Bull. Chem. Soc. Jpn., ***60,*** *1881—1886 (1987)*

In-beam EIMS and Molecular SIMS of Quaternary Ammonium Chlorides of Benzylamine Derivatives

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(Received December 1, 1986)

The in-beam EIMS and SIMS of three quaternary ammonium chlorides of benzylamine derivatives have been examined, and their fragmentation processes have been clarified by means of the B/E costant and B^2/E constant linked scanning techniques. The B/E constant linked scan of the benzyltrimethylammonium ion (m/z 150) in the in-beam EIMS indicated a fragment ion at m/z 126 as a daughter ion. A substitution reaction between the m/z 150 ion and a chlorine atom in the first field free region is proposed. The characteristics of SIMS of those compounds were demonstrated in comparison with those of EIMS and the fragmentation processes of the salts upon Xe^+ bombardment were established based on the linked scanning techniques.

In order to test the suitability of the unified model for soft ionization proposed by Vestal¹⁾ we have examined the matrix effects on the in-beam Electron Ionization Mass Spectrometry (EIMS) of quaternary ammonium salts.²⁾ During the course of this investigation we tried to clarify the fragmentation processes of those quaternary ammonium salts upon electron ionization (in-beam EI) and upon Xe^+ bombardment [molecular Secondary Ion Mass Spectrometry (SIMS)] on the basis of the B/E constant and the B^2/E constant linked scanning mass spectra. We found that the linked scans indicated the unusual behavior of the benzyltrimethylammonium ion in the in-beam EIMS. This article deals with the fragmentation processes of three quaternary ammonium salts of benzylamine derivatives upon electron impact and upon Xe^+ ion bombardment.

Experimental

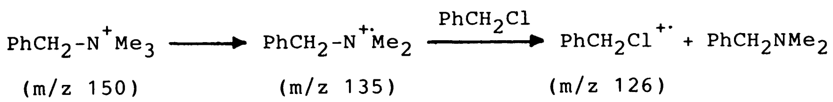
The in-beam EIMS were taken with a Hitachi RMU-6 and a Hitachi M-80 spectrometers. The in-beam EIMS were obtaind with an electron energy of 70 eV (80 μA) and at a source temperature of 200 °C. Samples were introduced into the in-beam system with probe heating at 300 °C. The molecular SIMS were performed with a double focusing Hitachi M-80B spectrometer. Xenon was used as the primary ion source and was accelerated to 8 kV. In these studies the samples dissolved in glycerol matrix were applied to the stainless steel target for the molecular SIMS. The B/E constant and the B^2/E constant linked scanning techniques were applied to each spectrum.

Benzyltrimethylammonium chloride (**1**), benzyltriethylammonium chloride (**2**) and benzyldimethylphenylammonium chloride (**3**) were purchased from Tokyo Kasei Co. and used without further purification.

Results and Discussion

1. In-beam EIMS. Figure 1a shows the in-beam EIMS of **1**. The intact quaternary ammonium ion is observed at m/z 150 (C^+), and the fragment ions at m/z 135 (C^+–Me), 126 ($PhCH_2Cl^+$), 91 ($C_7H_7^+$) and 58 ($CH_2{=}NMe_2$) are also abundant. The fragment ion at m/z 126 must contain chlorine atom because of the relative abundance of the isotope peak at m/z 128, and must correspond to the molecular ion of benzyl chloride. This ion seems to come from a thermal SN-2 type reaction under the in-beam conditions producing benzyl chloride molecules followed by electron ionization. In order to confirm the origins of the ion at m/z 126 as well as the other fragment ions, we examined the B/E constant linked scan of the C^+ at m/z 150. Figure 2a represents its spectrum. As expected, the ions at m/z 135, 134, 91, and 58 are shown to be derived from C^+ in accorded with the general fragmentation of quaternary ammonium salts in the in-beam EI.³⁻⁵⁾

