

distributions shown in Fig. 6 both for the low-voltage arc phase and the d. c. drawn arc very much resemble such SAHA distributions. Indeed, for the d. c. drawn arc discharge we were able to compute theoretical distributions which agree with the experi-

mental distributions far better than to a factor of two²³.

²³ J. FRANZEN and K. D. SCHUY, in preparation.

Acknowledgement

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Dissociation of Meta-stable Ions in Mass Spectrometers with Release of Internal Energy

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Certain of the "meta-stable peaks" in mass spectra are abnormally wide. This extra width is shown to be associated with release of kinetic energy during fragmentation. Methods are presented for measuring this energy release and values are given for various transitions in the spectra of aromatic nitro compounds.

Meta-stable ions are often detected in the mass spectra of organic compounds^{1, 2}. These ions may be detected if they dissociate near the entrance slit of the magnetic analyser in sector magnetic field mass spectrometers. If ions of original mass m_1 dissociate to produce ions of mass m_2 , a peak appears in the mass spectrum at a position m^* where

$$m^* \approx m_2^2/m_1. \quad (1)$$

These peaks are usually quite small and are much broader than peaks produced by normal stable ions. They often extend over a range of several mass numbers and usually have a shape resembling a GAUSSIAN distribution curve. Their maxima are usually sufficiently well defined to enable one to determine the values of m_1 and m_2 , from equation (1), for the ions involved in the transition. Occasionally, however, some of these "meta-stable peaks" are observed to be much broader than usual and to have a relatively flat top. Such peaks have been observed by NEWTON and SCIAMANNA corresponding to the meta-stable state of the doubly-charged carbon dioxide ion³. The length of this flat portion is found to vary inversely with the accelerating voltage. It is shown that the increased width of these peaks is caused by the release of a small amount of kinetic energy during the dissociation process.

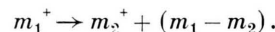
¹ J. A. HIPPLE and E. V. CONDON, Phys. Rev. **68**, 54 [1945].

² J. A. HIPPLE, R. E. FOX, and E. V. CONDON, Phys. Rev. **69**, 347 [1946].

Theoretical Considerations

In arriving at the approximate relationship of equation (1), HIPPLE and his co-workers² assumed that there was a negligible release of kinetic energy during the dissociation. In such a case the kinetic energy acquired by an ion of mass m_1 during the acceleration process is shared on dissociation between the two resulting particles in proportion to their masses.

Let us now consider an ion m_1^+ which is formed in the ionization chamber with zero kinetic energy and falls through a potential V_1 before dissociating into an ion m_2^+ and a neutral fragment $(m_1 - m_2)$, i. e.



At the dissociation let the velocities of m_1^+ , m_2^+ and $(m_1 - m_2)$ be v_a , v_b and v_c respectively. [If the total internal energy of m_2^+ and $(m_1 - m_2)$ remained the same as that of m_1 , then $v_a = v_b = v_c$, and we should say that there was no "kinetic energy of formation" of m_2^+ .] Further, let T represent the total decrease of internal energy. Then by the law of conservation of energy

$$T + \frac{1}{2} m_1 v_a^2 = \frac{1}{2} m_2 v_b^2 + \frac{1}{2} (m_1 - m_2) v_c^2. \quad (2)$$

By the law of conservation of momentum,

$$m_1 v_a = m_2 v_b + (m_1 - m_2) v_c. \quad (3)$$

³ A. S. NEWTON and A. F. SCIAMANNA, J. Chem. Phys. **40**, 718 [1964].



Let e be the electronic charge and v be the velocity of m_2^+ when it reaches the end of the accelerating region (potential = V).

$$\begin{aligned} \text{Then, } \frac{1}{2} m_2 v^2 &= \frac{1}{2} m_2 v_b^2 + e(V - V_1) \\ &= \frac{1}{2} m_1 v_a^2 \frac{m_2 v_b^2}{m_1 v_a^2} + e(V - V_1) \\ &= e V_1 \left(\frac{m_2}{m_1} \right) \left(\frac{v_b}{v_a} \right)^2 + e(V - V_1). \end{aligned} \quad (4)$$

Eliminating v_c between equations (2) and (3) and putting $v_b/v_a = x$, we have

$$x^2 - 2x + \left[\frac{m_1}{m_2} - \frac{m_1 - m_2}{m_2} \left(1 + \frac{T}{e V_1} \right) \right] = 0. \quad (5)$$

