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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Jones, Ian W. and Tebby, John C.(1978) 'THE MASS SPECTRA OF ALKYL ARYL SULPHIDES, DIARYL DISULPHIDES AND ALKYL ARYL SULPHONES', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 1, 57 — 60

To link to this Article: DOI: 10.1080/03086647808069863

URL: <http://dx.doi.org/10.1080/03086647808069863>

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THE MASS SPECTRA OF ALKYL ARYL SULPHIDES, DIARYL DISULPHIDES AND ALKYL ARYL SULPHONES

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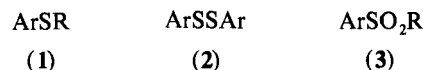
(Received February 13, 1978)

The electron impact mass spectra of a comprehensive series of each of the titled compounds have been studied. The spectra of the sulphides show that one or two methyl groups at the ortho position of the aryl rings markedly increase the intensity of the M-R and/or M-SR ions. The abundance of the latter also increase with increases in the size of the alkyl group. The fragmentation patterns of the diaryl disulphides are also sensitive to steric effects. The presence of an ortho methyl group inhibits the appearance of M-S₂ ions but leads to the formation of new ions at M-SH₃ mu. The spectra of ethyl phenyl sulphone and the ethyl tolyl sulphones are unique in that their spectra contain peaks at M-14 mu. Deuterium labelling indicates that these ions arise by the loss of a methyl radical from protonated (or deuteriated) molecular ions.

There has been wide interest in the mass spectra of sulphur compounds.¹ Comprehensive studies of alkyl thiols,^{2,3} aryl thiols,⁴ dialkyl disulphides,² alkyl aryl sulphides,^{5,6} dialkyl disulphides,⁷ various sulfoxides,^{5,8,9} and various sulphones,^{5,8,10} have been investigated. Diaryl sulphides¹¹ and diaryl disulphides have received less attention.

We have examined the electron impact mass spectra of a comprehensive series of alkyl aryl sulphides (1), diaryl disulphides (2) and alkyl aryl sulphones (3) in which the alkyl groups vary

through the series—methyl, ethyl, *i*-propyl, *t*-butyl; and the aryl groups vary through the series—phenyl, *o*-tolyl, *m*-tolyl, *p*-tolyl and mesityl. We have found some interesting facets which we now report.



The spectra of thioanisol and the corresponding tolyl compounds have been previously studied mainly with regard to the loss of SH by the re-

TABLE I
Relative abundances of selected ions in the mass spectra of alkyl aryl sulphides (1)

Compound	(1, Ar = phenyl)			(1, Ar = <i>o</i> -tolyl)		
	M	M-R	M-SR	M	M-R	M-SR
Me	100	43	8	100	59	42
Et	100	18	18	100	59	50
<i>i</i> -Pr	57	18	13	61	0	57
<i>t</i> -Bu	39	24	14	31	10	47

Compound	(1, Ar = <i>m</i> -tolyl)			(1, Ar = <i>p</i> -tolyl)			(1, Ar = mesityl)		
	M	M-R	M-SR	M	M-R	M-SR	M	M-R	M-SR
Me	100	23	35	100	31	44	100	60	23
Et	100	12	48	100	19	55	100	75	38
<i>i</i> -Pr	63	11	34	65	14	60	65	20	65
<i>t</i> -Bu	37	15	54	42	19	67	29	14	94

The base peaks of the iso-propyl and tert-butyl aryl sulphides correspond to ArSH⁺, i.e. *m/e* 110, 124 and 152 for the phenyl, tolyl and mesityl sulphides respectively.

TABLE II

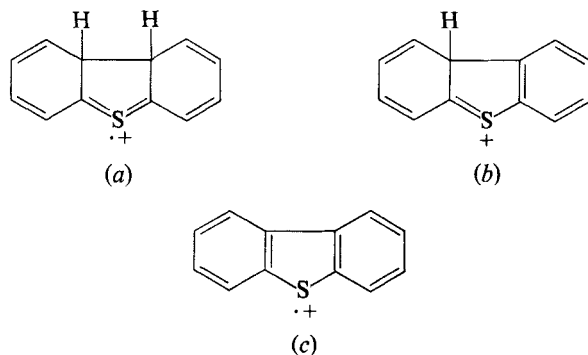
Relative abundancies of selected ions in the mass spectra of diaryl disulphides (2)

Ar	M	M-S	M-SH ₃	M-S ₂	ArSH	ArS
phenyl	95	19	0	12	76	100
<i>o</i> -tolyl	100	28	9	0	89	92
<i>m</i> -tolyl	100	6	0	13	15	79
<i>p</i> -tolyl	73	11	0	10	71	100
mesityl	87	6	0	0	96	100

