Collision-Induced Dissociation of the Alkali-Metal Adduct Ions $[M+c]^+$ and $[M+2c-H]^+$ ($c=Na$ and K): Trolox and a Phospholipid

Mitsuo TAKAYAMA*

(Received June 29, 1995)

Collision-induced dissociation (CID) spectra of sodium adduct $[M+Na]^+$ and $[M+2Na-H]^+$ ions of Trolox and a phospholipid *L*- α -phosphatidyl-*N*-monomethylethanolamine, produced under fastatom bombardment conditions, have been compared with the corresponding CID spectra of potassium adduct $[M+K]^+$ and $[M+2K-H]^+$ ions, in order to examine the influence of cation size on the CID patterns. While the CID spectra of mono-metal adduct ions $[M+c]^+$ ($c=Na$ and K) agreed with each other in pattern, the CID spectrum of dipotassium-adduct $[M+2K-H]^+$ ion of the phospholipid showed a definite pattern of charge-remote fragmentation and it was different from that of di-sodium adduct $[M+2Na-H]^+$ ion in fragment intensity. The CID spectra of di-metal adduct ions $[M+2c-H]^+$ ($c=Na$ and K) gave a number of di-metal containing fragments. On the basis of the results obtained, the structures of alkali metal adduct $[M+c]^+$ and $[M+2c-H]^+$ ions have been discussed.

1. Introduction

Alkali and alkaline-earth metals play an essential role in variety of biological processes.¹⁾ A significant process is the active transport through cell membranes, by which Na^+ ions are pumped from the inside and potassium ions (K^+) from the outside of a cell by a functional protein called Na^+/K^+ -activated ATPase.²⁾ It is important that Na^+ (K^+) cannot be replaced by K^+ (Na^+) for the ion transport, because the Na^+/K^+ -activated ATPase molecule inside and outside of the cell selectively binds to Na^+ and K^+ ions, respectively. It is of interest how one molecule recognizes one metal cation.

On the other hand, it is well known that positive-ion mass spectra of organic compounds give the peak of sodium adduct $[M+Na]^+$ ions in the desorption ionization methods such as field desorption (FD), laser desorption (LD), plasma desorption (PD), fast-atom bombardment (FAB), liquid secondary ion (LSI), and matrix-assisted laser desorption (MALD). Although sodium as a habitual metal is often disliked by researchers owing to the contamination for sample preparation, the formation and dissociation behaviors of $[M+Na]^+$ ions under mass spectrometric conditions have been extensively studied by many workers from the standpoints of structure elucidation and metal-ion chemistry.³⁾ The formation of adduct ions with other alkali metals, alkaline-earth metals, transition metals, and other metals have also been interestingly studied by using the desorption ionization, electrospray ionization (ESI), and collision-induced dissociation (CID) techniques.⁴⁾ With respect to the complexation between alkali metals c and organic compounds M under mass spectrometric conditions and the CID characteristics of resulting complex ions, the comparison of the CID spectra of adduct ions $[M+c]^+$ ($c=Li, Na, K, Rb,$ and Cs) has been reported by using FD⁵⁾ and FAB methods.⁶⁾

* Faculty of Pharmaceutical Sciences, Toho University (2-2-1 Miyama, Funabashi, Chiba 274, Japan)

