Mass Spectrometric Metastable Peak Shapes

By M. C. FLOWERS

(*Department of Chemistry, University College, Gower Street, London*)†

A recent communication reported the 'metastable' decomposition of the doubly-charged benzene ion in an A.E.I. MS9 mass spectrometer.[1] Two metastable peaks were observed from the decomposition

$$C_6H_6^{2+} \longrightarrow CH_3^+ + C_5H_3^+.$$

Each peak was centred at the mass predicted by the equation

$$m^* = 2m_2^2/m_1 \qquad (1)$$

where m_1 and m_2 are the masses of the parent and product ions respectively and m^* the apparent

---

† Present address: Chemistry Department, The University, Southampton.

[1] W. Higgins and K. R. Jennings, *Chem. Comm.*, 1965, 99.

mass of the metastable peak. The shapes of the peaks were similar to that shown in Figure 1.

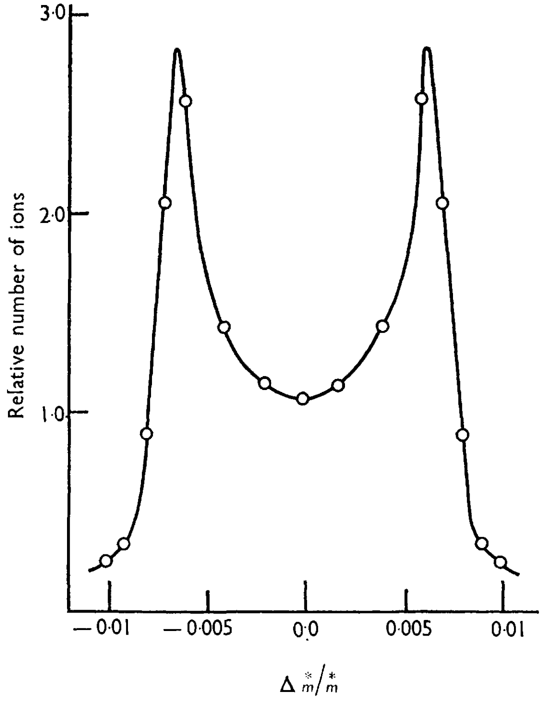

FIGURE 1. *Predicted metastable peak shape for reaction with* $\Delta v/v = 0{\cdot}0071$ (*estimated* $\Delta v/v$ *for peak* d, *Figure* 2) *abscissa*—$\Delta m^*/m^*$; *ordinate—relative number of ions*

Before the appearance of this work we had looked at the metastable peaks found in the mass spectra of various alkyl halides.[2] A large number of metastable peaks were identified. Pressure *versus* ion-current plots for all the largest peaks were linear over a ten-fold pressure range. This indicates that the decompositions are spontaneous and not collision-induced. No metastable peaks arising from doubly-charged ions were observed. None of the metastable peaks observed were of the shape found for the $C_6H_6^{2+}$ decomposition.

The trajectories of metastable ions after leaving the electrostatic analyser were calculated for decompositions occurring at different positions in the field-free region of a MS9 mass spectrometer. This gave

$$2\Delta m^*/m^* = \Delta v\{\cos\theta\,(2-\Delta v\cos\theta/v) \pm (2{\cdot}79-3{\cdot}95d/55)\sin\theta\}/v \tag{2}$$

where Δm^* is the shift from the expected value of m^* (calculated from equation 1) for the decomposition of an ion at a position d cm. from the start of the field-free region, v is the 'normal' velocity of the parent ion due to the accelerating voltage (V_a), Δv is the velocity increment resulting from any kinetic energy released in the decomposition of the parent ion, and θ is the angle to the main ion beam at which Δv acts, *i.e.* $\Delta v\cos\theta$ is the velocity vector adding to, or subtracting from, the overall velocity.