Putting $(m_1 - m_2)/m_2 = \mu$, we have

$$x^2 - 2x + (1 - \mu T/e V_1) = 0. \quad (6)$$

For the case where ions formed in meta-stable transitions are most readily detected, dissociation occurs after the ion m_1^+ has fallen through the entire accelerating voltage V (i. e. $V_1 = V$) and we have from equation (6)

$$x = v_b/v_a = 1 \pm \sqrt{\mu T/e V}. \quad (7)$$

From equation (3),

$$\frac{v_c}{v_a} = \frac{m_1 - (m_2 v_b/v_a)}{m_1 - m_2} = \frac{m_1 - m_2 [1 \pm \sqrt{\mu T/e V}]}{m_1 - m_2}. \quad (8)$$

Thus, if

$$\frac{v_b}{v_a} = (1 + \sqrt{\mu T/e V}) \text{ which } > 1, \text{ then } \frac{v_c}{v_a} < 1, \quad (9)$$

and if

$$\frac{v_b}{v_a} = (1 - \sqrt{\mu T/e V}) \text{ which } < 1, \text{ then } \frac{v_c}{v_a} > 1. \quad (10)$$

It is thus seen that the effect of a release of internal energy during a meta-stable transition is to cause the ion of mass m_2 to be given a velocity increment additional to that of the original ion of mass m_1 . The component of this velocity increment along the ion path, v_x say, is such that

$$-\sqrt{\mu T/e V} \leq v_x \leq +\sqrt{\mu T/e V}.$$

If we put $V = V_1$ in equation (4), we have

$$\frac{1}{2} m_2 v^2 = e V (m_2/m_1) (v_b/v_a)^2. \quad (11)$$

Now the radius of curvature, r , of the ion path in the magnetic field, H , is given by

$$r = m_2 v / H e. \quad (12)$$

Eliminating v between equations (11) and (12), we have

$$r = (\sqrt{2 e V} / H e) m^*$$

where m^* , the equivalent mass of the meta-stable ion, is given by

$$m^* = (m_2^2/m_1) (v_b/v_a)^2. \quad (13)$$

If we take the value of (v_b/v_a) from equation (7) and substitute it in (13), we have

$$\begin{aligned} m^* &= (m_2^2/m_1) [1 \pm \sqrt{\mu T/e V}]^2 \\ &= (m_2^2/m_1) [1 \pm 2\sqrt{\mu T/e V} + \mu T/e V]. \end{aligned} \quad (14)$$

Then if d is the width of the "meta-stable peak" in atomic mass units as shown in Fig. 1 (ignoring the "skirts" which are present even when the peak does not have a flat top), we have

$$d = (4 m_2^2/m_1) \sqrt{\mu T/e V}. \quad (15)$$

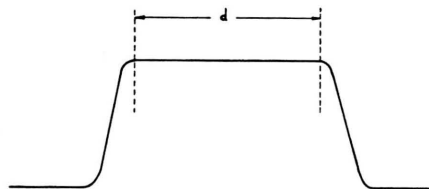
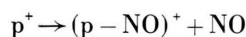


Fig. 1. "Meta-stable peak" with flat top.

Experimental

The meta-stable transition



where p^+ represents the parent ion, is observed in the mass spectra of the three isomeric nitrophenols at mass ⁴ 85.5. The peaks corresponding to the transitions in the ortho and para isomers are very similar in shape; the peaks in the spectrum of o-nitrophenol are shown in Fig. 2 recorded at four different accelerating voltages (2 kV, 4 kV, 6 kV and 8 kV). The "meta-stable peak" in the spectrum of m-nitrophenol has the usual shape without a plateau, and is shown in Fig. 3. The portions of the spectra shown in Figs. 2 and 3 were recorded on an A.E.I. mass spectrometer type MS 9.

In order to obtain a measure of the energy released during this meta-stable transition a potential was

⁴ J. H. BEYNON, R. A. SAUNDERS, and A. E. WILLIAMS, Ind. Chim. Belge **29**, 311 [1964].