It has been described in the reports that the adduct ions with Li^+ and Na^+ ions are more stable than those with K^+ , Rb^+ , and Cs^+ ions,^{6b)} and that the CID patterns and fragment abundances change significantly with increasing the cation size from Na^+ to K^+ .^{6d), 6f)} I have also described^{6f)} that relatively small cations (Li^+ and Na^+) and large cations (K^+ and Rb^+) can interact locally and widely, respectively, with a given molecule, and that the effect of cation size on the CID patterns may come from the difference in the structure of $[\text{M}+\text{c}]^+$ ions. It is of importance for the CID analysis of alkali metal adduct ions to assign the binding site(s) of organic molecules with cations and to give the structure of adduct ions. In this paper, the influence of cation size on the CID patterns of alkali metal adduct ions $[\text{M}+\text{c}]^+$ and $[\text{M}+2\text{c}-\text{H}]^+$ ($\text{c}=\text{Na}$ and K), produced under FAB conditions, will be examined by using 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) and a phospholipid *L*- α -phosphatidyl-*N*-monomethylethanolamine. It is convenient to use these compounds for the CID study of $[\text{M}+2\text{c}-\text{H}]^+$ ions, because the compounds have a carboxyl or a phospho group which is favorable for the formation of $[\text{M}+2\text{c}-\text{H}]^+$ ions. In particular, it is of interest to examine the CID characteristics of the phospholipid as a long-chain containing compound for an extension of the CID characteristics to the determination of length and double bond position in the long-chain of other compounds. The structure of the adduct ions will be discussed based on the CID characteristics obtained. A definite pattern of charge-remote fragmentation will be found in the CID spectrum of $[\text{M}+2\text{K}-\text{H}]^+$ ion of the phospholipid, as an effect of cation size.

2. Experimental

The FAB experiments were performed on a JEOL JMS-DX303 double-focusing mass spectrometer equipped with a JMA-DA5100 data system (JEOL Ltd., Tokyo, Japan). The fast argon atom was generated from Ar^{++} ions which were accelerated to 5 kV. The FAB gun emission current was 10 mA. The liquid matrix used was a 1 : 1 (v/v) mixture of dithiothreitol (DTT) and thioglycerol (TG) referred to as DTT/TG11. About 40 μg of sample was taken up into the tip of a 10 μL micropipet (Drummond Sci. Co., Pennsylvania, U.S.A.), and then matrix of 5 μL was introduced to the micropipet through capillary action. A saturated solution of an alkali metal chloride was added to the matrix solution. For the experiments, approximately 2 μL of the matrix solution was loaded onto a stainless steel tip. The B/E-constant linked-scanning experiments for CID spectra were done with helium gas collisions in the first field-free region, using the above JMS DX-303 mass spectrometer. The pressure of the collision gas was adjusted to reduce the precursor ion beam intensity by 50%. The spectra shown are profile data accumulated over five or ten scans. The samples Trolox and *L*- α -phosphatidyl-*N*-monomethylethanolamine were purchased from Aldrich and Sigma Chemical Companies, respectively.

3. Results and Discussion

3.1 Mass spectra with added alkali metal chlorides

The addition of alkali metal chloride (NaCl or KCl) to the matrix solutions of Trolox (1) and *L*- α -phosphatidyl-*N*-monomethylethanolamine (2) gave the peaks corresponding

Fig. 1. Positive-ion FAB mass spectra of Trolox (**1**) obtained with added (a) NaCl and (b) KCl.

to the adduct ions $[M+c]^+$ and $[M+2c-H]^+$ ($c=Na$ and K) in their FAB mass spectra, as shown in Figs. 1 and 2. For the acidic compounds containing carboxyl and phospho groups, it should be noted that the cation-exchange reaction between H^+ and c^+ occurs in matrix solution as follows:

This reaction will proceed to the formation of two types of mono-metal adduct ions, $[M+c]^+$ (**I**) and $[(M-H+c)+H]^+$ (**I'**), as shown in Scheme 1. The type **I'** is a protonated molecule of an alkali metal salt ($M-H+c$) formed by the forward reaction in (1). It is important to recognize that mono-metal adduct ion peaks observed here consist of types **I** and **I'**, because the structure of adduct ions will strongly affect the CID patterns. Furthermore, di-metal adduct $[M+2c-H]^+$ ions may be formed by the attachment reaction of c^+ to the salts ($M-H+c$). Possible structures of cesium adduct ions for **1** have been already presented by Nishimura *et al.*⁷⁾

3.2 CID characteristics of the adduct ions of Trolox

The CID spectra of adduct ions $[M+c]^+$ ($c=Na$ and K) of **1** are shown in Fig. 3. The CID spectrum of $[M+Na]^+$ ion showed some outstanding fragment ions at m/z 258, 228, 213, 199, 187, 186, and 109, as well as Na^+ , while the CID spectrum of $[M+K]^+$ ion showed only an intense peak of K^+ at m/z 39. This is an evidence for which the adduct ion with Na^+ ion is intrinsically more stable than that with K^+ ion, as pointed out by

Fig. 2. Positive-ion FAB mass spectra of L- α -phosphatidyl-N-monomethylethanolamine (2) obtained with added (a) NaCl and (b) KCl.