Figure 1 is a plot of the relative number of ions that would be collected at apparent mass m^*, calculated by determining the number of ways $\Delta m^*/m^*$ can be obtained for a given Δm^* increment with different values of d and θ, assuming the kinetic energy of decomposition was identical for each metastable decomposition. For the practical case with Δv having a range of values a reduction in the sharpness of the 'wings' of the curve would be expected. The distance between the maxima of the 'wings' is proportional to the most probable value of Δv. The shape of the calculated curve is in excellent agreement with that observed for the decomposition of the doubly-charged benzene ion. This would suggest that for this decomposition the kinetic energy released is sharply peaked at the value of 2·67 ev calculated by Higgins and

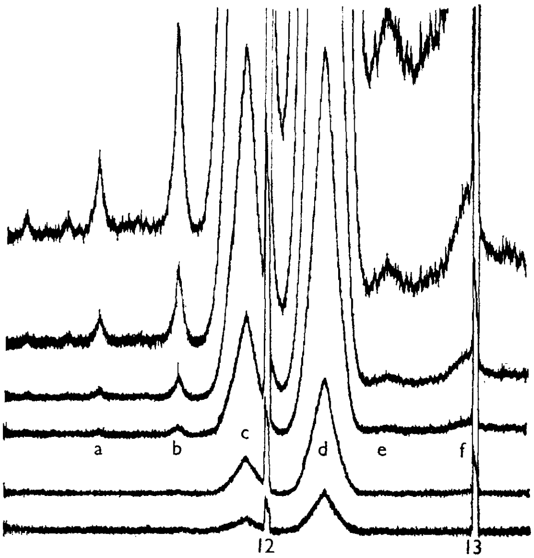

FIGURE 2. *Portion of the mass spectrum of ethyl chloride* (*mass* 12 *region*)

---

[2] Unpublished work.

Jennings.[1] The 'flat top' peaks of Beynon *et al.*[3] are presumably associated with decompositions involving a considerably larger range of kinetic energies.

Peak	Metastable Reaction	Measured m^*	Calculated
a	$C_2H_4{}^{37}Cl^+ \longrightarrow C_2H_3{}^+ + HCl$	11·238	11·239
b	$C_2H_4{}^{35}Cl^+ \longrightarrow C_2H_3{}^+ + HCl$	11·594	11·595
c	$C_2H_5{}^{37}Cl^+ \longrightarrow C_2H_4{}^+ + HCl$	11·909	11·908
d	$C_2H_5{}^{35}Cl^+ \longrightarrow C_2H_4{}^+ + HCl$	12·281	12·276
e	$^{12}C^{13}CH_5{}^{37}Cl^+ \longrightarrow C_2H_4{}^+ + HCl$	12·6	12·585
f	$^{12}C^{13}CH_5{}^{35}Cl^+ \longrightarrow C_2H_4{}^+ + HCl$	12·95	12·971

All observed metastable peaks in the mass spectra of the alkyl halides studied (ethyl chloride, bromide, and iodide; n- and iso-propyl chlorides; n-, s-, and t-butyl chlorides) had a single maximum, although the maxima may be sharp or quite rounded. Changing the accelerating voltage did broaden the peaks relative to 'normal' peaks but by less than the predicted $1/V_a{}^{\frac{1}{2}}$ relationship.

It was therefore concluded that, if the peak width of a metastable peak is due to kinetic energy of decomposition, the majority of decompositions, in the alkyl halides studied, occur with significantly less kinetic energy than 0·1 ev, unless there is a means of equilibrating this energy with other molecules. 0·1 ev is approximately equivalent to the value of Δv used in the calculation. The observation of double peaks from the decomposition of $C_6H_6{}^{2+}$ is evidence against significant collisional energy exchange. Such energy exchange may well be important in the source region and it is for this reason that the argument of Coggeshall,[4] which predicts that the relative peak widths of metastable and 'normal' peaks should be independent of v_a, may be invalidated.

It remains to be explained why the shapes and widths of various metastable peaks arising from the decomposition of singly-charged ions differ so distinctly (see Figure 2 for an example).

It has proved possible in favourable instances to measure the apparent mass of metastable peaks to 2 parts in 10,000. Excellent agreement with one half (singly-charged parent ion) the value calculated from equation 1 has been obtained in contrast to the consistently higher-than-predicted apparent mass found on single-focussing instruments[5] (see legend of Figure 2).

(*Received, April 8th,* 1965.)

---

[3] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

[4] N. D. Coggeshall, *J. Chem. Phys.*, 1962, **37**, 2167.

[5] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., 1960.