Loss of Carbon Monoxide in the Mass Spectrum of Methyl [1-^{13}C]Phenyl Sulphoxide

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Summary The carbon atom lost as carbon monoxide from the molecular ion ($M^{+\cdot}$) and the $(M - CH_3)^+$ ion of methyl [1-^{13}C]phenyl sulphoxide is shown to be the C-1 carbon atom of the aromatic ring.

Correlations of mass spectral and photochemical processes have been recognized for some time,[1] *e.g.*, Turro and McLafferty[2] have illustrated the correlation with pyruvic acid and isopropyl pyruvate, and the phenyl migration observed in the photodimerization of phenoxy-4,5-benzotropones[3] is duplicated in the mass spectrometer.

One of the more interesting mass spectral processes is that of new bond formation upon electron impact. A case in point is the loss of carbon monoxide from the molecular ion ($M^{+\cdot}$) and the $(M - CH_3)^+$ ion of methyl phenyl sulphoxide (I) despite the fact that no C–O bond exists in the original molecule.[4] This loss may be visualized as occurring by migration of the aryl ring to an electron-deficient oxygen atom (path a). Migration of unsaturated groups from sulphur to oxygen has been reported in the mass spectra of aromatic sulphoxides and sulphones,[5] vinyl sulphoxides,[6] and ethynyl sulphoxides and sulphones.[7] This path is analogous to the known photochemical conversion of sulphoxides and sulphones into sulphenate (II) and sulphinate esters, respectively.

Table. Low-resolution mass spectral peaks for unlabelled and labelled methyl phenyl sulphoxide[a]

Unlabelled *m/e*	Unlabelled Rel. abundance[b]	Labelled (III)[c] *m/e*	Labelled (III)[c] Rel. abundance[b]
113	—	113	—
112	0·185	112	0·169
111	—	111	0·280
110	0·272	110	0·551
109	0·543	109	—
98	0·060	98	0·058
97	0·625	97	0·620
96	0·030	96	0·038
95	0·092	95	0·210
94	0·193	94	0·074

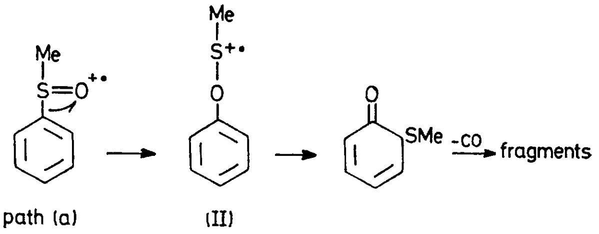
[a] Recorded on a Hewlett–Packard 5930 A mass spectrometer, average of five readings are given. [b] The sums of the relative abundances of the ions *m/e* 94—98 and 109—113, respectively, are both unity; corrected for naturally abundant ^{13}C and ^{34}S. [c] Calculated for 100% isotopic enrichment; sample contained 90·2% excess ^{13}C.

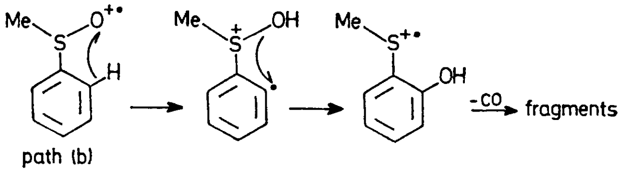
An alternative path (b) may involve migration of oxygen to an ionized aryl ring. This is based upon the known oxygen migrations in 1-nitronaphthalene[8] and thionylaniline[9] whose mass spectra show loss of carbon monoxide from their respective molecular ions. It is noteworthy that reversible oxygen to sulphur allyl and benzyl shifts have been reported in thermal sulphenate to sulphoxide rearrangements,[10] but phenyl sulphoxides do not appear to undergo thermal 1,2-migrations from sulphur to oxygen.[11]

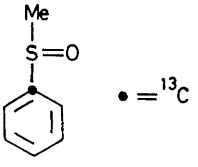
In order to distinguish between these two paths, the mass spectrum of methyl [1-^{13}C]phenyl sulphoxide (III) was determined. Compound (III) was synthesized from iodo-[1-^{13}C]benzene *via* conversion into the Grignard reagent[12] followed by successive treatment with elemental sulphur and methyl iodide. The resulting crude [1-^{13}C]thioanisole was oxidized to (III) with sodium metaperiodate.[13]

Loss of carbon monoxide from (III) *via* path (a) would result in total loss of label whereas loss of carbon monoxide from (III) *via* path (b) would result in total retention of label.

The observed data, showing the $(M^{+\cdot} - CO)$ and $(M - CH_3 - CO)^+$ regions, are given in the Table. It is clear that the relative peak intensities in the *m/e* 110—114 and *m/e* 96—100 regions for (I) and (III) indicate that prior to the loss of carbon monoxide, the C-1 atom of the ring has bonded to oxygen suggesting path (a) or its equivalent. Further, the peak at *m/e* 109 (C_6H_5S) is shifted to *m/e* 110, and the peak at *m/e* 94 (C_6H_6O), perhaps ionized phenol, is shifted to *m/e* 95 in accordance with path (a).







(III)

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