Scheme 1.

Mallis *et al.*^{6a)} However, the lower intensity ions at m/z 274, 244, 229, 215, 202, and 125 in the CID spectrum of $[M+K]^+$ ion are consistent with the above CID fragments of $[M+Na]^+$ ion in the loss of neutrals. This means that the CID characteristics of $[M+Na]^+$ and $[M+K]^+$ ions of 1 are almost the same to each other. Furthermore, the CID spectra of the $[M+c]^+$ ions here are in rough agreement with that of $[M+H]^+$ ion in the fragmentation characteristics.⁸⁾ Although the fragment ions from the $[M+c]^+$ ions

Fig. 3. Collision-induced dissociation spectra of alkali metal adduct ions (a) $[M+Na]^+$ at m/z 273 and (b) $[M+K]^+$ at m/z 289 of **1**.

could be assigned as shown in Scheme 1, this is inconsistent with the structures **I** and **I'** except for the ions of m/z 109 and 125. The proposed assignments for those fragment ions suggest that alkali metal (Na or K) binds to either phenol or carboxyl side, or that a metal rearrangement reaction occurs in the structures **I** and **I'**.

The CID spectra of $[M+2Na-H]^+$ and $[M+2K-H]^+$ ions of **1** also showed a very similar pattern to each other (Fig. 4). It is particularly interesting to pay attention to lower mass fragment ions such as at m/z 90, 63, and 46 for $[M+2Na-H]^+$ ion and at m/z 122, 95, and 78 for $[M+2K-H]^+$ ion, since such ions may provide the information regarding the sites of the first and second addition of alkali metal to analyte molecules. Jennings and co-workers⁹ have reported that in the CID study of the adduct $[M+2Cs-H]^+$ ion of leucine enkephalin the formation of a C-terminus ion $(Cs_2CO_2)^{+*}$ and a metal radical dimer ion $(2Cs)^{+*}$ occurs characteristically. According to their report, the fragment ions at m/z 90 (122) and 46 (78) in the CID spectrum of $[M+2Na-H]^+$ ($[M+2K-H]^+$) ion can be assigned as $(c_2CO_2)^{+*}$ and $(2c)^{+*}$ ions, respectively.

Furthermore, we can find an interesting ion at m/z 63 (95) in the CID spectrum of $[M+2Na-H]^+$ ($[M+2K-H]^+$) ion, which may correspond to $(c_2OH)^{+*}$ ion. In order to examine the formation of the $(c_2CO_2)^{+*}$, $(2c)^{+*}$, and $(c_2OH)^{+*}$ ions in the CID spectra of $[M+2c-H]^+$ ions, the FAB and CID spectra of **1** were obtained with added an equimolar solution of NaCl and KCl to the matrix solution. The FAB mass spectrum showed an adduct $[M+Na+K-H]^+$ ion peak at m/z 311, as well as the peaks of M^+ , $[M+Na]^+$,

Fig. 4. Collision-induced dissociation spectra of alkali metal adduct ions (a) $[M+2\text{Na}-\text{H}]^+$ at m/z 295 and (b) $[M+2\text{K}-\text{H}]^+$ at m/z 327 of **1**.

$[M+\text{K}]^-$, $[M+2\text{Na}-\text{H}]^+$, and $[M+2\text{K}-\text{H}]^+$ ions, as shown in Fig. 5a. The CID spectrum of adduct $[M+\text{Na}+\text{K}-\text{H}]^+$ ion showed the peaks corresponding to $(\text{Na}+\text{K}+\text{CO}_2)^{++}$ ion at m/z 106, $(\text{Na}+\text{K})^{++}$ ion at m/z 62, and $(\text{Na}+\text{K}+\text{OH})^{++}$ ion at m/z 79 (Fig. 5b), which are consistent with the result from the CID spectra of $[M+2\text{c}-\text{H}]^+$ ions described above. The assignments for the fragment ions from the possible structures of $[M+2\text{c}-\text{H}]^+$ ($\text{c} = \text{Na}$ and K) ions are proposed as shown in Scheme 2.