Surprisingly, this linked scan also indicates that the ion at m/z 126 is a daughter ion of C^+. The same technique showed that the m/z 126 ion is the parent ion of the m/z 91 ion, consistant with the structure of benzyl chloride. To ascertain the origin of the m/z 126 ion, we examined the B^2/E constant linked scan and found abroad weak peak around m/z 135 as the parent ion. Figure 3a shows the linked scanning spectrum. However, the B/E constant linked scan of m/z 135 ion did not show any peaks at m/z 126, but strong praks at m/z 91 and 58 as shown in Fig. 3b. If the ion at m/z 135 is the parent ion of m/z 126 ion, the fragmentation processes involving a charge exchange mechanism as shown in Scheme 1 may account for this unusual



$$\underset{(m/z\ 150)}{PhCH_2\text{-}\overset{+}{N}Me_3} \longrightarrow \underset{(m/z\ 135)}{PhCH_2\text{-}\overset{+\cdot}{N}Me_2} \xrightarrow{PhCH_2Cl} \underset{(m/z\ 126)}{PhCH_2Cl^{+\cdot}} + PhCH_2NMe_2$$

Scheme 1.

transition. However, it is hard to rationalize that collision between the m/z 135 ion and benzyl chloride transfers not only an electron but also the kinetic energy to each other.

The second possibility is a collision between the C^+ and a chlorine atom in the first field free region in accordance with the result of the B/E constant linked scan. Scheme 2 shows an example of the reaction. Since, under the in-beam conditions, large amounts of neutral species are vaporized in the ion source,[1] many

$$\underset{(m/z\ 150)}{PhCH_2\text{-}\overset{+}{N}Me_3} \xrightarrow{Cl} \underset{(m/z\ 126)}{PhCH_2Cl^{+\cdot}} + NMe_3$$

Scheme 2.

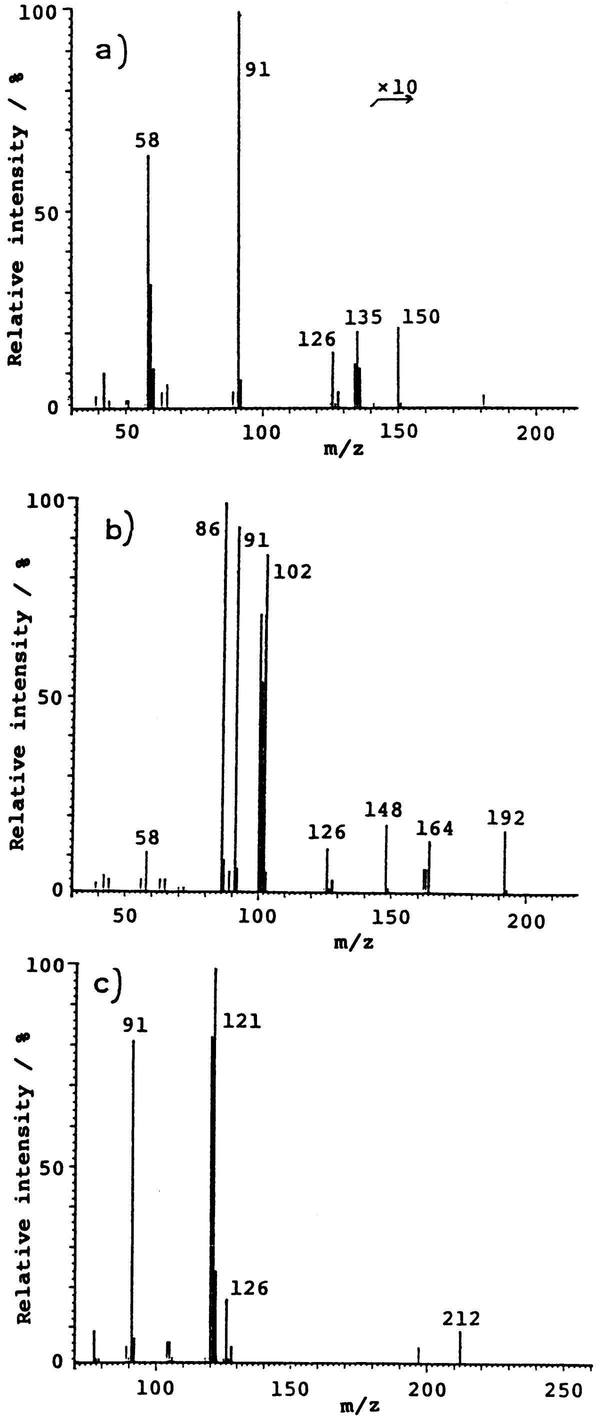


Fig. 1. In-beam EIMS of three quaternary ammonium chlorides of benzylamine derivatives.
a): **1**, b): **2**, c): **3**.

