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In-Beam Electron Ionization and Mass Analyzed Ion Kinetic Energy Studies on Choline and Several Long Chain Aliphatic Quaternary Ammonium Salts

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In-beam electron ionization (EI) and mass analyzed ion kinetic energy (MIKE) spectrometric techniques were used to study the EI-induced fragmentation of choline iodide, choline chloride, hexadecyltrimethylammonium bromide, ethylhexadecyldimethylammonium bromide, and methyltricaprylammonium chloride. The in-beam EI and MIKE spectra of these compounds are presented. The in-beam EI spectra exhibit intact quaternary ammonium cations as well as thermally and EI-induced fragment ions. The fragmentation pathways arising from the intact cations in the in-beam EI spectra were defined by using the MIKE technique. The general fragmentation processes are similar to those of simple tetraalkylammonium cations previously reported. The in-beam EI spectra of a sample of tricaprylmethylammonium chloride exhibit abundant ions that are due to lower and higher homologous cations, indicating that the sample is a mixture of at least three homologs.

Keywords——in-beam ionization; extended direct-inlet probe; EI mass spectrometry; choline salt; aliphatic quaternary ammonium cation; MIKES; fragmentation pathway

Until recently quaternary ammonium salts analyzed by mass spectrometry were believed to undergo thermal degradation to volatile neutral products prior to ionization in a mass spectrometer.[2] Consequently, investigations of the fragmentation of intact quaternary ammonium salts by electron ionization (EI) were not reported. More exotic ionization techniques, including field desorption (FD),[3] ^{252}Cf plasma desorption (PD),[4] laser desorption (LD),[4] secondary ion mass spectrometry (SIMS),[5] and fast atom bombardment (FAB)[6] have been used to study intact cations from quaternary ammonium salts. However, in 1980 Stoll and Röllgen[7] reported the presence of simple tetraalkylammonium cations in the gas phase. Lee *et al.*,[8] using an electron impact/flash desorption (EI/D) technique, also observed the quaternary ammonium cations of a series of simple tetraalkylammonium salts in addition to ions due to thermal dealkylation products. Similarly, Cotter and Yergey[9] reported thermal desorption spectra of simple quaternary ammonium cations. We also have shown that the corresponding tetraalkylammonium cations are routinely observed for tetramethyl- through tetrapentylammonium bromide salts by the in-beam EI technique.[10-12] The fragmentation processes of this series were determined by mass analyzed ion kinetic energy spectrometry (MIKES) and by high voltage (HV) scanning ion kinetic energy spectrometry (IKES).[13] Desorption chemical ionization (DCI) also has been shown to be a potent technique for observation of intact quaternary ammonium cations. For instance, Hunt *et al.*[14] obtained a methane CI spectrum of choline chloride by use of an FD emitter, whereas Horning *et al.*[15] described an ammonia CI spectrum of acetylcholine chloride. Both spectra exhibited responses due to the intact quaternary ammonium cations as well as ions due to thermal degradation and ion molecule reaction products. Hasiak *et al.*[16] also reported ammonia CI spectra of several quaternary ammonium salts.

In this paper we report the results of the mass spectrometric analyses of choline and several alkyl quaternary ammonium salts with surfactant properties, using in-beam EI coupled with the MIKE technique. The utility of the technique is demonstrated for the analysis of compounds more complex than simple tetraalkylammonium salts.

Experimental

In-beam EI mass spectra were recorded on a Varian-MAT 311A double focusing mass spectrometer equipped with a modified electron ionization/field ionization/field desorption (EI/FI/FD) ion source. FD emitters with nonactivated 110 μm diameter tungsten wires were used as solid sample holders with an FD insertion probe on which the heating current contact was modified to permit positioning of the wire approximately 3 mm from the ionizing electron beam. A similar modification was reported by Soltmann *et al.*[17] and described as an EI/D technique. The sample, usually 1 to 10 μg deposited on the wire, was inserted into the hot ion source (280—300 °C) and heated up to a maximum current of 50 mA,[18,19] using the standard emitter current module of the instrument. The spectra were recorded under the following conditions: ionizing energy 80 eV; source temperature 280—300 °C; sample heater 50 mA (no sample heater current was necessary for analysis of the long chain aliphatic quaternary ammonium compounds); emission current 500 μA; accelerating voltage 3 kV. MIKE spectra were obtained under similar conditions by electric sector scanning at 4 V/s and a recorder chart speed of 63 mm/min.