The results obtained here suggest that for the formation of $[M+2\text{c}-\text{H}]^+$ ions the second addition of alkali metal cation c^+ to the alkali metal salts ($\text{M}-\text{H}+\text{c}$) occurs in the neighborhood of functional group(s) of the first added metal c . This was first pointed out by Isa *et al.*^{6a)} Although the remarkable influence of cation size on the CID patterns of adduct ions $[M+\text{c}]^-$ and $[M+2\text{c}-\text{H}]^+$ ($\text{c} = \text{Na}$ and K) of **1** could not be observed, it seems to be useful for the structure analysis of organic compounds to obtain the CID spectra of $[M+2\text{c}-\text{H}]^+$ ions because of the charge localization which results in so-called charge-remote fragmentation,¹⁰⁾ as is described in the next subsection.

3.3 CID and charge-remote fragmentation characteristics of the adduct ions of *L*- α -phosphatidyl-*N*-monomethylethanolamine

The CID spectra of $[M+\text{H}]^+$, $[M+\text{Na}]^+$, and $[M+\text{K}]^+$ ions of the phospholipid, **2**, are shown in Fig. 6. The CID spectra of $[M+\text{Na}]^+$ and $[M+\text{K}]^+$ ions showed some informative peaks corresponding to $[M+\text{c}-57]^+$, $[M+\text{c}-238]^+$, $[M+\text{c}-295]^+$, and $[M+\text{c}-313]^+$ ions, whereas the CID spectrum of $[M+\text{H}]^+$ ion showed only a peak at m/z

Fig. 5. (a) Positive-ion FAB mass spectrum of **1** obtained with added an equimolar solution of NaCl and KCl, and (b) collision-induced dissociation spectrum of alkali metal adduct ion $[M+Na+K-H]^+$ at m/z 311 of **1**.

Scheme 2.

551 originating from the loss of a neutral $HOPO(OH)OC_2H_4NHCH_3$ from the $[M+H]^+$ ion, as shown in Scheme 3. The CID spectra of adduct $[M+c]^+$ ions quite differ from the CID spectrum of $[M+H]^+$ ion in the loss of neutrals, while the CID spectra of $[M+Na]^+$ and $[M+K]^+$ ions are almost the same in pattern. This implies that the structure of $[M+c]^+$ ions is quite different from that of $[M+H]^+$ ion, while the adduct ions $[M+c]^+$ ($c=Na$ and K) are very similar to each other in structure.

On the other hand, the CID spectra of adduct $[M+2c-H]^+$ ions of **2** gave considerable informative peaks over the lower to higher mass range, as shown in Fig. 7. The CID

Fig. 6. Collision-induced dissociation spectra of (a) $[M+H]^+$ at m/z 706, (b) $[M+Na]^+$ at m/z 728, and (c) $[M+K]^+$ at m/z 744 of 2.

spectra are partly consistent with the CID spectra of adduct $[M+c]^+$ ions in the loss of neutrals. That is, the fragment ions at m/z 693 (725), 512 (544), and 437 (469), indicated by arrows in the CID spectrum of $[M+2Na-H]^+$ ($[M+2K-H]^+$) ion, correspond to the fragment $[M+c-57]^+$, $[M+c-238]^+$, and $[M+c-313]^+$ ions in the CID spectra of $[M+c]^+$ ions, respectively. It is interesting that the relative abundances of those ions at m/z 693 (725), 512 (544), and 437 (469) changed drastically according to cation size. This may be due to the structural difference of $[M+2Na-H]^+$ and $[M+2K-H]^+$ ions. As described in the previous report,^{6f)} relatively large cations such as K^+ and Rb^+ can widely interact with the cation-accepting groups in a given molecule to form multi-

Collision-Induced Dissociation of the Alkali-Metal Adduct Ions $[M+c]^+$

Scheme 3.