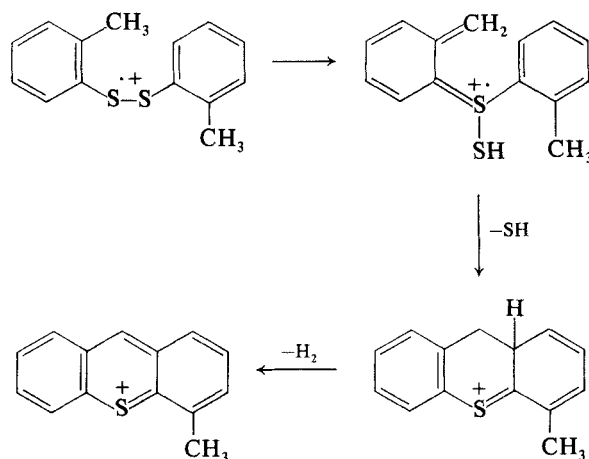
arranged molecular ions.⁶ It was found that the abundance of the M-Me ions was greatest in the spectrum of the *o*-tolyl sulphide. We confirm these results and find (see Table I) that the M-Et ions in the spectra of the corresponding ethyl sulphides follow the same trends and that the effect is greater still for the mesityl derivatives in which the aryl rings bear two methyl groups at the ortho position.

Peaks corresponding to M-SR ions appear in the spectra of all the sulphides (see Table I). In the mesityl series their intensity increases markedly as the size of the *S*-alkyl group increases. However, a meta-stable ion for the formation of these ions by the direct cleavage of the *S*-aryl bond in the molecular ion, was observed only in the spectrum of methyl *p*-tolyl sulphide. There can be little doubt that there is an alternative pathway leading to the M-SR ions for the higher alkyl compounds which involves loss of HS from the M-alkene ion.

The mass spectra of the phenyl, tolyl and mesityl disulphides shows that the major fragmentation paths involve the cleavage of the disulphide bond to give ArS⁺ and ArSH⁺ ions. The former ions of the molecular ions are the base peaks of the spectra. Peaks corresponding to M-S ions are observed in the spectra of all five disulphides (see Table II). This ion appears at *m/e* 186 in the spectrum of diphenyl disulphide and is accompanied by peaks at *m/e* 185 and *m/e* 184. We suggest that these ions have the cyclic structures *a*, *b* and *c*. Peaks corresponding to



M-S₂ are observed only in those disulphides which do not possess a methyl group at the ortho position of the aryl ring. On the other hand the di-ortho-tolyl disulphide was unique in giving a peak corresponding to a M-SH₃ ion which can be readily explained by the fragmentation path shown in the Scheme. It has been suggested that di-ortho-tolyl sulphone fragments via similar methylene-bridged ions.⁸



A number of alkyl aryl sulphones have been studied previously.^{6,7} We confirm the presence of peaks corresponding to ArOH and/or ArO ions in all the spectra, which supports the generally accepted proposal that migrations of the aryl group from sulphur to oxygen is facile. We also find (see Table III) peaks corresponding to ArSO ions (M-OR) which tend to become more evident as the branching of the alkyl group (R) increases. Although these ions could also arise via the migration of the alkyl group from sulphur to oxygen it is also possible for them to arise via loss of HO from the M-alkene ions. This latter pathway is probably predominant because the spectra which exhibit no ArSO peaks also show no or very low abundant ions corresponding to M-alkene.

TABLE III
Relative abundances of selected ions in the mass spectra of alkyl aryl sulphones (3)

Compound	(3, Ar = phenyl)				(3, Ar = <i>o</i> -tolyl)			
R	M	ArSO	ArOH	ArO	M	ArSO	ArOH	ArO
Me	29	0	33	7	49	0	9	35
Et	83	19	83	10	83	11	19	28
<i>i</i> -Pr	39	26	50	13	64	7	34	10
<i>t</i> -Bu	6	35	9	0	10	10	10	0

Compound	(3, Ar = <i>m</i> -tolyl)				(3, Ar = <i>p</i> -tolyl)			
R	M	ArSO	ArOH	ArO	M	ArSO	ArOH	ArO
Me	58	8	28	18	84	7	13	67
Et	76	50	67	61	45	0	15	28
<i>i</i> -Pr	55	20	50	17	25	21	12	12
<i>t</i> -Bu	22	37	19	0	26	76	20	26