The quaternary ammonium salts were all commercially available and were used without further purification: choline iodide (I), Aldrich Chemical Co., Inc., Milwaukee, WI; choline chloride (II), Merck & Co., Inc., Rahway, NJ; hexadecyltrimethylammonium bromide (III), Eastman Organic Chemicals, Rochester, NY; ethylhexadecyldimethylammonium bromide (IV), Chem Service, Inc., West Chester, PA; methyltricaprylammonium chloride (V), General Mills, Inc., Chemical Div., Kankakee, IL.

Results and Discussion

Choline

The in-beam EI spectra of choline iodide (I) and choline chloride (II) are shown in Fig. 1(a) and (b), respectively. In the spectrum of I, ionic responses due to thermal alteration products appear in the mass region above the quaternary ammonium cation at *m/z* 104. These ions include *m/z* 127 $(I)^+$, 128 $(HI)^{+}$, 142 $(CH_3I)^{+}$, and 172 $(HOCH_2CH_2I)^{+}$. In II, an analogous response appears at *m/z* 50 $(CH_3Cl)^{+}$ with the isotopic ion for ^{37}Cl at *m/z* 52. Overall, the general fragmentation patterns of both compounds are similar except that the intensity of the ion at *m/z* 58 is enhanced in the spectrum of II. The MIKE spectrum of I, shown in Fig. 2, indicates that the major ions in the in-beam EI spectrum are produced directly from the quaternary ammonium cation by EI.

The MIKE data for I, shown in Chart 1, confirm the transitions leading to the fragment ions a (*m/z* 89), b (*m/z* 88), f (*m/z* 60), g (*m/z* 59), and h (*m/z* 58), which are similar to those

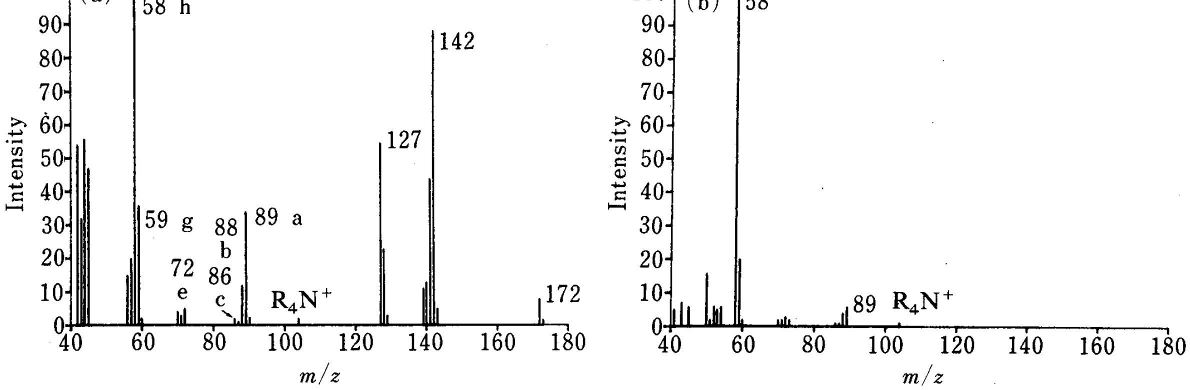

Fig. 1. In-Beam EI Spectra of Choline Iodide (a) and Choline Chloride (b)

