Experimental Study on Gas-phase Ionization Process for Ion Attachment Mass Spectrometry

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In this study, in order to investigate the mechanism of Li^+ attachment process, dimethylarsinic acid (DMAA) was detected by selective-ion monitoring mode of ion attachment mass spectrometry (IAMS) and the Li^+ binding energy of N_2 and DMAA was also calculated. The results indicated the possibility of the transfer of Li^+ from N_2Li^+ to DMAA in IAMS analysis. This study could contribute to the development and application of IAMS technique.

The technical advances of the past years have led to a vast widening of the scope of the mass spectrometer for the investigation of ion-molecule reaction and many studies led to the recognition that the ion-molecule reactions display third-order kinetics. In previous studies, two kinds of mechanisms have been reported for the ion-molecule reaction.[1] One is "energy-transfer" process, like the following equation indicated.

$$I + A + M \rightleftharpoons IM + A \tag{1}$$

$$I + M \rightleftharpoons IM^* \tag{2}$$

$$IM^* + A \rightarrow IM + A \tag{3}$$

Where I denotes a positively charged ion and M and A are neutral species. Eq 1 is the overall reaction and the eqs 2 and 3 are the elementary reaction. With no activation energy, the initial combination step is brought about by ion-permanent dipole or ion-induced dipole attraction between the reactants. The energy thus liberated in the reaction complex could be lost by collision with a third body (A).

Another alternative mechanism was considered as an "ion transfer" process, like eqs 4 and 5 indicated.

$$I + A \rightleftharpoons IA^* \tag{4}$$

$$IA^* + M \rightleftharpoons IM + A \tag{5}$$

In this case, the initial combination produces the species IA*, which then undergoes "ion transfer" with M. This process also accounts for the observed reaction products and for the rate law. Using this mechanism, chemical ionization mass spectrometry was developed and it was indicated that the compound (A), which has lower positively charged ion binding energy, would be easier to transfer positively charged ion to the other compounds.[2–4]

Recently, a soft ionization mass spectrometry named IAMS has been developed. The principle of IAMS is considered as "energy-transfer" process.[5,6] Like what shown in eqs 2 and 3, when I is lithium ion (Li^+) and A is nitrogen gas (N_2), the mechanism of IAMS was considered as the following equation.

$$M + Li^+ \rightleftharpoons MLi^{+*} \tag{6}$$

$$MLi^{+*} + N_2 \rightarrow MLi^+ + N_2 \tag{7}$$

Li^+ attaches to a sample molecule (M) firstly (eq 6). Then, in order to prevent Li^+ detaching from MLi^+, N_2, which exists in ionization chamber as the third body, was used to remove the excess energy produced from the attached ion. Under this condition, the attached ions become so stable that they can be analyzed and detected by mass spectrometer, while still retaining their shape (eq 7).

With IAMS, compound's structure cannot be destroyed and only Li^+ attached ion peak per one ingredient appears on a mass spectrum.[5,6] Thus, IAMS has been used to analyze many kinds of compounds directly and simply.[7–11] In our former study, a new method named direct sample insertion probe ion attachment mass spectrometer (DIP-IAMS) was developed to detect organoarsenic compounds, including DMAA, trimethylarsine oxide (TMAO), and arsenic ethoxide (AsE) successfully.[12]

However, no experimental study has been carried out to investigate the possibility of "ion transfer" process in IAMS analyses. Therefore, in this study, we focused on N_2, which may be possible to transfer Li^+ to sample molecule in IAMS and measured the intensity of Li^+, N_2Li^+, and $DMAALi^+$ by selective-ion monitoring (SIM) mode of IAMS, in order to investigate the possibility of lithium ion transfer mechanism. Moreover, theoretical calculations of Li^+ binding energy of N_2, and DMAA were performed and compared with the experimental results.

DMAA of HPLC grade was detected by DIP-IAMS.[8] IAMS was operated in both scan and SIM mode. SIM was used to monitor selected ions of interest and helped in real-time monitoring of the reaction process. In this study, Li^+ (*m/z* 7), N_2Li^+ (*m/z* 35), and $DMAALi^+$ (*m/z* 145) were selected for SIM experiment.

Hybrid functional B3LYP method with the 6-311+G* basis set was used to calculate the Li^+ binding energy. Both the zero point energies and thermal energy corrections have been included in the results. All the calculations were performed using the Gaussian 98.[13]

Figure 1 shows the background mass spectrum without sample introduction. Nitrogen is highly detected as N_2Li^+ (*m/z* 35) due to the high concentration of N_2 in the reaction

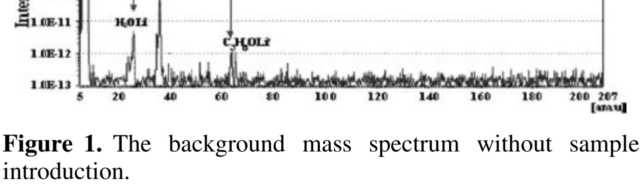

Figure 1. The background mass spectrum without sample introduction.