Compound	(3, Ar = mesityl)			
R	M	ArSO	ArOH	ArO
Me	98	0	0	70
Et	36	0	0	25
<i>i</i> -Pr	49	6	21	49
<i>t</i> -Bu	23	13	34	68

The base peaks of the methyl, ethyl and iso-propyl sulphones correspond to Ar⁺, i.e. *m/e* 77, 91 and 119 for the phenyl, tolyl and mesityl sulphones respectively except for (a) iso-propyl phenyl sulphone whose base peak at *m/e* 142 corresponds to M⁺-propene and (b) iso-propyl mesityl sulphone whose base peak at *m/e* corresponds to mesitylene⁺. The base peaks of the tert-butyl aryl sulphones appear at *m/e* 57 which corresponds to C₄H₉⁺.

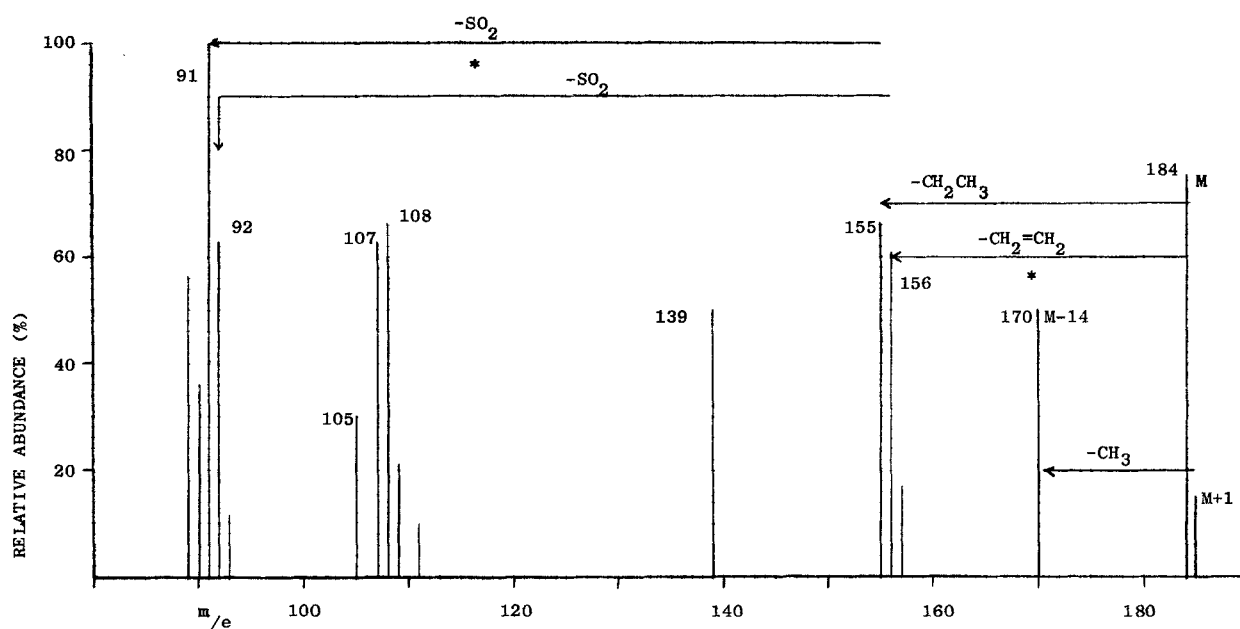


FIGURE 1 Mass spectrum of ethyl *m*-tolyl sulphone.

The spectra of ethyl phenyl sulphone and the ethyl tolyl sulphones also contain M-14 peaks which have abundances varying from 13 to 50%, see Figure 1. Loss of methylene is a very uncommon fragmentation and therefore the spectra of the α -dideuteriated ethyl sulphones were determined. The above ions appear at M-13 μ in the spectra of the dideuteriated compounds indicating that the fragmentation involves loss of a CH_3 radical and gain of a proton or deuterium atom.

EXPERIMENTAL

The mass spectra were determined on a Perkin-Elmer Hitachi R.M.U.-6 spectrometer operating at 70 eV. Samples were introduced through a heated inlet system. The compounds were prepared by standard procedures and all gave satisfactory uv, ir, nmr and mass spectra, and (for solids) melting points in agreement with published values. The dideuterio sulphones were prepared by heating the sulphone in 0.2 M sodium deuterioxide in deuterium oxide for 16 hr.

ACKNOWLEDGEMENTS

We thank the University of Keele for making their mass spectroscopy facilities available to us.

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