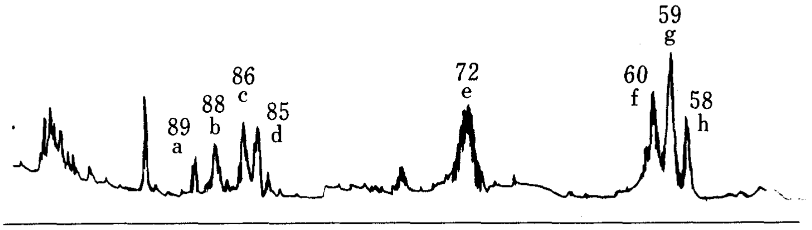

Fig. 2. MIKE Spectrum of Choline Iodide

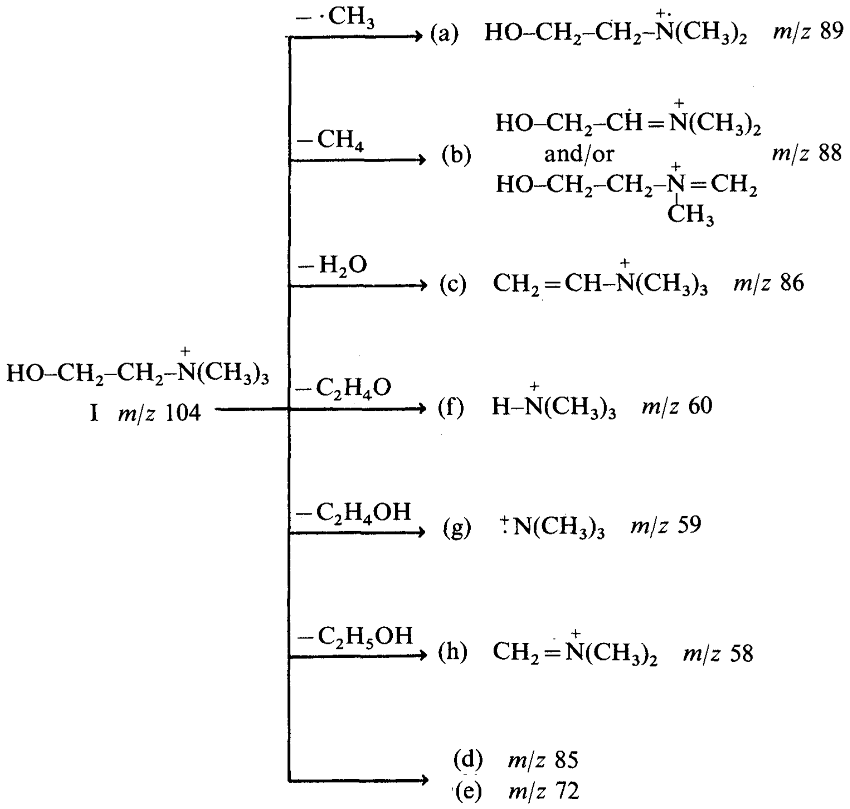

Chart 1

observed for the simple tetraalkylammonium salts.[10] These MIKE data, representing the reactions in the second field-free region of the reversed Nier–Johnson geometry instrument, provide evidence that the formation of the trialkylamine ion at *m*/*z* 59 is formed, at least partially, by EI-induced decomposition of the tetraalkyl cation. These data, however, do not exclude the contribution of ionization produced by thermal decomposition, particularly since strong responses in the in-beam EI spectrum appear for thermal rearrangement products, *i.e.*, CH_3I, HI, CH_3Cl, *etc.* The transition leading to the ion at *m*/*z* 86 corresponds to the loss of water, whereas the mechanism giving rise to the ions at *m*/*z* 72 and 85 remains uncharacterized.

In the SIMS spectrum of II, Day *et al.*[5] assigned the $(C^+ - 2CH_4)$ structure, where $C^+ =$ cation, to the ion at *m*/*z* 72, whereas Shabanowitz *et al.*[20] postulated a structure of $((CH_3)_2NHCH=CH_2)^+$ for this ion as a thermal degradation product in the CI spectrum. HV scanning IKES was investigated to determine the origin and composition of the ion. However, the HV scanning IKE spectrum of I proved to be broad and thus prevented the determination of the mass to charge ratio of the precursor ions. An example of the spectral broadening exhibited a few minutes after insertion of the sample into the ion source is shown

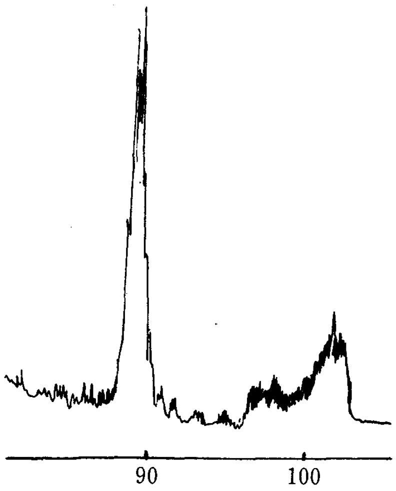

Fig. 3. HV Scanning IKE Spectrum (m/z 72) of Choline Iodide

in Fig. 3. The peak, at approximately $V/V_0 = 1.2$, is too diffuse to allow differentiation of m/z 88 (loss of CH_4) or m/z 89 (loss of OH) as the precursor ion. The presence of other unresolved interfering peaks, however, cannot be excluded as a possible reason for the broadening.[21]

