# Mass Spectrometry: Inter-charge Distance in Doubly-charged Organic Ions

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DECOMPOSITION of metastable ions gives rise to diffuse peaks in mass spectra which are commonly referred to as "metastable peaks". It has recently been noted[1,2] that not all "metastable peaks" are of the same shape; some have distinctive flat tops whilst others show "lobes" on either end of a plateau top and are referred to as dish-shaped.

Broadened "metastable peaks" arise whenever

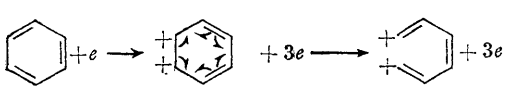
the decomposition of a metastable ion is accompanied by the release of kinetic energy.[1] This can arise if the two fragments formed by decomposition are together more stable than the decomposing ion. The measurement of peak widths is indeed used to deduce that particularly stable fragments have been formed, and thence to infer structural information.

When a doubly-charged metastable ion decomposes into two charged fragments there is a release of energy due to the repulsion between the two charges. This process may or may not be accompanied by a further energy release due to the stability of the fragments formed. In decompositions of doubly-charged ions which have been reported, there has always been a release of energy of at least 2 ev, and the accompanying peaks have always been dish-shaped. From the widths of these peaks, the total energy release can be arrived at. For example, Jennings[2] has shown that in the decomposition:

$$C_6H_6^{2+} \rightarrow CH_3^+ + C_5H_3^+$$

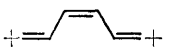
there is a release of energy of 2·8 ev. If all this energy is the result of repulsion between the two positive charges in the doubly-charged $C_6H_6$ ion it is equal to the work required to bring two charges from infinity to a distance apart equal to the charge separation in the doubly-charged $C_6H_6$ ion. If the fragments formed in the decomposition have assumed particularly stable forms, then only part of the energy release will arise from the separation of the two charges. The energy release on separation of the charges is equal to $e^2/r$ where $e$ is the electronic charge and $r$ the initial inter-charge distance. For an energy release of 2·8 ev the inter-charge distance is 5·14 Å. If only part of the energy release in the decomposition arises from the charge separation then the inter-charge distance in the decomposing ion will be greater than 5·14 Å.

Loss of two $\pi$-electrons from benzene must therefore be visualized as leading to opening of the ring and this will involve electron rearrangement perhaps in the manner shown below:



(a) (b)

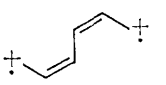
The "half arrow" ("fish-hook") symbol is used to represent transfer of a single electron.[3,4] Rotation about the single bonds will lead to separation of the positive charges even without further electron rearrangement to give an ion



(c)

Assuming a value of 1·37 Å for C=C and 1·47 Å for C–C and that all bond angles are 120°, the intercharge distance in this ion is 5·58 Å.

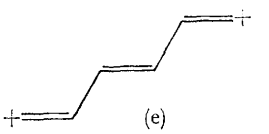
If, however, one visualises ring-opening of (a) without electron rearrangement, a doubly-charged biradical is produced, which by rotation about single bonds can assume the configuration



(d)

The inter-charge distance in (d) is 5·13 Å.

If electron rearrangement and rotation are possible, the ion could attain a more linear configuration such as



(e)

in which the inter-charge distance is 6·13 Å.

The coulombic repulsion between the charges would be insufficient to produce appreciable extension of structures such as (c), (d), or (e).

Field and Franklin[5] give the following appearance potentials:

$C_6H_6 \rightarrow$
$C_5H_3^+ + CH_3\cdot\ (?) + e$ requires 16·6 ev

$CH_3\cdot \rightarrow CH_3^+ + e$ requires 10·0 ev

$C_6H_6 \rightarrow C_6H_6^{2+} + 2e$ requires 27·2 ev

$\therefore C_6H_6 \rightarrow$
$C_5H_3^+$ and $CH_3^+ + 2e$ requires 26·6 ev

and

$C_6H_6^{2+} \rightarrow C_5H_3^+ + CH_3^+$ yields
27·2 − 26·6 ev = 0·6 ev

There is considerable uncertainty in these figures, that for the appearance potential of $C_6H_6^{2+}$ from

benzene being given only to $\pm 1$ ev, but nevertheless, the errors do not cast doubt on the hypothesis that the $C_6H_6^{2+}$ ion has an open configuration.

The results suggest a general method for estimating inter-charge distances in multiply-charged ions, information which is necessary in thermodynamic calculations.

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[1] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.
[2] W. Higgins and K. R. Jennings, *Chem. Comm.*, 1965, 99.
[3] J. S. Shannon, *Tetrahedron Letters*, 1963, 801.
[4] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964.
[5] F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press, New York, 1957.