Formation of M^{+} Ions and Electronic Excitation under Fast-Atom Bombardment Conditions by Using a Liquid Matrix*

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The mechanism for the formation of molecular ions M^{+} under fast-atom bombardment (FAB) conditions with a liquid matrix is discussed on the basis of the mass spectra of pyrene, coronene, and fullerene C_{60} obtained by using electron impact, gas-phase fast-atom bombardment, and gas-phase fast-molecule bombardment techniques. The obtained results suggest that formation of the M^{+} ions under FAB conditions is not due to direct collisions between analytes M and fast atoms A , but is due to collision interactions between M and recoiling matrix molecules B or matrix ions. It has been confirmed, furthermore, that the FAB conditions with a liquid matrix are sufficient in energy for formation of singly charged ions M^{+} and insufficient for the formation of multiply charged ions M^{z+} ($z = 2, 3$) of pyrene, coronene, and C_{60} . (*J Am Soc Mass Spectrom* 1995, 6, 114–119)

Ionization events under fast-atom bombardment (FAB) with a liquid matrix (matrix FAB or liquid secondary ion mass spectrometry) are diverse and complex to understand, as noted by Sunner [1]. Recently, we described [2] that the formation of M^{+} and $[M + H]^{+}$ ions under matrix FAB conditions occurs competitively and that FAB conditions can enable organic compounds M to ionize to M^{+} ions even when a liquid matrix is used. Although some ideas for the formation of M^{+} ions under matrix FAB conditions have been presented so far [3–7], the mechanism has not yet been clarified. Kralj et al. [4], Dube [5], and Huang et al. [7] believed that the formation of M^{+} ions occurs by a mechanism in which neutral analytes M are sputtered and then impacted by a high energy argon or xenon beam in the gas phase:

This is known as gas-phase FAB [4–7], where gaseous samples are ionized by collision with high energy He, Ar, or Xe beams [8–11]. According to De Pauw [3], the formation of M^{+} ions may occur alternatively through formation of a charge-transfer (CT) complex between analyte M and matrix B molecules under matrix FAB conditions:

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Here, $[MB]$ represents a CT complex. Furthermore, Bojesen et al. [6] described that a most likely process for the M^{+} ion formation is the charge exchange between analytes M and xenon ions Xe^{+} , which slightly form in the fast neutral xenon beam, that is,

To clarify the major processes for the M^{+} ion formation, we have examined the behavior of ion formation under FAB conditions by using an electron acceptor such as *p*-benzoquinone, positive- and negative-ion FAB, gas-phase FAB, and electron impact ionization (EI) techniques [12]. The following suggestions were obtained: (1) the liquid matrix plays some essential role in the M^{+} ion formation, (2) the addition of electron acceptor to the matrix solutions does not enhance the M^{+} ion formation, (3) one-electron transfer between neutral molecules does not occur, and (4) the abundant formation of M^{+} ions under FAB conditions cannot be explained by mechanisms (1) and (3) because of the rare flux of the fast-atom beam. It was pointed out [12], subsequently, that the formation of M^{+} ions under matrix FAB conditions cannot be successfully explained by mechanisms (1)–(3).

It is important to know the range of electronic excitation that occurs under matrix FAB conditions in connection with the mechanism of M^{+} ion formation. For this purpose, here we employ samples of pyrene, coronene, and fullerene C_{60} for which ionization energies for multiply charged molecular ions M^{z+} ($z = 1-3$) have been estimated already. These samples are convenient for our experiments because they are of relatively high molecular weight and therefore are not expected to evaporate out of the matrix solution and

be ionized in the gas phase. In this communication, we will present a suggestion that the formation of M^{+} ions under matrix FAB conditions is not due to direct collisions between M and fast atoms A_{fast} , but due to collision interactions between M and B or matrix ions such as B^{+} . By using the previously cited samples, gas-phase FAB, matrix FAB, gas-phase fast-molecule bombardment (FMB), and EI techniques, the range of collisional electronic excitation that occurs under matrix FAB conditions will be estimated.

