Doubly Charged Parent Ions of Higher Abundance than the Corresponding Singly Charged Species

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Summary The mass spectra of some phosphorus- and arsenic-substituted biphenyl systems show doubly charged parent ions of higher abundance than the singly charged molecular ions.

IN general, doubly charged parent ions, produced under electron impact, must be of lower abundance than the corresponding singly-charged ions.[1] Exceptions are only possible when the doubly charged species is, for some reason, *more stable* and therefore decomposes more slowly. The first report of a M^{2+} ion with greater intensity than the corresponding $M^{+\cdot}$ ion was published only recently and is ascribed to an intramolecular rearrangement which stabilizes the doubly charged species relative to the directly fragmenting singly charged ion.[2]

We now report further cases of highly abundant doubly charged parent ions. 2,2′-Bis-(2,2′-biphenylylenearsino)-biphenyl (I)[3] shows in the 70 ev mass spectrum‡ a doubly charged molecular ion (relative intensity 0·94) which is about 19 times more abundant than the singly charged parent ion (relative intensity 0·05) (see Scheme 1). The most abundant ion, which has the spiro-arsonium structure (II), has a mass number of 379.

The mass spectral features can be interpreted by assuming that the ($I^{+\cdot}$) ion easily decomposes to the stable bis-(2,2′-biphenylylenearsonium)ion (II)[4] and the 2,2′-biphenylylenearsino-radical (III), whereas the doubly-charged species (I^{2+}) undergoes a similar cleavage to the spiro-cation (II) and the 2,2′-biphenylylenearsonium cation (IV) (relative intensity 12%)§ only to a minor extent. Instead, the bi-radical ion (I^{2+}) probably rearranges to the doubly charged ion (V) which has only paired electrons and a favourable charge separation.[2,5] [The doubly charged species at mass numbers 189½ and 113½ corresponding to the mono-cations (II) and (IV) have relative intensities of 0·1% and 0·06%.] The charges on the heteroatoms[6] can be further separated and stabilized by delocalisation into the outer 2,2′-biphenylylene systems.

Similar observations are made in the mass spectra of two other compounds, containing ter- and quinque-valent phosphorus and arsenic. The compounds (VIa; M = P) and (VIb; M = As)[8] (see Scheme 2) show doubly charged

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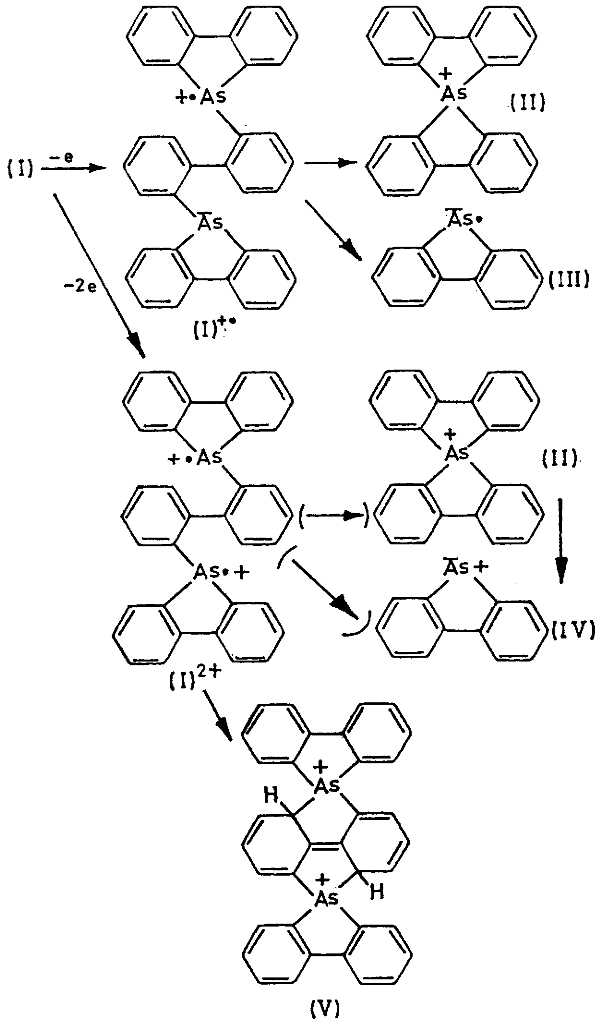
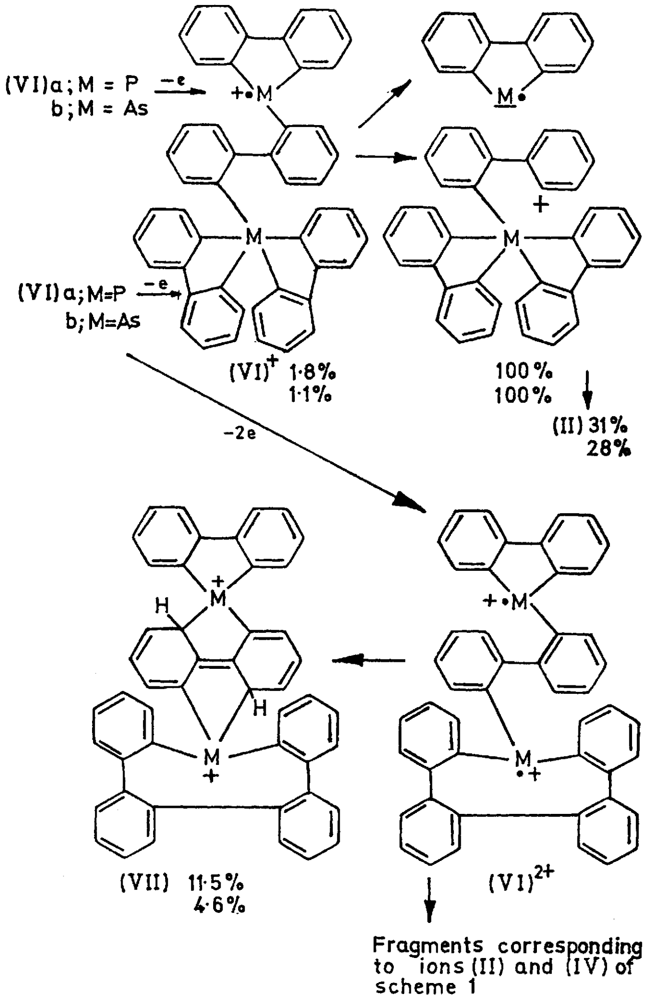
‡ Mass spectra were obtained on an Atlas CH4 mass spectrometer; high-resolution measurements were made on a CEC 21-110 B double-focusing mass spectrometer.

§ This cation can also be formed by further decomposition of cation (II).

parent peaks which are 6·4 and 4·2 times as intensive as those of the corresponding singly charged molecular ions.



SCHEME 1



SCHEME 2

Again one can assume that the singly charged radical ions decompose easily whereas the doubly charged bi-radical species rearrange at least to a certain extent to the relatively stable doubly-charged ions (VIIa) and (VIIb) with paired electrons. This includes the primary rearrangement of the quinquevalent part of these molecules to a tervalent state. Such rearrangements are known to occur thermally with related compounds of quinquevalent phosphorus[9] and arsenic.[3,4,7]

On the basis of these results we hope to produce further examples of highly abundant doubly charged molecular ions by examining related phenyl and polyphenyl systems bearing one, two, or even more heteroatoms (or heteroatom-containing groups) with easily ionizable free electron pairs.[6]

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