Fig. 7. Collision-induced dissociation spectra of alkali metal adduct ions (a) $[M+2Na-H]^+$ at m/z 750 and (b) $[M+2K-H]^+$ at m/z 782 of 2.

dentate structures. If the amine nitrogen of 2 strongly binds to K^+ rather than Na^+ owing to the larger cation radius ($0.95\text{\AA}$ for Na^+ and $1.33\text{\AA}$ for K^+), the intrinsic weak bond $PO-(CH_2)_2NHCH_3$ which results in the preferential loss of 57 mass unit from the adduct $[M+Na]^+$, $[M+K]^+$, and $[M+2Na-H]^+$ ions may hardly break in the case of $[M+2K-H]^+$ ion. In fact, the CID spectrum of $[M+2K-H]^+$ ion showed the preferential peak of m/z 544 originating from the loss of a palmitoyl group (238 mass unit) rather than the loss of 57 mass unit. The proposed structure and fragment assignments in the

Scheme 4.

Fig. 8. Partial spectra of collision-induced dissociation of alkali metal adduct ions (a) $[M+2Na-H]^+$ at m/z 750 and (b) $[M+2K-H]^+$ at m/z 782 of 2.

CID spectra of the $[M + 2c - H]^+$ ions for **2** are shown in Scheme 4. The CID pattern of alkali metal adducts may be dependent on the functional groups, steric factors, and molecular size of analytes, as well as cation size. Regarding this further study is required.

Furthermore, new informative ion peaks at m/z 566 (598) and 494 (526) indicated by asterisks were observed in the CID spectrum of $[M + 2Na - H]^+$ ($[M + 2K - H]^+$) ion, originating from the loss of 184 and 256 mass units, respectively, from the $[M + 2c - H]^+$ ions (Scheme 4). It is interesting that observed fragment ions at m/z 312, 240, 200, 182, 143, and 125 in Fig. 7a correspond to the ions at m/z 344, 272, 232, 214, 175, and 157 in Fig. 7b, respectively. These ions are di-metal containing fragments. Particularly, the fragments of m/z 125 and 143 could be assigned as the phospho containing $(Na_2PO_3)^{++}$ and $(Na_2PO(OH))^{++}$ ions, respectively, and all the ion peaks observed in Fig. 7 are dimetal containing fragments. This suggests that both the first and second added alkali metals *c* in the adduct $[M + 2c - H]^+$ ions of **2** localize on the phospho group.

Interestingly, the CID spectrum of $[M + 2K - H]^+$ ion showed a definite pattern of CH_2 losses originating from the cleavage of the *N*-acyl chain. As pointed out by Adams *et al.*^{6e)} this is a typical one of the charge-remote fragmentation which is often useful for the identification of alkyl chains. It may be considered that the charge-remote fragment ions here appeared as an effect of cation size, as shown in Fig. 8. This fact indicates that in the CID study of alkali metal adduct ions the use of alkali metals of differing ion radius is very useful for the structure elucidation of organic compounds.

4. Conclusion

The influence of Na^+ and K^+ ion size on the CID pattern of alkali metal adduct ions was observed in the CID spectra of di-metal adduct $[M + 2c - H]^+$ ions of **2**, whereas such influence was not observed in the CID spectra of mono-metal adduct $[M + c]^+$ ions of **1** and **2**, and of di-metal adduct $[M + 2c - H]^+$ ions of **1**. This result means that the influence of cation size on the CID spectra of metal adduct ions comes from the functional groups, steric factors, and molecular size of analytes, as well as cation size. This has already been shown in the CID study in which the CID pattern of adduct $[M + c]^+$ ions of diglycosides changes drastically with increasing the cation size from Na^+ to K^+ , while that of $[M + c]^+$ ions of mono-glycosides does not change.^{6f)} Further study regarding both the effects of cation and analyte size on the complexation and CID characteristics is necessary to apply the CID technique to the structure elucidation of organic compounds, and the metal-ion chemistry combined with the CID technique will become increasingly important in the future.