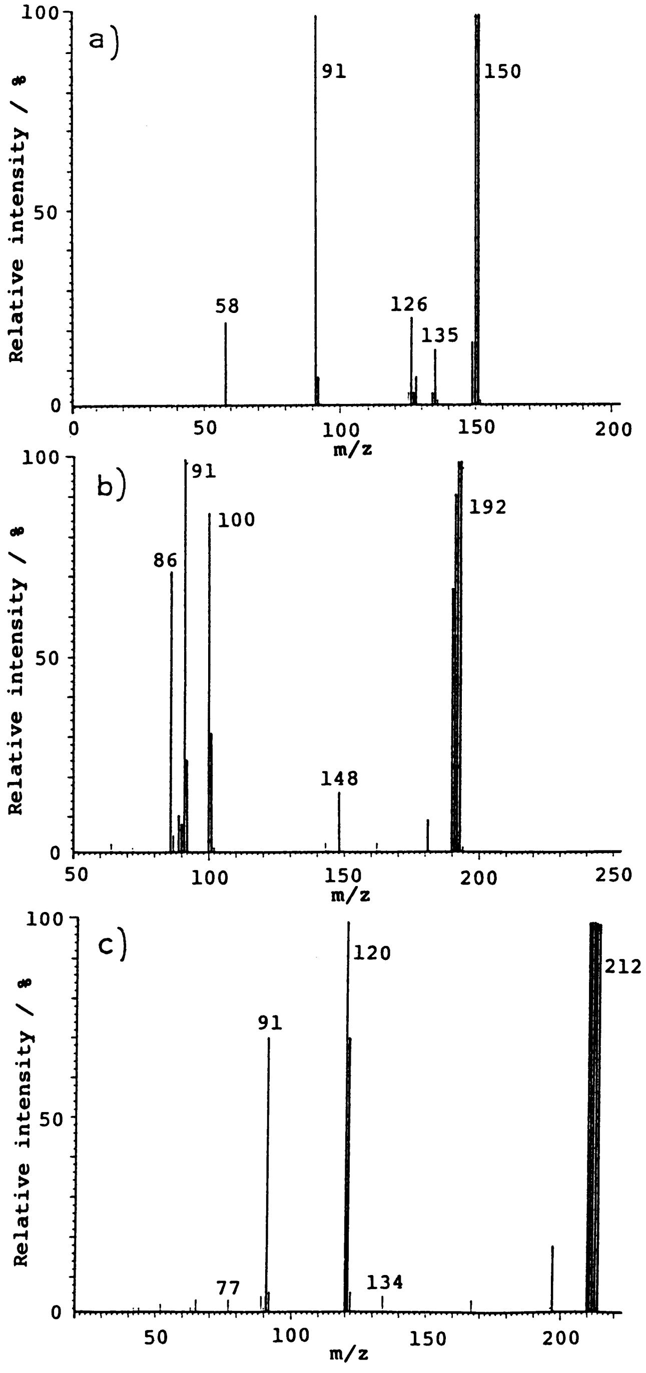


Fig. 2. B/E constant linked scanning spectra of C^+ in the in-beam EIMS.
a): **1**, m/z 150, b): **2**, m/z 192, c): **3**, m/z 212.

ion-molecular reactions are also expected to happen in the first field free region. At this stage, the processes shown in Scheme 2 are reasonably conceivable. The third possibility is the so-called "artifact peak" discussed by Beynon et al.[6] Suppose that there are a parent ion m_1, a daughter ion m_2, and another ion m_3 formed in the source and fully accelerated, which then decomposes to give an ion m_4. The only necessary condition for the detection of m_4 in the B/E constant linked scanning spectra is as follows;