Experimental

Experiments were performed with a JEOL (Tokyo, Japan) JMS-DX303 double-focusing mass spectrometer equipped with a JMA-DA5100 data system. The fast argon beam was generated from Ar^{+} ions, which were accelerated to 5 kV. The FAB gun emission current was 10 mA. The mass resolution was approximately 2000. The liquid matrices used were *m*-nitrobenzylalcohol (NBA) and a 1:2 mixture of dithiothreitol (DTT) and thioglycerol (TG) (referred to as DTT/TG12 [13]). A sample of $\sim 40 \mu\text{g}$ was taken up into the tip of a $10\text{-}\mu\text{L}$ micropipet (Drummond Scientific Co., Broomall, Pennsylvania) and the matrix of $5 \mu\text{L}$ was introduced to the micropipet through capillary action. For the experiments, approximately $2 \mu\text{L}$ of the matrix solution was loaded onto a stainless steel tip. Pyrene, coronene, and the matrices NBA and DTT were purchased from Tokyo Kasei (Tokyo, Japan) and TG was purchased from Fluka (Buchs, Switzerland). The experimental details concerning the preparation of fullerene C_{60} (99%) have been described elsewhere [14]. The electron impact energy in the EI mode varied from 12 to 32 eV or was 70 eV. The ionization current and the chamber temperature were $100 \mu\text{A}$ and 200°C , respectively.

The experiments of gas-phase FAB with an argon beam [8-11] and gas-phase FMB with an isobutane beam [15, 16] were carried out by using the same mass spectrometry system described in the preceding text and the sample was introduced via a direct inlet system. The vacuum, which was read by a gauge attached to the pumping line for the ion source, was typically at 1×10^{-5} torr. The spectra shown are profile data accumulated over 5 or 10 scans.

Results and Discussion

Mass spectra of pyrene by EI (70 eV) and gas-phase FAB (Ar, 5 keV) methods are shown in Figures 1 and 2, respectively. These spectra are very similar to each other and show the peaks that correspond to doubly and triply charged molecular ions M^{2+} and M^{3+} , as well as M^{+} ions at m/z 202. Further multiply charged ions were not observed. Under 32-eV EI conditions, the M^{3+} ion was not observed. The M^{2+} ion disappeared at about 20 to 22 eV, which is consistent with the known ionization energies (IE) of pyrene—7.4 eV for

Figure 1. EI mass spectra of pyrene in (a) full, (b) triply charged ion ($200 \times A$), and (c) doubly charged ion ($12 \times A$) regions.

M^{+} , 21.8 eV for M^{2+} , and 38.7 eV for M^{3+} [17]. The obtained gas-phase FAB spectrum indicates that high energy direct collision between M and Ar in the gas phase causes electronic excitation of at least 38.7 eV.

On the other hand, the FAB spectrum of pyrene with NBA matrix did not show any multiply charged ion peaks as shown in Figure 3. Figure 3b and c represent partial spectra of triply and doubly charged molecular ion regions, respectively. In all of the spectra, asterisks indicate the peaks that originate from the

Figure 2. Gas-phase FAB mass spectra of pyrene in (a) full, (b) triply charged ion ($200 \times A$), and (c) doubly charged ion ($8 \times A$) regions.

Figure 3. Matrix FAB mass spectra of pyrene in (a) full, (b) triply charged ion ($100 \times A$), and (c) doubly charged ion ($100 \times A$) regions.