It should be noted that the radical ions a and g correspond to the molecular ions of possible thermal degradation products, β-*N*,*N*-dimethylaminoethanol and trimethylamine, respectively. However, these ions are shown by MIKES to be produced directly from the quaternary ammonium cation by EI, although some thermal contributions cannot be excluded from the data. In the conventional EI spectrum of II, only the ions associated with β-*N*,*N*-dimethylaminoethanol and methyl chloride appear.[22] The source insertion CI (DCI) spectra of II acquired on a Finnigan 4023 quadrupole mass spectrometer in this laboratory also fail to show the intact cation but show responses at m/z 90 $(R_4N^+ - CH_3 + 1)^+$, m/z 72 $((CH_3)_2NHCH{=}CH_2)^+$, and m/z 60 $((CH_3)_3NH)^+$.[20] These results demonstrate that the in-beam EI spectra of I coupled with the MIKE technique give information not only on the intact cation, as in the case of DCI,[14] FD,[23] and SIMS,[5] but also on previously unreported fragmentation of the quaternary ammonium compounds upon EI.

Long Chain Aliphatic Quaternary Ammonium Salts

The in-beam EI spectra of III and IV are shown in Figs. 4 and 5, respectively. The spectrum of III exhibits ions at m/z 284, 269, and 268, corresponding to the $(R_4N)^+$, $(R_4N^+ - CH_3)$, and $(R_4N^+ - CH_4)$ ions, respectively. The base peak appears at m/z 58 $(R_4N^+ - C_{16}H_{34})$ in addition to an abundant ion at m/z 59, corresponding to $((CH_3)_3N)^+$, *i.e.*, $(R_4N^+ - C_{16}H_{33})$. In the spectrum of IV, ions at m/z 298, 283, 282, 269, and 268 correspond to $(R_4N)^+$, $(R_4N^+ - CH_3)$, $(R_4N^+ - CH_4)$, $(R_4N^+ - C_2H_5)$, and $(R_4N^+ - C_2H_6)$, respectively. The ions at m/z 73 $(R_4N^+ - C_{16}H_{33})$ and at m/z 72 $(R_4N^+ - C_{16}H_{34})$ are also intense. The significant rearrangement ion at m/z 58 is consistently present in the spectra of long chain aliphatic quaternary ammonium cations and appears to be diagnostic for this class of compounds. Both spectra exhibit responses due to the alkylbromide ion: at m/z 94 $(CH_3Br)^+$ with an isotopic ion at m/z 96, at m/z 135 and 137 $(C_4H_8Br)^+$, and at m/z 108 and 110 $(C_2H_5Br)^+$ (Fig. 5). These data suggest some contribution from thermal degradation products to the in-beam EI spectra.

The MIKE spectra of III and IV are shown in Figs. 6 and 7, respectively. The transitions observed in the MIKE spectrum of IV are presented in Chart 2 and are in accordance with the general fragmentation established in the cases of simple tetraalkylammonium salts.[10] The transitions observed in the spectrum of III can also be explained similarly. The in-beam EI spectrum and MIKES data of IV exhibit the formation of the m/z 58 ion (h), which is characteristic of this class of compounds and is possibly produced *via* a rearrangement of the