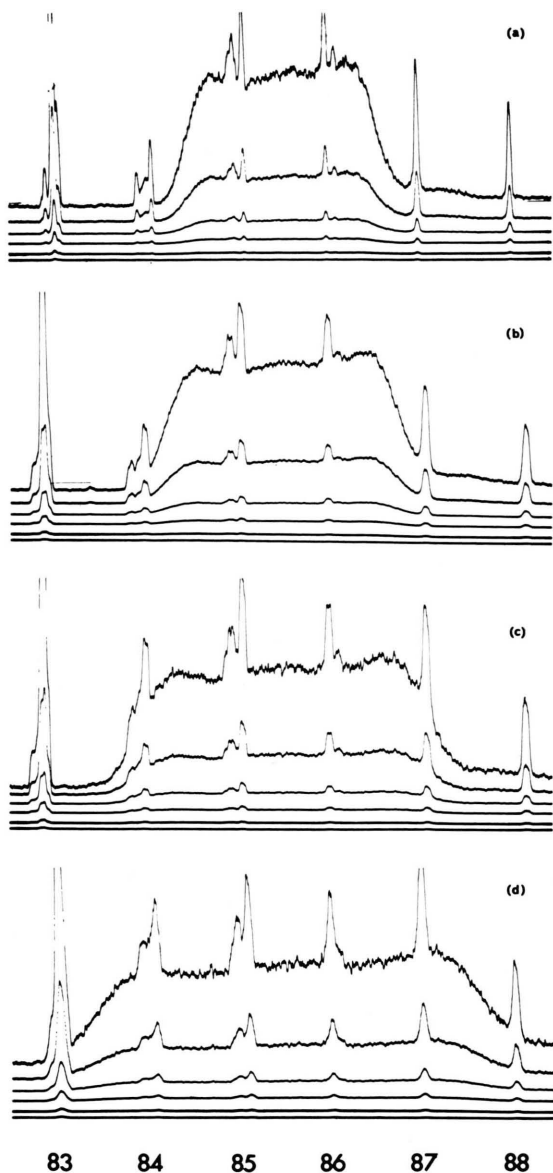


Fig. 2. "Meta-stable peak" in the spectrum of *o*-nitrophenol recorded at accelerating voltages of (a) 8 kV, (b) 6 kV, (c) 4 kV, and (d) 2 kV.

applied to an electrode placed in front of the ion collector. These measurements were carried out using a mass spectrometer of the NIER, single-focussing, 90° sector magnetic field design⁵. It could not be performed on the MS 9 mass spectrometer because it does not have a suitable electrode to which the retarding potential can be applied. However, the

⁵ A. O. NIER, *Rev. Sci. Instrum.* **11**, 212 [1940].

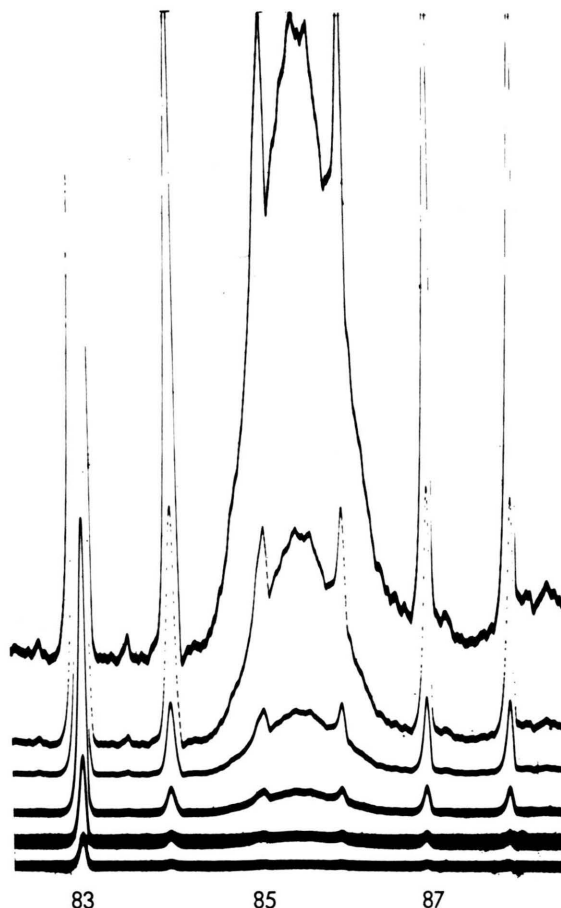


Fig. 3. "Meta-stable peak" in the spectrum of *m*-nitrophenol recorded at an accelerating voltage of 8 kV.