References

- 1) R. W. Hay, "Bio-Inorganic Chemistry," Ellis Harwood Ltd., Chichester (1984).
- 2) L. Stryer, "Biochemistry," 2nd Ed., W. H. Freeman and Company, San Francisco (1981), pp. 861-867.
- 3) (a) G. Puzo and J. C. Promé, *Org. Mass Spectrom.*, **20**, 288 (1985); (b) M. E. Castro, L. M. Mallis, and D. H. Russell, *J. Am. Chem. Soc.*, **107**, 5652 (1985); (c) J. M. Miller, S. J. Brown, R. Theberge, and J. H. Clark, *J. Chem. Soc. Dalton Trans.*, 2525 (1986); (d) D. Renner and G. Spiteller, *Biomed. Environ. Mass Spectrom.*, **15**, 75 (1988); (e) X. Tang, W. Ens, K. G. Standing, and J. B. Westmore, *Anal. Chem.*, **60**, 1791 (1988); (f) D. H. Russell, E. S. McGlohon, and L. M. Mallis, *Anal. Chem.*, **60**, 1818 (1988); (g) W. Kulik, W. Heerma, and J.

- K. Terlouw, *Rapid Commun. Mass Spectrom.*, **3**, 276 (1989); (h) R. Orlando, C. A. Bush, and C. Fenselau, *Biomed. Environ. Mass Spectrom.*, **19**, 747 (1990); (i) L. M. Teesch, R. C. Orlando, and J. Adams, *J. Am. Chem. Soc.*, **113**, 3668 (1991); (j) M. Takayama, T. Fukai, T. Nomura, and T. Yamauchi, *Org. Mass Spectrom.*, **26**, 655 (1991); (k) M. Takayama, Y. Tanaka, and T. Nomura, *Rapid Commun. Mass Spectrom.*, **7**, 172 (1993); (l) H. Zhao and J. Adams, *Int. J. Mass Spectrom. Ion Processes*, **125**, 195 (1993); (m) T. Fujita, Y. Itagaki, H. Naoki, T. Nakajima, and K. Hagiwara, *Rapid Commun. Mass Spectrom.*, **9**, 365 (1995); (n) T. Ii, M. Kubota, S. Okuda, T. Hirano, and M. Ohashi, *Eur. Mass Spectrom.*, **1**, 11 (1995).
- 4) (a) H. Grade and R. G. Cooks, *J. Am. Chem. Soc.*, **100**, 5615 (1978); (b) R. J. Day, S. E. Unger, and R. G. Cooks, *J. Am. Chem. Soc.*, **101**, 499 (1979); (c) D. Zakett, A. E. Schoen, and R. G. Cooks, *J. Am. Chem. Soc.*, **103**, 1295 (1981); (d) R. A. W. Johnstone and I. A. S. Lewis, *Int. J. Mass Spectrom. Ion Phys.*, **46**, 451 (1983); (e) R. A. W. Johnstone, I. A. S. Lewis, and M. E. Rose *Tetrahedron*, **39**, 1597 (1983); (f) M. A. Baldwin, K. J. Welham, and D. B. Davies, "Advances in Mass Spectrometry," Part B, ed. by J. F. J. Todd, John Wiley & Sons, Chichester (1985), p. 1585; (g) J. M. Miller and R. Theberge, *Org. Mass Spectrom.*, **20**, 600 (1985); (h) J. L. Aubagnac, B. Elamrani, F. M. Devienne, R. Combarieu, and J. C. Roustan, *Int. J. Mass Spectrom. Ion Processes*, **65**, 159 (1985); (i) L. M. Mallis and D. H. Russell, *Int. J. Mass Spectrom. Ion Processes*, **78**, 147 (1987); (j) J. Adams and M. L. Gross, *Anal. Chem.*, **59**, 1576 (1987); (k) R. P. Grese, R. L. Cerny, and M. L. Gross, *J. Am. Chem. Soc.*, **111**, 2835 (1989); (l) M. Sawada, L. Ouyang, Y. Takai, H. Yamada, T. Hanafusa, T. Kinoshita, and T. Mochizuki, *Chem. Lett.