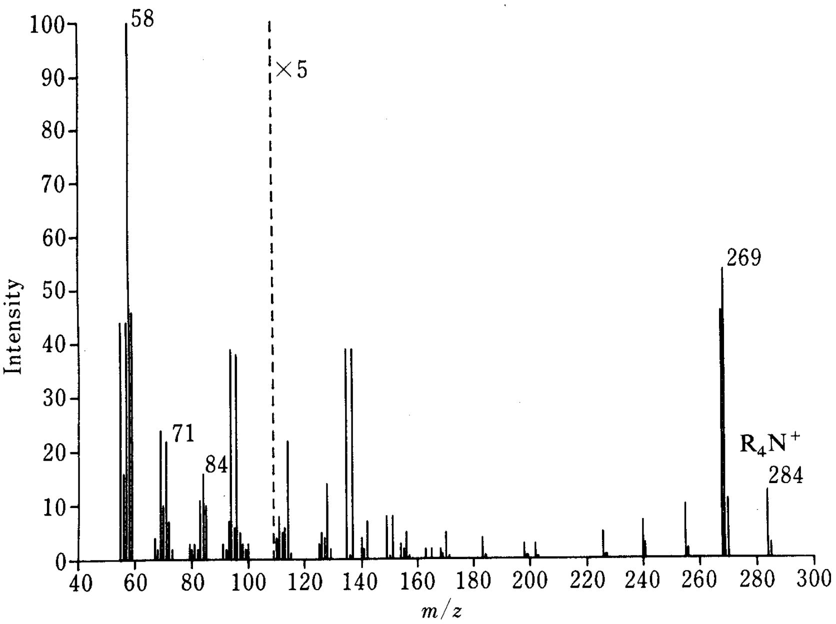

Fig. 4. In-Beam EI Spectrum of Hexadecyltrimethylammonium Bromide

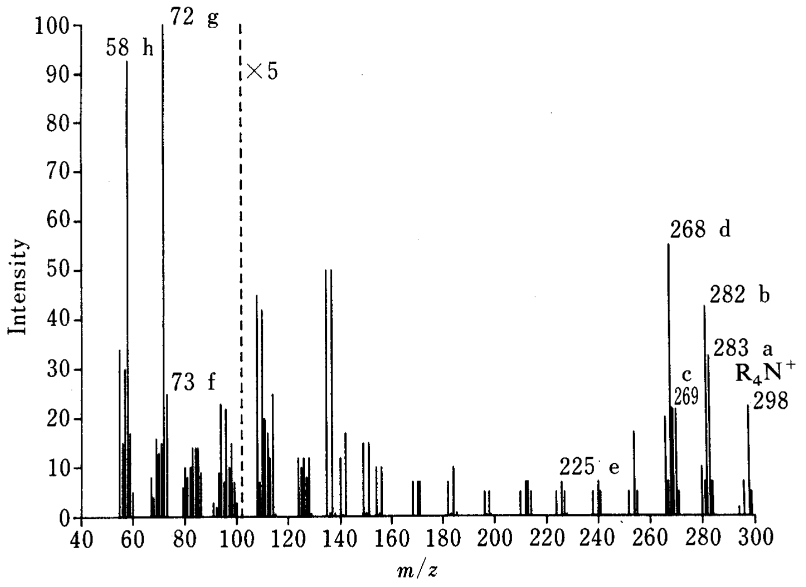

Fig. 5. In-Beam EI Spectrum of Ethylhexadecyldimethylammonium Bromide

imminium species, as detailed in Chart 2, b′ or d′. A similar rearrangement of imminium cations was studied extensively by Djerassi and Fenselau[24)] during mass spectrometric investigations of aliphatic tertiary amines.

The structures of the ions at *m*/*z* 282 and 268 can be formulated in two ways (b *vs*. b′, and d *vs*. d′, in Chart 2) with possibly both structures participating. The MIKE spectrum of III (Fig. 6) also shows the transitions leading to *m*/*z* 71 and 85. These transitions also appear as a series of peaks at *m*/*z* 85 and 99 in the spectrum of IV (Fig. 7). The mechanism of these transitions is uncertain, but probably involves simple C–C bond cleavage of the long chain aliphatic moiety of species b in the transitions.

