Detection of Aromatic Sulphinyl (ArSO·) Radicals during the Photolysis and Thermolysis of *S*-Aryl Arenethiosulphonates and Diaryl Sulphoxides

By Bruce C. Gilbert* and Barbara Gill
(*Department of Chemistry, University of York, Heslington, York* YO1 5DD)
and Michael D. Sexton
(*Paramins Technology Division, Esso Chemical Research Centre, Abingdon, Oxfordshire* OX13 6BB)

Summary Evidence has been obtained using e.s.r. spectroscopy that arenesulphinyl radicals (ArSO·) are produced during the thermal and photolytic homolysis of both diaryl sulphoxides and *S*-aryl arenethiosulphonates, in the latter case *via* the initial production of the corresponding sulphonyl and thiyl radicals, ArSO$_2$· and ArS·, respectively.

Sulphur-containing organic compounds have been employed for some time as antioxidants for operation under both thermolytic and photolytic conditions, and there has recently been renewed interest in their mechanisms of action.[1] We now report results of an e.s.r. study of the reactions of two classes of compounds, namely some *S*-aryl arenethiosulphonates (I) and diaryl sulphoxides (II).

When solutions of some *S*-aryl arenethiosulphonates (*ca.* 10^{-4} M) in deoxygenated methylbenzene are photolysed at *ca.* 210 K in the cavity of a Varian E-104 e.s.r. spectrometer with the radiation from an Hanovia 977B-1 1 kW mercury–xenon compact arc, signals attributed to sulphinyl radicals[2] (III) are detected (see Table).

Similar, though somewhat broader, signals are also detected when mixtures of some thiosulphonates and naphthalene (with the concentration of the former *ca.* 10^{-4} M) are heated to *ca.* 400 K in the e.s.r. cavity.

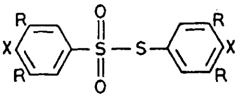
Table

E.s.r. spectra of radicals derived from some *S*-aryl arenethiosulphonates and diaryl sulphoxides

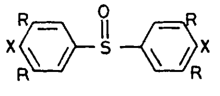
Radical	Hyperfine splittings/mT	g	Method of generation[a]	
			$h\nu$	Heat
(III; R=X=H)	a(*o,p*-H), 0·239; a(*m*-H), 0·070	2·0091	(I; R=X=H (II; R=X=H)	
(III; R=H, X=NO$_2$)	a(*o*-H), 0·227[b]	2·0091	(I; R=H, X = NO$_2$)	(I; R=H, X=NO$_2$)
(III; R=H, X=Br)	a(*o*-H), 0·230[b]	2·0101	(I; R=H, X=Br) (II; R=H, X=Br)	(I; R=H, X=Br)
(III; R=H, X=Me)	a(*o*-H) and a(Me), 0·264[b]	2·0092	(I; R=H, X=Me) (II; R=H, X=Me)	
(III; R=Bu^t, X=OH)	a(*o*-H), 0·227	2·0090	(I; R=Bu^t, X=OH) (II; R=Bu^t, X=OH)	(I; R=Bu^t, X=OH) (II; R=Bu^t, X=OH)
(IV)	a(N), 1·712	2·0066	(I; R=H, X=Me)[c]	
(V)	a(N), 1·208	2·0061	(I; R=H, X=Me)[c] (II; R=H, X=Me)[c]	(I; R=H, X=Me)[c]

[a] For conditions, see text. [b] Splittings from *m*-H not resolved. [c] In the presence of 2-methyl-2-nitrosopropane.

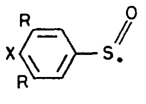
Thermal and photochemical decomposition of *S*-aryl arenethiosulphonates in the presence of spin traps provides evidence for the formation of radicals of different types. For example, photolysis of (I; R = H, X = Me) in methylbenzene in the presence of 2-methyl-2-nitrosopropane (Bu^tNO) leads to the detection of signals from the adducts formed by trapping the appropriate aromatic thiyl (RS·) and sulphonyl radicals ($RSO_2·$) (see Table and refs. 3 and 4); we have independently generated these adducts from photolysis of the appropriate disulphide and sulphonyl chloride, respectively, in the presence of the trap. We have found no evidence that arenesulphinyl radicals are trapped by either nitroso or nitrone traps.