*, 1361 (1990); (m) L. M. Teesch and J. Adams, *J. Am. Chem. Soc.*, **112**, 4110 (1990); (n) R. P. Grese and M. L. Gross, *J. Am. Chem. Soc.*, **112**, 5098 (1990); (o) R. B. Cole, J.-C. Tabet, and J.-C. Blais, *Int. J. Mass Spectrom. Ion Processes*, **98**, 269 (1990); (p) M. L. Gross, R. L. Cerny, D. E. Giblin, D. L. Rempel, D. K. MacMillan, P. Hu, and C. L. Holliman, *Anal. Chim. Acta*, **250**, 105 (1991); (q) C. Lange, C. Mulheim, A. Vey, and M. Pais, *Rapid Commun. Mass Spectrom.*, **5**, 503 (1991); (r) H. Zhang and D. V. Dearden, *J. Am. Chem. Soc.*, **114**, 2754 (1992); (s) S. Maleknia and J. Brodbelt, *J. Am. Chem. Soc.*, **114**, 4295 (1992); (t) P. Hu and M. L. Gross, *J. Am. Chem. Soc.*, **114**, 9161 (1992); (u) M. Sawada, M. Shizuma, Y. Takai, H. Yamada, T. Tanaka, Y. Okumura, Y. Hidaka, T. Hanafusa, and S. Takahashi, *Bull. Chem. Soc. Jpn.*, **65**, 1275 (1992); (v) S. Maleknia and J. Brodbelt, *Rapid Commun. Mass Spectrom.*, **6**, 376 (1992); (w) K. P. Madhusudanan, A. Rani, B. Kumar, and S. N. Suryawanshi, *Org. Mass Spectrom.*, **28**, 892 (1993); (x) I.-H. Chu, H. Zhang, and D. V. Dearden, *J. Am. Chem. Soc.*, **115**, 5736 (1993); (y) P. Hu and M. L. Gross, *J. Am. Chem. Soc.*, **115**, 8821 (1993); (z) A. Chapeaurouge, L. Bigler, A. Schäfer, and S. Bienz, *J. Am. Soc. Mass Spectrom.*, **6**, 207 (1995).
- 5) F. W. Röllgen, U. Giessmann, F. Borchers, and K. Levsen, *Org. Mass Spectrom.*, **13**, 459 (1978).
- 6) (a) K. Isa, T. Kinoshita, H. Kido, R. Nakata, and K. Mizuta, *Nippon Kagaku Kaishi*, 1657 (1986); (b) L. M. Mallis and D. H. Russell, *Anal. Chem.*, **58**, 1076 (1986); (c) K. Isa and Y. Takeuchi, *Org. Mass Spectrom.*, **24**, 153 (1989); (d) L. M. Teesch and J. Adams, *J. Am. Chem. Soc.*, **113**, 812 (1991); (e) Q. Ann and J. Adams, *Anal. Chem.*, **65**, 7 (1993); (f) M. Takayama, *Org. Mass Spectrom.*, **28**, 878 (1993); (g) M. Takayama, *Int. J. Mass Spectrom. Ion Processes*, **136**, 35 (1994).
- 7) T. Nishimura and M. Takayama, *J. Mass Spectrom. Soc. Jpn.*, **43**, 85 (1995).
- 8) M. Takayama, T. Kosaka, and T. Kinoshita, submitted.
- 9) S. G. Summerfield, D. Despeyroux, and K. R. Jennings, in Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, U.S.A. (1994), p. 465.
- 10) (a) M. L. Gross, *Int. J. Mass Spectrom. Ion Processes*, **118/119**, 137 (1992); (b) M. Claeys, H. Van den Heuvel, J. Claereboudt, J. Corthout, L. Pieters, and A. J. Vlietinck, *Biol. Mass Spectrom.*, **22**, 647 (1993); (c) M. Claeys and H. Van den Heuvel, *Biol. Mass Spectrom.*, **23**, 20 (1994).

Keywords

Fast-atom bombardment mass spectrometry
Alkali metal adducts
Collision-induced dissociation
Charge-remote fragmentation
Metal-ion chemistry