$$m_3 = m_2^2/m_1, \quad m_4 = m_2 m_3/m_1.$$

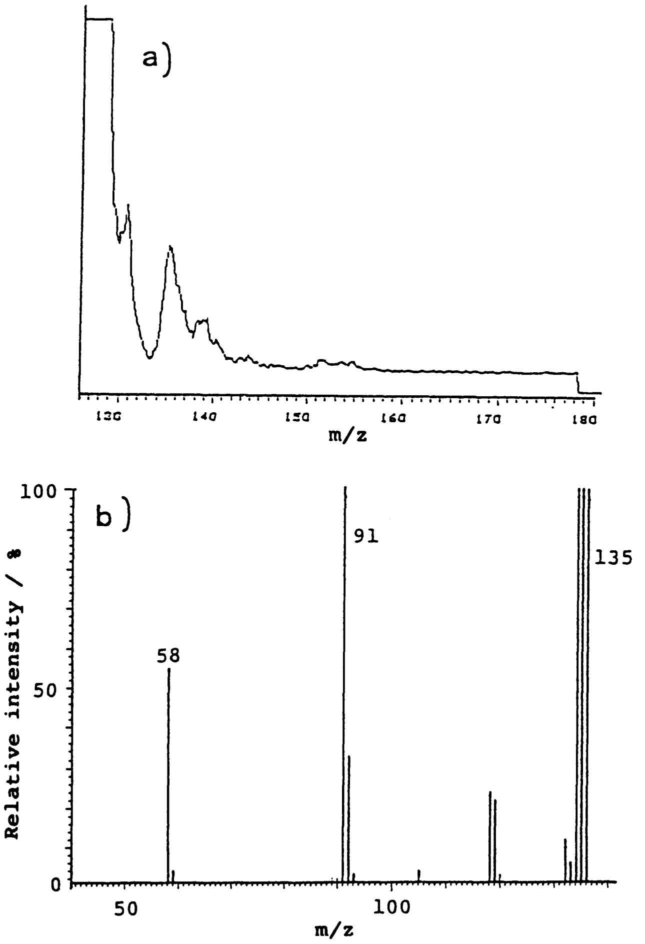
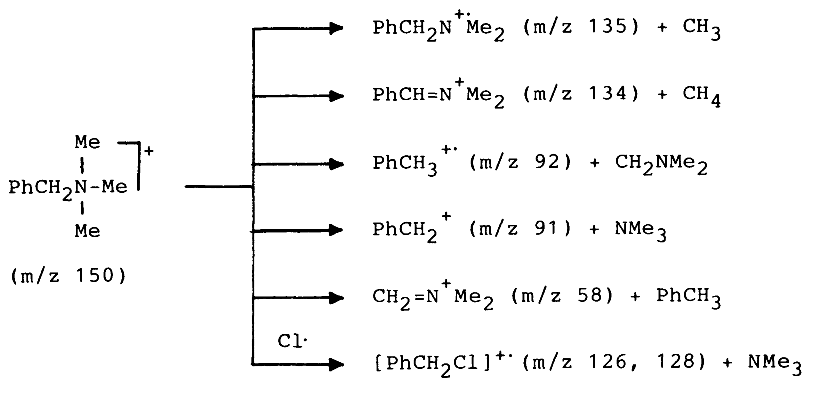


Fig. 3. a) B^2/E constant linked scanning spectrum of m/z 126 ion, and b) B/E constant linked scannining spectrum of m/z 135 ion of the in-beam EI spectrum of **1**.

In our case, $m_1=150$ and $m_2=126$. Then substituting these values for the equations, we obtained $m_3=106$, $m_4=89$. However, we found no peak corresponding to those ions. Thus the possibility of the artifact peak is excluded. The fragmentation processes of the in-beam EIMS of **1** are summarized in Scheme 3.

The in-beam EIMS of **2** and **3** are shown in Figs. 1b and 1c, respectively. The B/E constant linked scanning spectra of each C^+ at m/z 192 or 212 are shown in Figs. 2b and 2c, respectively. Figures 2b and 2c also show the presence of benzyl chloride ion at m/z 126 and 128, but the linked scanning spectra do not. Thus we conclude that the unusual behavior of **1** in the B/E constant linked scan is not general, but very specific. The fragmentation processes of **2** and **3** upon in-beam EI are summarized in Scheme 4 and 5, respectively.

