Detection of Meta-Stable Peaks by Mattauch-Herzog Mass Spectrometer*

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Daughter ions from metastable ions were detected on photo plate in Mattauch-Herzog geometry by the gradual shift of accelerating voltage. By this technique the most possible fragmentations of 3, 4-epoxymenthane, *l*-menthone and piperitol were presented.

The observation of meta-stable ions is very important in the study of fragmentation of mass spectra. In Mattauch-Herzog geometry, however, a daughter ion from a meta-stable ion produced between the object slit and the electrostatic field has insufficient kinetic energy and so cannot pass through the electrostatic field¹⁾; therefore none of these daughter ions can be detected on the photo plate.

In the case of a decomposition of $m_1^+ \rightarrow m_2^+ + (m_1 - m_2)$ which shows meta-stable ion formation, the energy of the ion m_1^+ , at the accelerating voltage V , is distributed as follows:

$$eV \rightarrow \frac{m_2}{m_1} eV + \frac{m_1 - m_2}{m_1} eV \quad (1)$$

The ion m_2^+ cannot pass the electrostatic field because it has an energy of only $m_2/m_1 \cdot eV$. So, if the accelerating voltage is increased to $V' = m_1/m_2 \cdot V$, the energy of ion m_2^+ produced between the object slit and the electrostatic field will be as follows:

$$\frac{m_1}{m_2} eV' = \frac{m_2}{m_1} e \left(\left(\frac{m_1}{m_2} \right) V \right) = eV \quad (2)$$

This energy of eV for the ion m_2^+ (produced between the object slit and the electrostatic field), in the case of accelerating voltage V' , is the same as that of m_1^+ at an accelerating voltage V . In other words, the ion m_2^+ (produced between the object slit and the electrostatic field) can be detected at the same place as the ion m_2^+ (produced in the ionisation chamber just as m_1^+ , at the accelerating voltage of V) by varying the accelerating voltage from V to V' . (Fig. 1)

Fig. 2 shows the actual example of noteworthy daughter ions from meta-stable ions which have been detected in 3, 4-epoxymenthane^{2,3)} by this method. The observed and calculated daughter ions from meta-stable ions and possible break-down reactions deduced from them are shown in Table I.

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Fig. 1. Daughter ions from meta-stable ions detected on photo plate by the shift of accelerating voltage ($V \rightarrow V'$)
 (a) a daughter ion from meta-stable ion presenting the transition of $m_1^+ \rightarrow m_2^+$ (b) $m_2^+ \rightarrow m_i^+$ (c) $m_1^+ \rightarrow m_i^+$
 (d) $m_2^+ \rightarrow m_j^+$ (e) $m_i^+ \rightarrow m_j^+$

Furthermore the exact mass measurements for several prominent peaks of this compound are carried out, and the values thereof are shown in Table II. These values indicate that the ions at m/e 71 and 83 in 3,4-epoxymenthane are contributed by two different ions: the former $C_5H_{11}^+$ and $C_4H_7O^+$, and the latter $C_6H_{11}^+$ and $C_5H_7O^+$, respectively.

Fig. 2. Daughter ions from meta-stable ions of 3,4-epoxymenthane detected on photo plate by the shift of accelerating voltage (3.5 KV $\rightarrow$ 7.6 KV)

Table I. Possible break-down reactions of 3,4-epoxymenthane deduced from the daughter ions from meta-stable ions (See Fig. 2)

obsd.		calcd.		transition
V'/V	V'	V'/V	V'	
1.11	3.88	1.11	3.88	$154^+ \rightarrow 139^+ + 15$

1.26	4.41	1.23	4.31	$154^+ \rightarrow 125^+ + 29$
1.40	4.90	1.39	4.86	$154^+ \rightarrow 111^+ + 43$
1.58	5.53	1.56	5.46	$154^+ \rightarrow 99^+ + 55$
2.17	7.59	2.17	7.59	$154^+ \rightarrow 71^+ + 83$

Table II. Exact mass measurements of 3,4-epoxymenthane

	obsd.	calcd.	composition
m/e 99	.081	.084	$C_6H_{11}O$
m/e 83	.086	.085	C_6H_{11}
	.050	.047	C_5H_7O
m/e 71	.086	.083	C_5H_{11}
	.050	.048	C_4H_7O
m/e 43	.055	.055	C_3H_7

Mass values are based on $C^{12}=12.000$

Thus the combination of the detection of daughter ions from meta-stable ions by above-mentioned technique and the ordinary exact mass measurements suggests the following fragmentation process for 3,4-epoxymenthane. (Fig. 3)

The transition marked with * is deduced only by the exact mass measurements of the ions $C_5H_{11}^+$ and $C_5H_7O^+$.

Fig. 3. Fragmentation of 3,4-epoxymenthane established by the detection of daughter ions from meta-stable ions and the exact mass measurements

Furthermore, the fragmentation pathways are suggested as follows for *l*-menthone and piperitol by the technique to detect daughter ions from meta-stable ions. (Fig. 4 and 5)

Fig. 4. Fragmentation process of *l*-menthone

- Transition in which the meta-stable ion has been observed.
- Another transition is also conceivable because the daughter ion has not been displayed as a doublet, despite the fact that the meta-stable ion has been observed.
- *** Number of asterisk corresponds to intensity of ions.

Experiment

The mass spectra were measured with JMS-OISG mass spectrometer with ionizing voltage 75 eV, ionizing current 150 μ A, ion accelerating voltage 3.5 kV→8 kV, exposed time 1 min., and the temperature of ion source 130→140°C.

Fig. 5. Fragmentation process of piperitol

- Transition in which the meta-stable ion has been observed.
- - -→ Another transition is also conceivable because the daughter ion has not been displayed as a doublet, despite the fact that the meta-stable ion has been observed.
- *** Number of asterisk corresponds to intensity of ions.

3, 4-Epoxymenthane was synthesized by the epoxidation of 3-menthene.³⁾ *l*-Menthone and piperitol are commercially available.

Literatures

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