, O. Ito, M. Iino, and M. Matsuda, *J. Phys. Chem.*, 1978, **82**, 314.
- 13 A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 626.
- 14 G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 6803.
- 15 M. C. R. Symons, *J. Am. Chem. Soc.*, 1969, **91**, 5924.
- 16 H. Schuh and H. Fischer, *Int. J. Chem. Kinet.*, 1976, **8**, 341; *Helv. Chim. Acta*, 1978, **61**, 2130; M. Lezni, H. Schuh, and H. Fischer, *Int. J. Chem. Kinet.*, 1979, **11**, 705.
- 17 J. A. Howard and E. Furimsky, *Can. J. Chem.*, 1974, **52**, 555.
- 18 J. A. Howard and J. E. Bennett, *Can. J. Chem.*, 1972, **50**, 2374.
- 19 J. E. Bennett, G. Brunton, and R. Summers, *J. Chem. Soc., Perkin Trans. 2*, 1980, 981.
- 20 J. E. Bennett, G. Brunton, J. R. Lindsay Smith, T. M. F. Salmon, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1987, 2421.
- 21 J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Am. Chem. Soc.*, 1972, **94**, 7040.
- 22 S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 1958, **29**, 546.
- 23 S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haughen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
- 24 S. W. Benson, 'Thermochemical Kinetics,' John Wiley, New York, 1st edition, 1968.
- 25 J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, 1970, **35**, 114.
- 26 C. M. M. da Silva Corrêa and W. A. Waters, *J. Chem. Soc. C*, 1968, 1874.
- 27 J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, 1964, **86**, 4898.
- 28 J. L. Kice, H. C. Margolis, W. S. Johnson, and C. A. Wulff, *J. Org. Chem.*, 1977, **42**, 2933.
- 29 M. Geoffroy and E. A. C. Lucken, *J. Chem. Phys.*, 1971, **55**, 2719.
- 30 I. B. Douglass and R. V. Norton, *J. Org. Chem.*, 1968, **33**, 2104.

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