2. **SIMS.** Figures 4a—c show the glycerol assisted SIMS os **1**, **2**, and **3**, respectively. The major fragment ions from the quaternary ammonium ion (C^+) are similar to those of the in-beam EIMS. Several major differences between the SIMS and the in-beam EIMS are also noticed: i.e., (1) the cluster ions of $(R_4N^+)_2Cl$ are observed in the SIMS but not in the in-beam EIMS, (2) the ions at m/z 126 and 128 due to the benzyl chloride molecular ion observed in the in-beam EIMS are absent in the SIMS, (3) the fragment ions having not only even electrons but also odd electrons are often observed in the in-beam EIMS but the ions carrying only even electrons are observed in the SIMS. For instance, in the SIMS spectrum of **2** (Fig. 4b), the peaks at m/z 163, 102, and 101 observed in the in-beam EIMS are absent, but the peaks at m/z 192, 162, 148, 100, 91, and 86 are commonly observed in both spectra. Similarly, in the case of **3**, the peaks at m/z 212, 121,



Scheme 3.

and 91 are common in both spectra, but strong peak at *m/z* 120 observed in the in-beam EIMS is absent in the SIMS.

The *B/E* constant and B^2/E constant linked scanning spectra of major peaks of **1** are shown in Figs. 5 and 6, respectively. On the basis of these spectra, the fragment processes of **1** are summarized as shown in Scheme 6: i.e., the cluster ion at *m/z* 335 forms only a C^+ ion at *m/z* 150, which decomposes to yield ions at *m/z* 134, 91, and 58 and the ion at *m/z* 134 also produces the *m/z* 91 ion.

Similarly, the fragmentation processes of **2** and **3** in the SIMS are also summarized in Scheme 7 and 8, respectively.

In conclusion we have clarified the characteristics of the in-beam EIMS and the SIMS of three quaternary

