Metastable Transitions of the Doubly-Charged Benzene Ion

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IN the mass spectra of many organic substances, CH_3^+ ions formed with excess kinetic energy give rise to a satellite peak on the high mass side of the normal $m/e = 15$ peak. Such ions may be formed by the dissociation of a highly-excited singly-charged ion or more probably by the dissociation of a doubly-charged ion into a CH_3^+ ion and a further ion.[1]

If the process

$$m_1^{2+} \rightarrow CH_3^+ + (m_1 - 15)^+ \quad .. \quad (1)$$

is a significant source of CH_3^+ ions, metastable peaks at $550/m_1$ and at $2(m_1 - 15)^2/m_1$ might be observed under favourable conditions. Meyerson and van der Haar[2] have reported the occurrence of doubly- and triply-charged ions in the mass spectra of many aromatic compounds and cite a number of examples in which metastable peaks for the processes

$$m_1^{2+} \rightarrow m_2^{2+} + C_2H_2 \text{ or } C_2H_4 \quad .. \quad (2)$$

have been observed. No case of metastable peaks arising from process (1) has been reported, although metastable peaks due to the dissociation of CO_2^{2+} into CO^+ and O^+ have recently been observed.[3]

We now report the observation of the two metastable peaks which correspond to the process

$$C_6H_6^{2+} \rightarrow CH_3^+ + C_5H_3^+ \quad .. \quad (3)$$

in the mass spectrum of benzene obtained with 70 volt electrons, using an A.E.I. MS9 mass spectrometer. If no kinetic energy is released in the process, the metastable peaks are expected to be observed at $m/e = 5{\cdot}77$ and $101{\cdot}8$. The peaks actually observed are shown in the Figure, and it can be seen that the mid-points of the peaks correspond very closely to the expected values. The peak at $m/e = 5{\cdot}77$ was much less intense than that at $m/e = 101{\cdot}8$, presumably because the greater part of the kinetic energy released is imparted to the CH_3^+ ions. The pressure in the analyser tube could only be varied by a factor of 2·3 because of the low intensities of the metastable peaks but, over this pressure range, the ratio of the intensities of the $m/e = 78$ and $m/e = 101{\cdot}8$ peaks remained constant. This confirms that the decomposition process is truly unimolecular rather than collision-induced.

The width of metastable peaks has been interpreted in terms of the kinetic energy released in the decomposition of the original ion.[4] For the process

$$m_1^+ \rightarrow m_2^+ + (m_1 - m_2) \; .. \quad .. \quad (4)$$

the metastable peak resulting from the formation of m_2^+ will occur at a m/e value of m^* given by

$$m^* = \frac{m_2^2}{m_1}\left[1 \pm \left(\frac{\mu T}{Ve}\right)^{\frac{1}{2}}\right]^2,$$

where V is the accelerating voltage, e is the

[1] J. Olmsted, K. Street, and A. S. Newton, *J. Chem. Phys.*, 1964, **40**, 2114.
[2] S. Meyerson and R. W. van der Haar, *J. Chem. Phys.*, 1962, **37**, 2458.
[3] A. S. Newton and A. F. Sciamanna, *J. Chem. Phys.*, 1964, **40**, 718.
[4] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

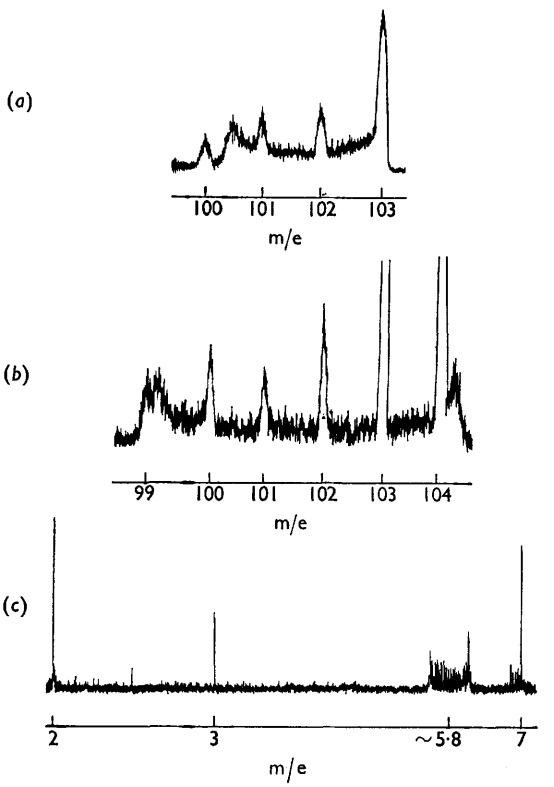
electronic charge, $\mu = (m_1 - m_2)/m_2$, and T is the total kinetic energy released in the decomposition. If the initial ion is doubly-charged however, its kinetic energy before decomposition is $2Ve$, and m^* is given by

$$m^* = \frac{2m_2^2}{m_1}\left[1 \pm \left(\frac{\mu T}{2Ve}\right)^{\frac{1}{2}}\right]^2.$$

The width of the metastable peak is therefore proportional to $1/V^{\frac{1}{2}}$. The $m/e = 101{\cdot}8$ peak was observed using accelerating voltages of 8 kv, 4 kv, and 2 kv, and extended over 2·6, 3·6, and 5·4 mass numbers, in agreement with this equation.

The kinetic energy released in the decomposition of the $C_6H_6^{2+}$ ion was calculated from the widths of the peak at $m/e = 101{\cdot}8$ obtained using accelerating voltages of 8 kv, 4 kv, and 2 kv, and from the width of the peak at $m/e = 5{\cdot}77$ obtained using an accelerating voltage of 8 kv only. An average value of $2{\cdot}67 \pm 0{\cdot}1$ ev was found, of which $2{\cdot}16 \pm 0{\cdot}08$ ev is the kinetic energy associated with the CH_3^+ ion. This is in very good agreement with the value of 2·27 ev recently obtained from the normal and satellite peaks of the CH_3^+ ion.[1]

These observations provide unequivocal evidence that in the case of benzene, at least, CH_3^+ ions formed with excess kinetic energy arise from the decomposition of the doubly-charged parent ion. Preliminary observations on the mass spectra of other aromatic compounds suggest that process (1) provides a general route for the formation of such ions.



(a) *Metastable peak arising from* $78^{2+} \rightarrow 63^+$, $V_a = 8$kv.
(b) *As in* (a), *but* $V_a = 2$kv.
(c) *Metastable peak arising from* $78^{2+} \rightarrow 15^+$, $V_a = 8$ kv, *with a trace of air added to provide the* N^{2+} *peak at* $m/e = 7$.

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