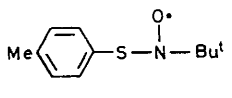
(I)



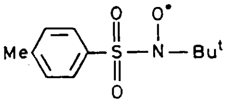
(II)



(III)



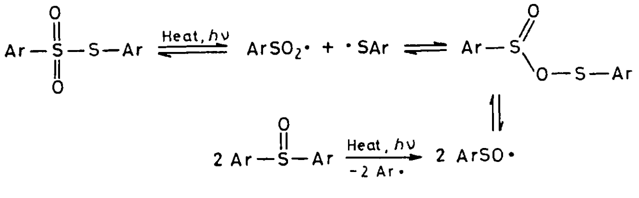
(IV)



(V)

Decomposition of *S*-aryl arenethiosulphonates evidently proceeds, under these conditions, at least in part *via* a homolytic mechanism (evidence for heterolytic thermal decomposition of some *S*-aryl thiosulphonates has been summarized[5]). In the absence of a trap, the first-formed radicals $ArSO_2·$ and ArS· can recombine and thence give the appropriate arenesulphinyl radical, probably *via* the S–O shift shown in the Scheme. It seems likely that the stability of the arenesulphinyl radical is such that it is not itself trapped.

Arenesulphinyl radicals are also detected during the photolysis of solutions of diaryl sulphoxides in deoxygenated methylbenzene and in the thermolysis of the antioxidant (II; R = Bu^t, X = OH) (*ca.* 10^{-4} M solution in naphthalene at *ca.* 400 K). Aromatic sulphonyl radicals are trapped during the photolysis of some sulphoxides (*e.g.*, II; R = H, X = Br or Me) and during the thermolysis of (II; R = Bu^t, X = OH) (under these conditions thiyl radicals were not trapped).



Scheme

It is known that decomposition of aryl sulphoxides leads, *inter alia*, to thiosulphonates (*cf.* the photolysis of phenyl t-butyl sulphoxide[6] and thermolysis[7] of benzyl 4-methylphenyl sulphoxide); our results provide support for a mechanism which involves a reversible route for the interconversion of ArSO· and the radical pair $ArSO_2·$–ArS· (see Scheme). The formation at some intermediate stage of the symmetrical sulphinyl dimer ArS(O)S(O)Ar (*cf.* ref. 8) cannot be ruled out.

We thank the S.R.C. and Esso Chemicals Ltd. for a C.A.S.E. award (to B.G.).

(*Received*, 12*th October* 1977; *Com.* 1066.)

---

[1] J. R. Shelton, *Rubber Chem. Technol.*, 1974, **47**, 949; J. R. Shelton and E. R. Harrington, *ibid.*, 1976, **49**, 147; W. J. M. van Tilborg and P. Smael, *Rec. Trav. chim.*, 1976, **95**, 132, 138; P. Koelewijn and H. Berger, *ibid.*, 1972, **91**, 1275; 1974, **93**, 63; G. Scott, *Pure Appl. Chem.*, 1972, **30**, 267.

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

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

[4] E. Flesia and J.-M. Surzur, *Tetrahedron Letters*, 1974, 123; Th. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 696; M. Kobayashi, E. Akiyama, H. Minato, and N. Kito, *Bull. Chem. Soc. Japan*, 1974, **47**, 1504.

[5] J. L. Kice, in 'The Chemistry of Organic Sulphur Compounds,' eds. N. Kharasch and C. Y. Meyers, 1966, Vol. 2, p. 129.

[6] D. Barnard, *J. Chem. Soc.*, 1957, 4673, 4675.

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

[8] R. M. Topping and N. Kharasch, *J. Org. Chem.*, 1962, **27**, 4353; M. M. Chau and J. L. Kice, *J. Amer. Chem. Soc.*, 1976, **98**, 7711.