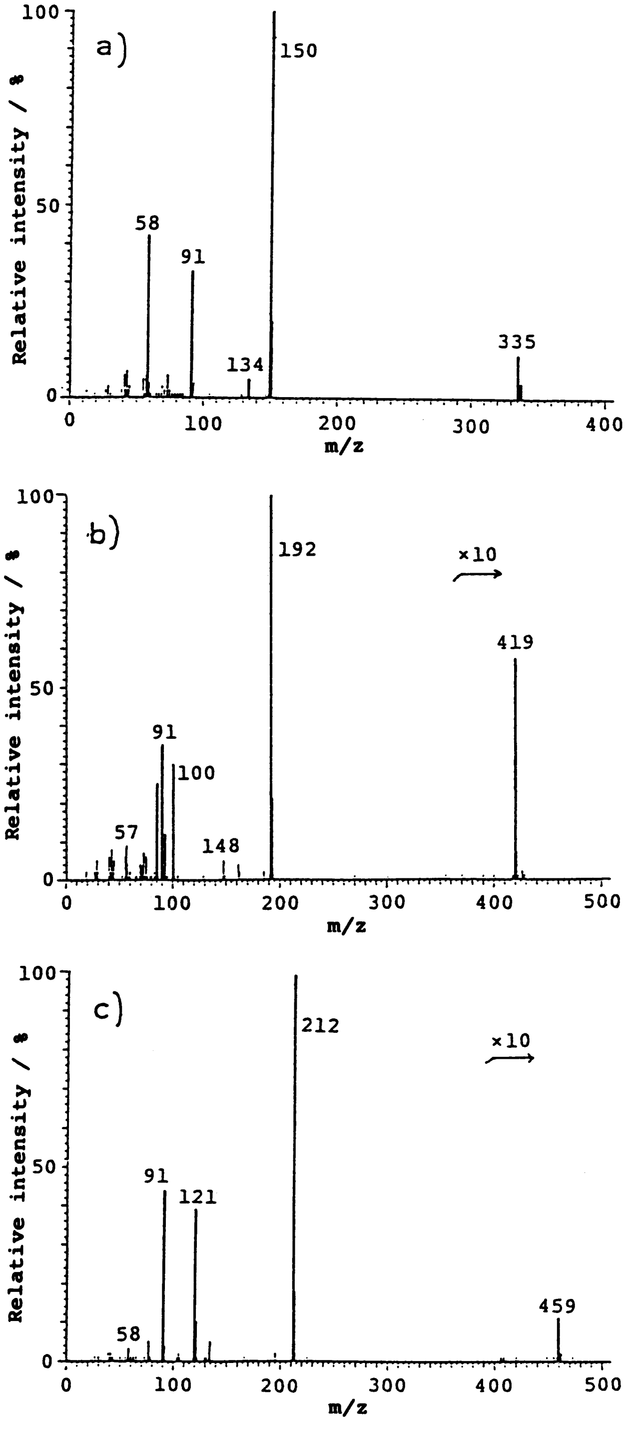


Fig. 4. Molecular SIMS (glycerol assisted) of a) **1**, b) **2**, and c) **3**.

