

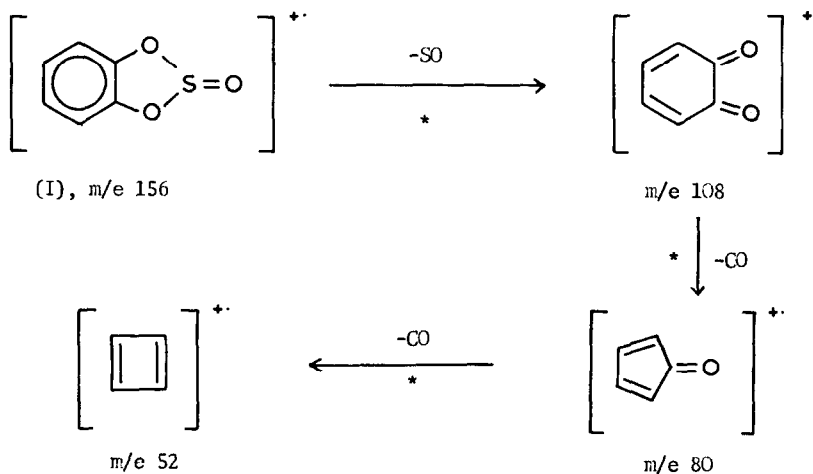
SO VERSUS SO<sub>2</sub> ELIMINATION IN CYCLIC AROMATIC SULPHITES

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De Jongh et al. (1) have shown that the 70 ev mass spectrum of *o*-phenylene sulphite (I) contains ions arising from initial loss of sulphur monoxide followed by successive losses of two molecules of carbon monoxide (Scheme 1). We have confirmed this fragmentation scheme by observation of the appropriate metastable ions (marked \* - see Table). The (M-SO<sub>2</sub>) ion is of very low



Scheme 1

intensity. This is in marked contrast to the behaviour of alicyclic (2) and di-alkyl sulphites (3) for which the loss of SO<sub>2</sub> is a major fragmentation pathway. To determine whether the behaviour of *o*-phenylene sulphite is anomalous we have studied the mass spectra of three further cyclic aromatic sulphites (II - IV).

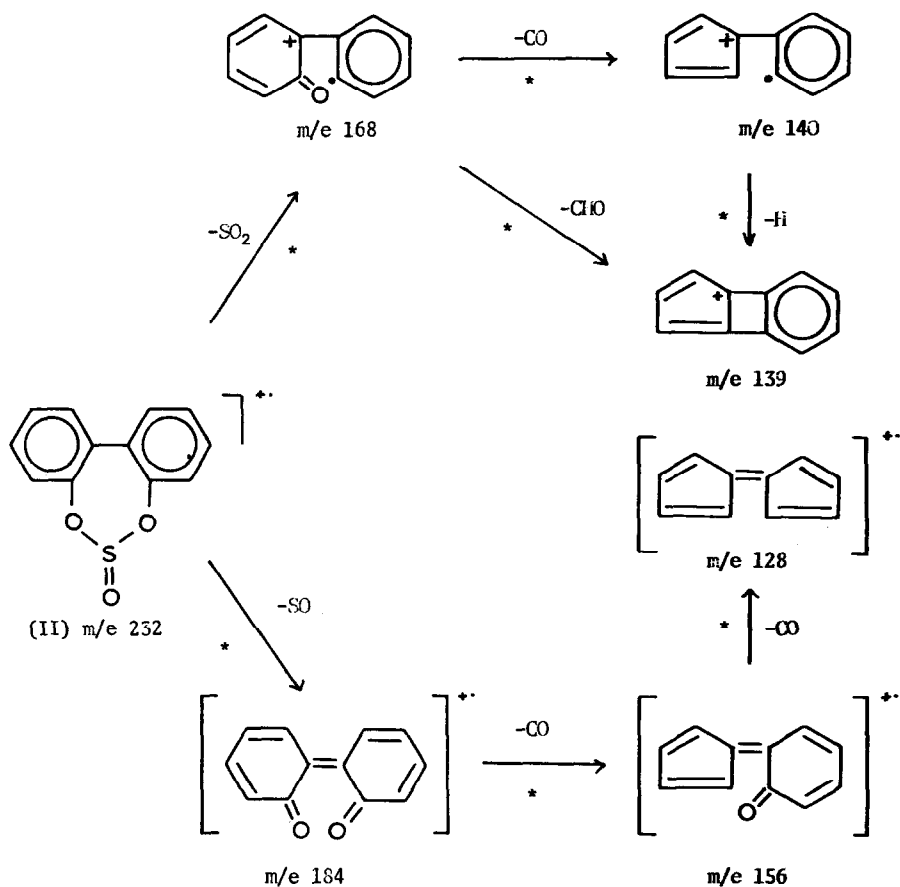
The mass spectrum of 2,2'-biphenylene sulphite (II) has peaks at m/e 168 and 184 showing that loss of both SO<sub>2</sub> and SO occurs. Scheme 2 outlines possible fragmentation pathways supported by metastable ions (Table).