On the basis of these findings, together with previous results on tetraalkylammonium bromide salts, a commercial sample of V was examined. The in-beam EI spectrum of this sample is shown in Fig. 8. As expected from its structure, ions at *m*/*z* 368 $(R_4N)^+$, 353

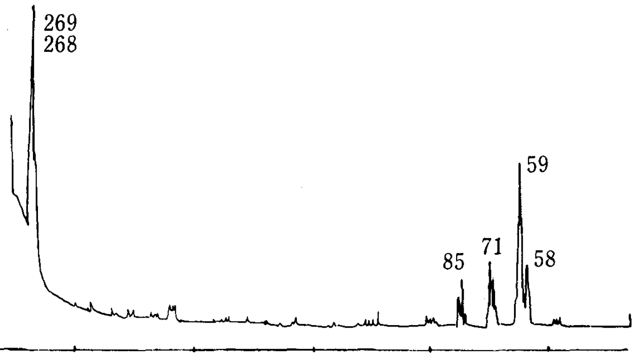

Fig. 6. MIKE Spectrum of Hexadecyltrimethylammonium Bromide

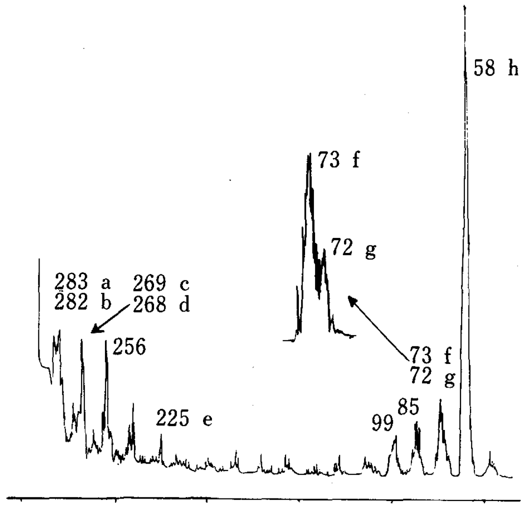

Fig. 7. MIKE Spectrum of Ethylhexadecyldimethylammonium Bromide

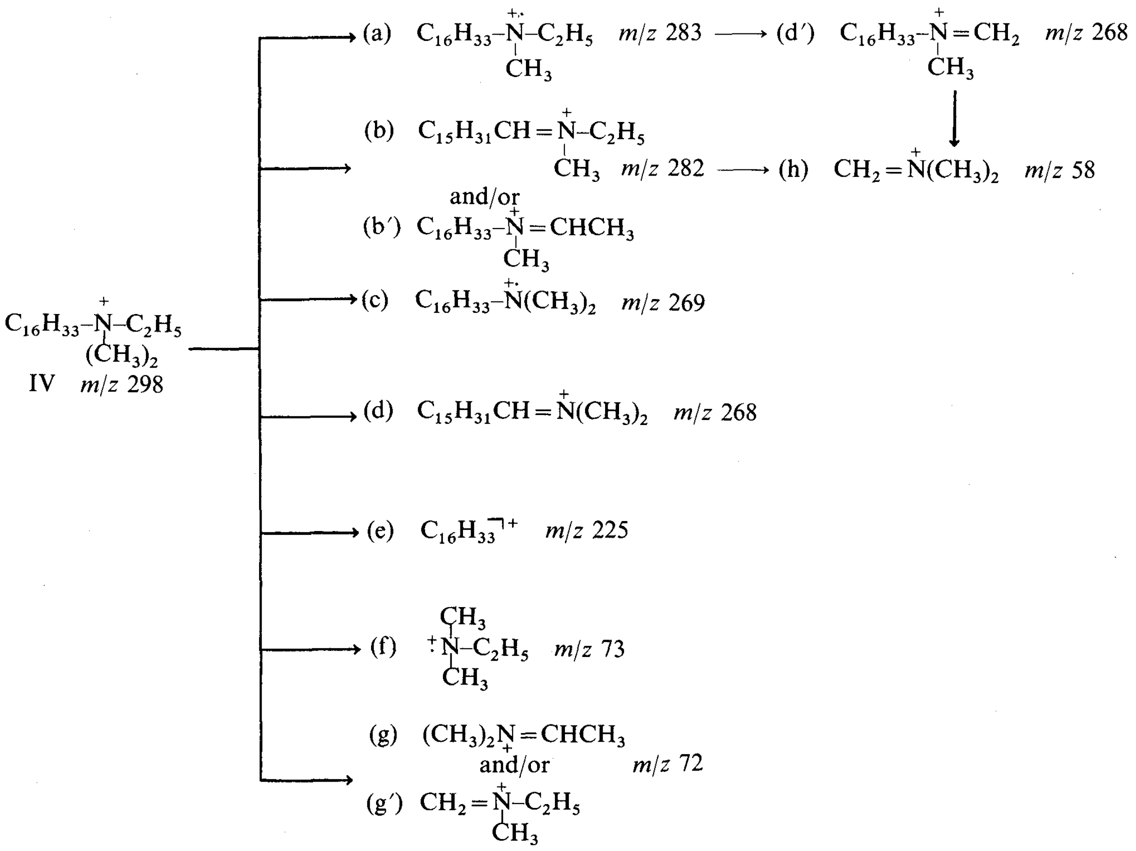

Chart 2

$(R_4N^+-CH_3)$, 352 $(R_4N^+-CH_4)$, 255 $(R_4N^+-C_8H_{17})$, 254 $(R_4N^+-C_8H_{18})$, 156 $(CH_3(C_8H_{17})N=CH_2)^+$, and 58 $((CH_3)_2N=CH_2)^+$ are present in the spectrum. In addition to these, a series of other intense ions appear, which on analysis proved to be responses due to homologous compounds. These results, summarized in Table I, clearly confirm that the sample is a mixture of at least three compounds (V, VI, and VII), with relative intensities of 3 : 10 : 12 for the cations in the spectrum. However, any attempt to quantify or determine the ratios of these impurities from such values is tenuous because the intensities of the cations are