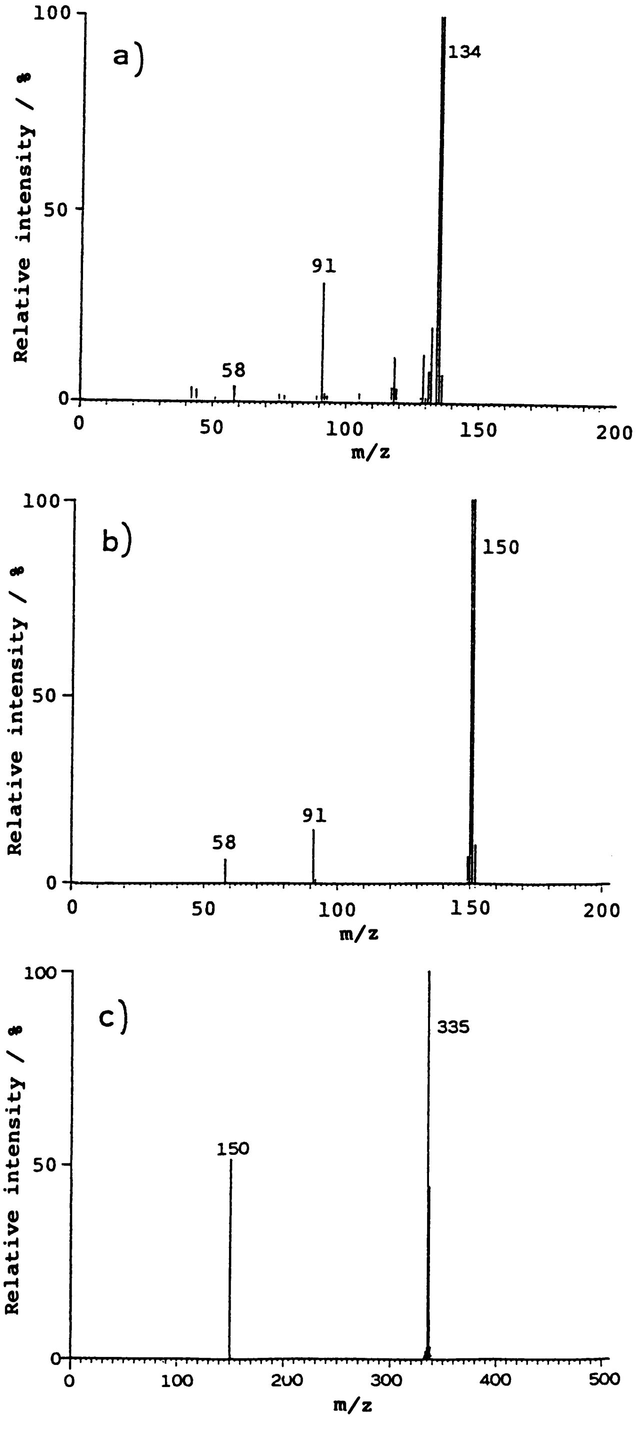
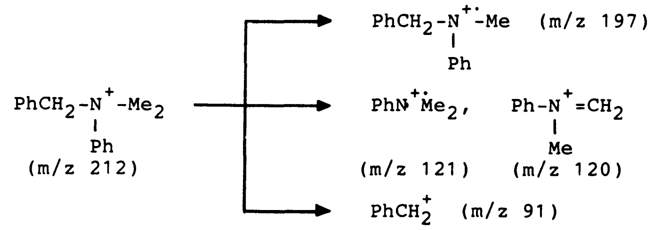
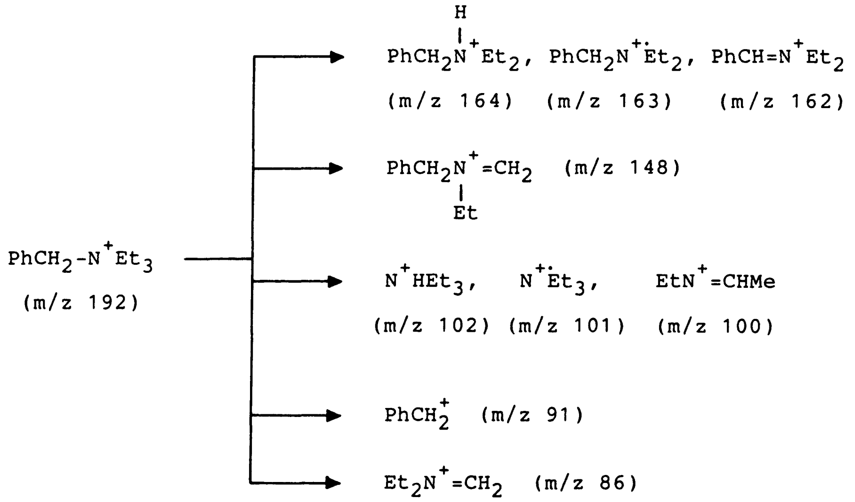