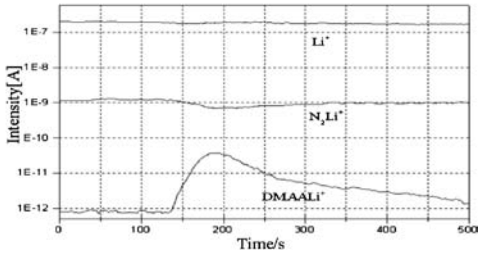

Figure 2. The detection of DMAA by SIM mode of IAMS: the intensity of Li^+, N_2Li^+, and $DMAALi^+$ with time increasing.

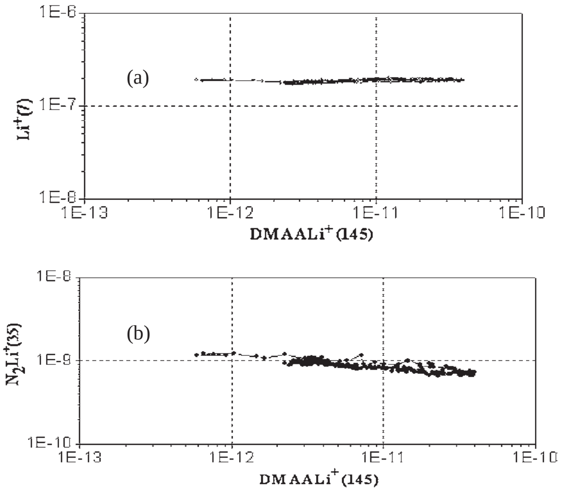

Figure 3. (a) The relationship of Li^+ and $DMAALi^+$ intensity. (b) The relationship of N_2Li^+ and $DMAALi^+$ intensity.

chamber. H_2OLi^+ (m/z 25) are derived from the ever-present water in the nitrogen gas. The m/z 65 peak is assigned as Li^+ attachment to the frequently used solvent acetone.

The intensity of Li^+, N_2Li^+, and $DMAALi^+$ measured by SIM mode are shown in Figure 2. Before DMAA introduction (from 0 to 140 s), the Li^+ and N_2Li^+ can be detected as same as background and the intensity of them is stable. After DMAA introduction, the intensity of N_2Li^+ is decreasing with the detection of $DMAALi^+$, and when the intensity of $DMAALi^+$ reaches to the highest point, almost at the same time, that of N_2Li^+ reaches to the lowest point. And then the intensity of N_2Li^+ returns to the background level gradually. Figures 3a and 3b indicate the intensity relationship of Li^+, $DMAALi^+$, and N_2Li^+, $DMAALi^+$ (from 140 to 190 s). The intensity of Li^+ has almost no change during $DMAALi^+$ detection. While, the intensity of N_2Li^+ is almost linearly decreasing, with the increasing of $DMAALi^+$. Therefore, these results suggest the possibility that $DMAALi^+$ would be produced by transferring Li^+ from N_2Li^+ to DMAA, and the "ion transfer" process exists in IAMS analysis. It was also considered that the reaction rate of termolecular reaction is much lower than that of ion-molecule reaction and the kinetic energy of the production can dissipate easily for exothermic reaction.

In order to investigate this possibility of Li^+ ion transfer, we also performed theoretical calculations of Li^+ binding energy of N_2 and DMAA (Table 1). The binding energy of Li^+ to N_2 is 12.25 kcal/mol, which is much lower than that of DMAA (60.57 kcal/mol). Previous studies indicate that the compound, which has lower Li^+ binding energy, would be easier to transfer Li^+ to the other compounds.[2–4] Therefore, for the observation of $DMAALi^+$, it is possible that DMAA reacts to N_2Li^+, due to high Li^+ binding energy of DMAA and high intensity of N_2Li^+ (Figure 1). Then more stable complex, $DMAALi^+$ and N_2, were produced, which well agree with the conclusion from previous SIM experiment.

Table 1. Li^+ binding energy of the complexes at B3LYP/6-311+G* level

Complex	Binding energy/kcal mol^{-1}
Li^+–N_2	12.2504
Li^+–DMAA	60.5691

From the experimental and calculational results, it was indicated that Li^+ transfer mechanism that N_2Li^+ transfers Li^+ to the sample molecule, would be also included in IAMS analysis (eqs 8 and 9).

$$Li^+ + N_2 \rightleftharpoons N_2Li^{+*} \tag{8}$$

$$N_2Li^{+*} + M \rightarrow MLi^+ + N_2 \tag{9}$$

This mechanism was thought to be suitable to not only DMAA, but also the other kind of sample, such as water and acetone which shown in Figure 1. More quantitative study for the ion attachment mechanism is desired in order to understand this process clearly. The well understanding of reaction mechanism of IAMS will be very important for the development and improvement of IAMS apparatus and the application of this technique, especially in the analysis of biochemical and environmental samples, such as organometallic compounds and diesel particles.

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