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 field\(^1\); 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:

\[
eV = \frac{m_2}{m_1} \cdot eV + \frac{m_1 - m_2}{m_1} \cdot eV
\]

(1)

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

\[
\frac{m_1}{m_2} \cdot eV' = \frac{m_2}{m_1} \cdot e\left(\frac{m_1}{m_2}\right) V = eV
\]

(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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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 C₅H₁₁⁺ and C₄H₇O⁺, and the latter C₆H₁₁⁺ and C₅H₇O⁺, respectively.

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

<table>
<thead>
<tr>
<th>obsd.</th>
<th>calcd.</th>
<th>transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>V'/V</td>
<td>V'</td>
<td>V'/V</td>
</tr>
<tr>
<td>1.11</td>
<td>3.88</td>
<td>1.11</td>
</tr>
</tbody>
</table>
Table II. Exact mass measurements of 3,4-epoxymenthane

<table>
<thead>
<tr>
<th>m/e</th>
<th>obsd.</th>
<th>calcd.</th>
<th>composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>0.081</td>
<td>0.084</td>
<td>C₆H₁₁O</td>
</tr>
<tr>
<td>83</td>
<td>0.086</td>
<td>0.085</td>
<td>C₆H₁₁</td>
</tr>
<tr>
<td>71</td>
<td>0.086</td>
<td>0.083</td>
<td>C₅H₁₁</td>
</tr>
<tr>
<td>43</td>
<td>0.055</td>
<td>0.055</td>
<td>C₄H₇O</td>
</tr>
</tbody>
</table>

Mass values are based on C₁₂=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 C₅H₁₁⁺ and C₅H₇O⁺.

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)

Experiment

The mass spectra were measured with JMS-OISG mass spectrometer with ionizing voltage 75 eV, ionizing current 150 µA, ion accelerating voltage 3.5 kV–8 kV, exposed time 1 min., and the temperature of ion source 130–140°C.
3, 4-Epoxymenthane was synthesized by the epoxidation of 3-menthene.\textsuperscript{3)} \(l\)-Menthone and piperitol are commercially available.

**Literatures**