Fig. 5. *B/E* constant linked scanning spectra of C^+ in the SIMS: a) *m/z* 134; b) *m/z* 150; c) *m/z* 335.

ammonium chlorides of benzylamine derivatives, and indicated the unusual behavior of benzyltrimethylammonium chloride in the *B/E* constant linked scanning spectra. Care must be taken for the interpretation of the *B/E* constant linked scanning spectra, considering the possibilities of the ion-molecular reactions in the first field free region in the in-beam EIMS.



Scheme 5.



Scheme 4.

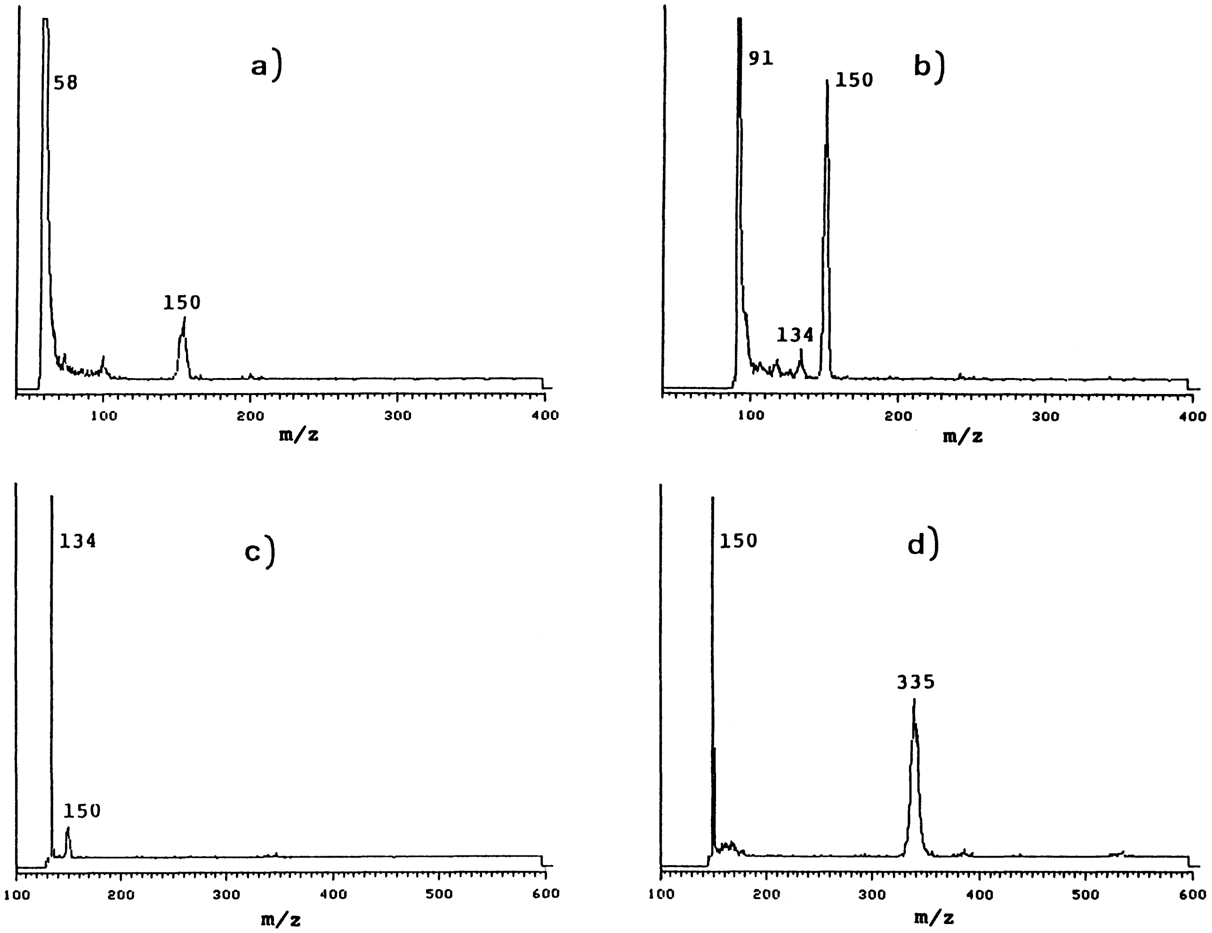
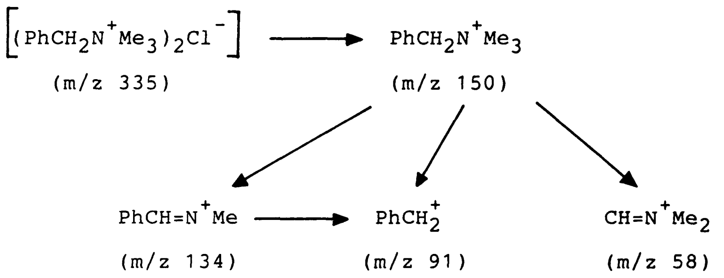
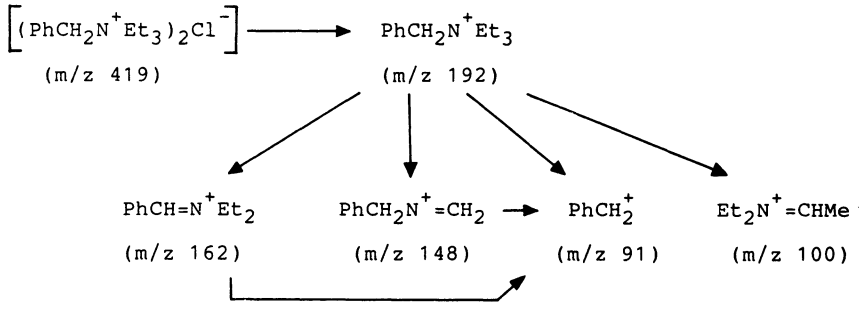


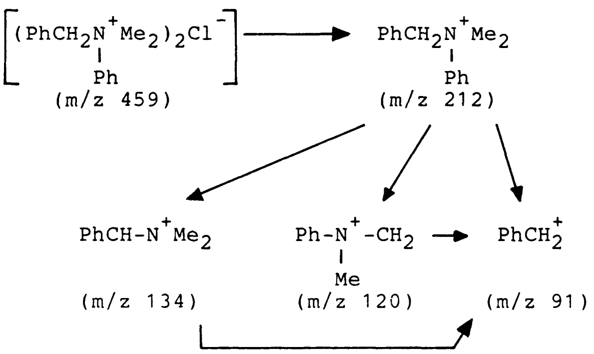
Fig. 6. B^2/E constant linked scanning spectra of a) *m/z* 58, b) *m/z* 91, c) *m/z* 134, and d) *m/z* 150 in the SIMS of **1**.



Scheme 6.



Scheme 7.



Scheme 8.

This work was supported by the Grant-in-Aid for Scientific Research No. 60430007 from the Ministry of Education, Science and Culture.

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