"meta-stable peak" shape was very similar in the two instruments when operated at the same accelerating voltage. By adjusting this retarding potential it was found that at a certain value the low mass end of the "meta-stable peak" began to disappear. Increasing the potential caused more and more of the peak to disappear until, finally, the whole peak vanished. The potentials at which the peak began to disappear and at which all trace of it had vanished were found to be in the ranges 780–785 volts and 825–830 volts, for the peak in the spectrum of *o*-nitrophenol, when the accelerating voltage was 1020 volts.

Discussion of Results

The retarding potential range between which the peak began to disappear and at which it finally vanished was measured as (45 ± 5) volts. If the

dissociation occurs when $V = V_1$, using the same notation as above, then this potential represents the variation in energy that the dissociating ions possess, i. e. the variation in $\frac{1}{2} m_2 v_b^2$. From equation (7), we have

$$v_b^2 = v_a^2 [1 \pm \sqrt{\mu T/eV}]^2.$$

Therefore

$$\frac{1}{2} m_2 v_b^2 = \frac{1}{2} m_2 v_a^2 (1 + \mu T/eV \pm 2\sqrt{\mu T/eV}).$$

Therefore

$$\begin{aligned} \text{Spread in } \frac{1}{2} m_2 v_b^2 &= 45 \text{ eV (approx.)} \\ &= (m_2/m_1) \cdot \frac{1}{2} m_1 v_a^2 \cdot 4\sqrt{\mu T/eV}. \end{aligned}$$

Substituting the values of m_1 , m_2 , μ , $\frac{1}{2} m_1 v_a^2$ and eV for the meta-stable transition in o-nitrophenol, i. e. $m_1 = 139$, $m_2 = 109$, $\frac{1}{2} m_1 v_a^2 = eV = 1020$ electron volts we have

$$T = 0.74 \text{ electron volts.}$$

If we consider the uncertainty in measuring the 45 eV energy spread, this may be written $T = (0.74 \pm 0.16) \text{ eV}$.

If no energy were released during the transition, the energy required to repel the ion m_2^+ would be given by

$$(m_2/m_1) eV$$

which in the present circumstances is equal to

$$(109/139) \times 1020 = 800 \text{ electron volts.}$$

It is seen that this value lies almost exactly in the middle of the range of energies that the ions actually possessed.

As an alternative, a value of T may be calculated from equation (15) using data derived from the widths of the peaks recorded in Fig. 2 at different accelerating voltages. We have the results listed in Table 1.

It can be seen immediately that each of these results is well within the limits of the value obtained

Accelerating Voltages [kV]	d [u]	$T = \left(\frac{d^2 m_1^2 eV}{4 \cdot 4 m_2^4} \right)$ [eV]
8.0	1.7	0.76
6.0	2.0	0.78
4.0	2.5	0.75
2.0	3.5	0.76

Table 1.

from the retarding method. It would appear then that by measurement of peak widths we have a reasonably accurate method of measuring the energy liberated during meta-stable transitions. A search has been made of the spectra of some further aromatic nitro compounds⁴, and several other meta-stable transitions were found that involved a release of kinetic energy. These transitions are listed in Table 2.

Two interesting points emerge from a study of this table: (a) the meta-stable transition involving the release of energy does not occur in the meta isomer of the nitroanilines but only in the cases of the ortho and para isomers. (This is similar to the behaviour of the nitrophenols). (b) The neutral fragment in each of the above cases is a stable molecule either NO or CO.

Conclusions

Peaks with flat tops, corresponding to meta-stable ions, are often observed in the mass spectra of organic compounds. These are shown to correspond to transitions in which a small quantity of energy is liberated during the dissociation. From measurements of the width of these peaks and a knowledge of the operating conditions of the mass spectrometer, it is possible to obtain a measure of this energy. Measurements have been carried out on the retarding potentials necessary to suppress a "meta-stable peak" and the results of these confirm the data from the former measurements.

Compound	Meta-stable ion	m_1	m_2	Neutral fragment	d [u]	T [eV]
o-nitrophenol	(p - NO) ⁺	109	81	CO	0.7	0.25
p-nitrophenol	(p - NO) ⁺	109	81	CO	0.7	0.25
o-nitroaniline	p ⁺	138	108	NO	1.8	0.81
p-nitroaniline	p ⁺	138	108	NO	1.8	0.81
3-nitro-p-toluidine	p ⁺	152	122	NO	2.0	0.85
1-nitronaphthalene	p ⁺	173	145	CO	1.0	0.18

Table 2. Meta-stable transitions in the spectra of some aromatic nitro compounds involving the release of kinetic energy.