Table

Principal Metastable Ions in the Mass Spectra of Cyclic Aromatic Sulphites<sup>†</sup>

<u>Sulphite</u>	<u>m/e</u>		<u>Assignment</u>	<u>Parent</u>	<u>Neutral Fragment</u>
	<u>obs.</u>	<u>calc.</u>			
(I)	74.7	74.8	156 → 108	C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub>	SO
	59.2	59.3	108 → 80	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	CO
	33.8	33.8	80 → 52	C <sub>5</sub> H <sub>4</sub> O	CO
(II)	105.0	105.0	156 → 128	C <sub>11</sub> H <sub>8</sub> O	CO
	115.0	115.0	168 → 139	C <sub>12</sub> H <sub>8</sub> O	CHO
	116.5	116.7	168 → 140	C <sub>12</sub> H <sub>8</sub> O	CO
	121.7	121.7	232 → 168	C <sub>12</sub> H <sub>8</sub> SO <sub>3</sub>	SO <sub>2</sub>
	132.4	132.3	184 → 156	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub>	CO
	138.0	138.0	140 → 139	C <sub>11</sub> H <sub>8</sub>	H
	145.9	145.9	232 → 184	C <sub>12</sub> H <sub>8</sub> SO <sub>3</sub>	SO
(III)	68.0	67.9	114 → 88	C <sub>9</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>
	91.5	91.5	142 → 114	C <sub>10</sub> H <sub>6</sub> O	CO
	98.0	97.9	206 → 142	C <sub>10</sub> H <sub>6</sub> SO <sub>3</sub>	SO <sub>2</sub>
	112.0	112.0	114 → 113	C <sub>9</sub> H <sub>6</sub>	H
(IV)	199	199	314 → 250	C <sub>13</sub> H <sub>8</sub> SO <sub>3</sub> <sup>35</sup> Cl <sub>2</sub>	SO <sub>2</sub>
	225	225	314 → 266	C <sub>13</sub> H <sub>8</sub> SO <sub>3</sub> <sup>35</sup> Cl <sub>2</sub>	SO

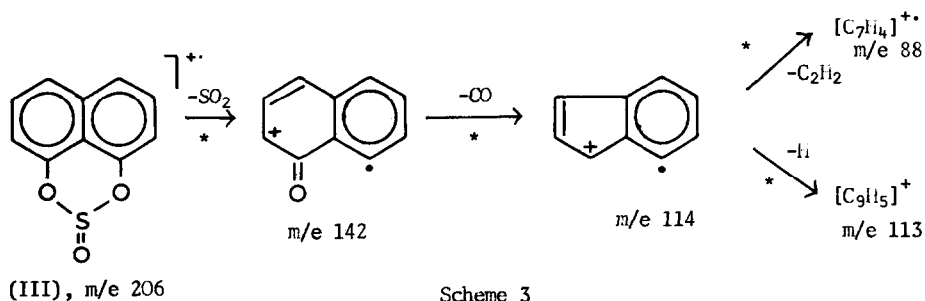
<sup>†</sup> Mass spectra measured on an A.E.I. M.S. 12 spectrometer operating at 70 ev using either an all glass heated inlet system or a direct insertion probe at 100°.



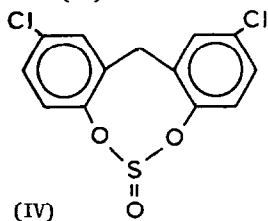
Scheme 2

The appearance of the  $(M-\text{SO}_2)$  ion is probably due mainly to the increased resonance stabilization of this radical ion compared to the corresponding ion from I. Both the  $(M-\text{SO}_2)$  and  $(M-\text{SO})$  ions fragment subsequently with loss of  $\text{CO}$ . Further fragmentations (not shown here) characteristic of aromatic compounds involving loss of  $\text{C}_2\text{H}_2$  units also occur.

The electron-impact induced fragmentation of naphthylene 1,8-sulphite (III), however, is similar to that of alicyclic sulphites; loss of  $\text{SO}_2$  occurs almost exclusively (Scheme 3).



The absence of an (M-SO) ion in the spectrum of (III) is presumably due to its lack of stability compared with those ions derived from (I) and (II). The mass spectrum of dichlorophene sulphite (IV) has ions corresponding to the loss of both SO and SO<sub>2</sub> from the molecular ion.



The relative intensities of these ions, however, are much lower than for (II). The lower stabilities of these ions probably arise from the lack of resonance interaction between the rings due to the intervening methylene group.

Thus the nature of the neutral species eliminated in the fragmentation of cyclic aromatic sulphites depends to a large extent on the stability of the daughter ion resulting from such an elimination and the more energetically favourable pathway can be predicted from simple valence bond considerations.

#### References

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3. A.A. Gamble, J.R. Gilbert, J.G. Tillett, R.E. Coombs and A.J. Wilkinson, J. Chem. Soc.(B), 655 (1969).