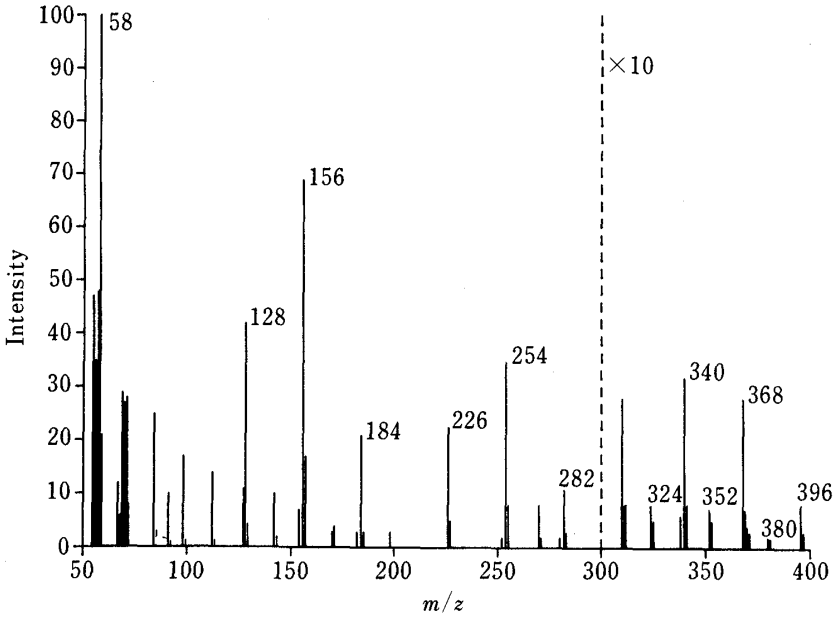

Fig. 8. In-Beam EI Spectrum of a Commercial Sample of Methyltricaprylammonium Chloride

TABLE I. Major Ions in the In-Beam EI Spectrum of $((C_8H_{17})_2NRCH_3)^+Cl^-$

Compound[a]	$(R_4N)^+$	$(R_4N^+-CH_3)$	$(R_4N^+-CH_4)$	$(R_4N^+-C_8H_{17})$	$(R_4N^+-C_8H_{18})$	$(CH_3(R)N=CH_2)^+$ [b]
V	368	353	352	255	254	156
VI	396	381	380	283	282	184
VII	340	325	324	227	226	128

a) Where: V, $R=C_8H_{17}$; VI, $R=C_{10}H_{21}$; VII, $R=C_6H_{13}$. b) Ion due to loss of C_8H_{18} and C_7H_{14} from corresponding cation.

very sensitive both to the volatilities of the compounds and to measurement conditions of the in-beam EI spectra. Nevertheless, qualitatively we can conclude on the basis of the in-beam spectra that the sample contains a fairly large amount of homologs relative to the labeled component.

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