NBA matrix. The obtained result indicates that the gas-phase FAB process by which the $M^{+•}$ ion formation occurs by direct collisions between M and A in the gas phase is very unlikely to be the mechanism of $M^{+•}$ ion formation under matrix FAB conditions. Furthermore, the obtained result gives evidence that matrix FAB conditions are sufficient in energy for the formation of singly charged ion $M^{+•}$ and insufficient for the formation of multiply charged ions M^{z+} ($z = 2, 3$) of pyrene. In other words, the matrix FAB process causes electronic excitation of at least 7.4 eV, but less than 21.8 eV. This seems to be a significant observation for the understanding of ion formation under matrix FAB conditions. To confirm this and to examine the range of electronic excitation further, coronene and C_{60} were used, because the ionization energies for M^{z+} ($z = 1-3$) formation are known. Similar results were obtained in the FAB spectra of coronene and C_{60} by using the techniques of gas-phase FAB with the Ar beam and matrix FAB with NBA. Figures 4 and 5 show the gas-phase FAB and matrix FAB spectra of coronene, respectively. Figures 6 and 7 show the gas-phase FAB and matrix FAB spectra of C_{60} , respectively. In these compounds, the matrix FAB spectra did not show any multiply charged ion peaks, whereas the gas-phase FAB spectra showed peaks that correspond to M^{z+} ($z = 1-3$) ions. The known ionization energies of coronene are 7.4 eV for $M^{+•}$, 21.0 eV for M^{2+} , and 37.1 eV for M^{3+} [17], and the energies for C_{60} are 7.6 eV for $M^{+•}$, 19.9 eV for M^{2+} , and 36.9 eV for M^{3+} [18]. Here we again state that in the case of C_{60} the matrix FAB process causes electronic excitation of at least 7.6 eV, but less than 19.9 eV.

However, the foregoing results of gas-phase FAB experiments indicate that we cannot deny the forma-

Figure 4. Gas-phase FAB mass spectra of coronene in (a) full, (b) triply charged ion ($50 \times A$), and (c) doubly charged ion ($5 \times A$) regions.

tion of M^{z+} ($z = 1-3$) ions that may occur in the early stages of high energy direct collision between A_{fast} and the matrix surface. One reason why the peak of multiply charged ions M^{z+} ($z = 2, 3$) could not be observed in the matrix FAB spectra may be due to the neutralization reaction of the M^{z+} ions through frequent collisions between M^{z+} and matrix molecules B in the dense gaslike phase, that is,

Figure 5. Matrix FAB mass spectra of coronene in (a) full, (b) triply charged ion ($100 \times A$), and (c) doubly charged ion ($100 \times A$) regions.

Figure 6. Gas-phase FAB mass spectra of C_{60} in (a) full, (b) triply charged ion ($5 \times A$), and (c) doubly charged ion ($1 \times A$) regions.

This is a charge exchange reaction. The condition for the progress of this reaction can be given by $IE(M^{(z-1)+} \rightarrow M^{z+}) > IE(B \rightarrow B^+)$. The IEs (electronvolts) of pyrene are 7.4 for $M \rightarrow M^+$, 14.4 for $M^+ \rightarrow M^{2+}$, and 16.9 for $M^{2+} \rightarrow M^{3+}$ [17]. Because the IE of NBA is 9 eV [19], M^{2+} and M^{3+} ions of pyrene can ionize the NBA molecules B, and M^+ ions will be left in the ion source. Furthermore, the matrix ions B^+ that are formed will enable pyrene molecules M to ion-

ize to M^+ ions in accordance with the condition of $IE(B) > IE(M)$.

In accordance with the latest model for ionization under matrix FAB conditions [12, 20-22], on the other hand, the formation of various ion species occurs competitively through extensive collisions and ion-molecule reactions in a dense gaslike phase that enables analyte M and matrix B molecules of high translational energy to collide frequently with each other. The formation of molecular ions M^+ may occur by such frequent collisions between neutrals and/or ion species in the dense gaslike phase. To examine the possibility of ion formation due to collisions between neutral molecules, the FMB spectrum of pyrene was obtained by colliding a high energy isobutane beam (5 keV) with gas-phase pyrene molecules (Figure 8). The FMB spectrum is very similar to the gas-phase FAB spectrum in Figure 2, and it shows the peaks that correspond to M^{z+} ($z = 1-3$) ions. The FMB spectra of coronene and C_{60} also showed multiply charged molecular ions M^{z+} ($z = 1-3$); these spectra are not presented in this communication. This seems to be an important observation for understanding the M^+ formation, although it does not give direct evidence that formation of the M^+ ions occurs due to direct collisions between M and B in a dense gaslike phase produced under matrix FAB conditions. We propose a possible mechanism for the M^+ ion formation under matrix FAB conditions:

Here, B_{gas} represents the recoiling matrix molecules formed immediately after the collision cascade caused by particle bombardment. We noted a significant matrix effect: the extent of fragmentation, which is related to the internal energy, in the molecular ions M^+ produced under FAB conditions is affected by the matrix material used [12, 23]. Because the mechanism (5) proposed here requires collision interactions between analyte M and matrix B molecules, the matrix effect might be explained by the collision processes.

In the sense of collision interactions, however, we also have to consider the mechanism of charge exchange between M and matrix ion species such as B^+ as previously described, that is,

Ligon [24] has reported that formation of the matrix radical cations B^+ is one of the primary events in the FAB ionization. To examine the validity of charge exchange reaction (6), positive- and negative-ion FAB spectra of pyrene were obtained by using two different matrix systems—NBA and DTT/TG12. In all of the spectra, asterisks indicate the peaks that originate from the matrix used. Figure 9a and b are positive- and negative-ion FAB spectra of pyrene with NBA matrix, respectively. The positive-ion spectrum shows an intense M^+ ion peak at m/z 202, a protonated matrix

Figure 7. Matrix FAB mass spectra of C_{60} in (a) full, (b) triply charged ion ($2 \times A$), and (c) doubly charged ion ($10 \times A$) regions.

Figure 8. Gas-phase FMB mass spectra of pyrene in (a) full, (b) triply charged ion ($200 \times A$), and (c) doubly charged ion ($10 \times A$) regions.

peak $[NBA + H]^+$ at m/z 154, and a weak matrix ion $[NBA]^+$ at m/z 153, whereas the negative-ion spectrum shows an intense matrix ion $[NBA]^-$ at m/z 153. Although these spectra imply that one-electron transfer like reaction (2) occurs rather than charge exchange (6), the origin of the electron of $[NBA]^-$ ions is not necessarily the analyte molecules M because the negative-ion FAB spectrum of neat NBA gives a pattern quite similar to figure 9b. This observation will be confirmed by using another matrix system that is not a strong electron scavenger. Positive- and negative-ion FAB spectra of pyrene with a thiol-containing matrix

Figure 9. (a) Positive-ion and (b) negative-ion matrix FAB mass spectra of pyrene with NBA matrix.

Figure 10. (a) Positive-ion and (b) negative-ion matrix FAB mass spectra of pyrene with DTT/TG12 matrix.

system DTT/TG12 are shown in Figure 10a and b, respectively. The positive-ion spectrum shows an intense M^+ ion peak at m/z 202 and matrix ions $[DTT]^+$ and $[DTT + H]^+$, whereas the negative-ion spectrum does not show matrix ions $[DTT]^-$ and $[TG]^-$. The obtained results are not definite evidence for both charge exchange (6) and one-electron transfer (2).

Conclusion

The formation of M^+ ions under matrix FAB conditions is a rather unusual phenomenon, so our understanding of it is incomplete. Although direct evidence for the mechanism of M^+ ion formation could not be obtained in the experiments here, it seems clear that formation of the M^+ ions occurs due to collision interactions between analytes M and matrix molecules or ions in a dense gaslike phase formed immediately after the collision cascade caused by particle bombardment. The point is that matrix FAB conditions are sufficient in energy for the formation of singly charged ions M^+ and insufficient for the formation of multiply charged ions M^{z+} ($z = 2, 3$), which requires relatively high electronic excitation of about 20 eV or greater. This important fact suggests that M^+ ion formation under matrix FAB conditions occurs through charge exchange (6) rather than high energy collision processes (1) and (5). Further experiments in this regard are in progress.

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