Atomic nitrogen adduct formation at sp^3 carbon in the electrospray ionization process

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Atomic nitrogen attachment to an sp^3 carbon during the electrospray ionization process was proved by experiments using $^{15}N_2$ and other evidence.

Electrospray ionization (ESI) has been adopted for the study of various small organic compounds as well as large biomolecules in recent years.[1–5] In the course of our mass spectrometric studies of unstable organic compounds in solution, we have found some unexpected mass shifts of 14 atomic mass units (u).‡ This phenomenon was observed in some aliphatic and aliphatic ether compounds containing sp^3 carbons (Fig. 1). Since this shift was found in compounds that mainly consisted of aliphatic moieties, the participation of a CH_2 unit was the most promising hypothesis to explain this mass difference. However, we propose here that atomic nitrogen attachment in the ESI process is the reason for this shift, based on several electrospray mass spectrometric studies including an $^{15}N_2$ experiment.

An electrospray is produced under atmospheric pressure using a strong electric field. This field induces a charge accumulation at the liquid surface located at the end of the nebulizing capillary, which will break to form highly charged droplets.[6–8] In this process, N_2 is frequently used as a sheath gas and sometimes as a drying gas to evaporate the droplets. Ionspray (IS), a form of electrospray using the sheath gas as a pneumatic nebulizer, made it possible to introduce relatively large amounts of solution.[9] The ionization of non-polar compounds is also possible using IS. This method was adopted for our study using N_2 as the sheath gas. A double focus tandem mass spectrometer equipped with an atmospheric ESI source was used for this experiment in order to obtain detailed characteristics of the single charged ion species to be discussed here. Typical conditions for the ESI measurement were as follows: acceleration voltage; 5 kV, resolution; 2000–5000, needle voltage (current); 2.5–5.0 kV (700 to $>$20000 nA), desolvation chamber temperature; 100 °C, sample flow; 7 mL h^{-1} and sheath gas flow; 1.5 l min^{-1} (JEOL, JMS–700T). The neat chemicals were sprayed without dilution. In the case of THF, for instance, the $[M + 14]^+$ ion is clearly detected using molecular nitrogen as a pneumatic nebulizing gas in the atmospheric ESI source, as can be seen in Fig. 1(*b*). The ions of *m/z* 71 $[THF - H]^+$ and 145 $[(THF)_2 + H]^+$ are also observed[10] in this spectrum. The results from ESI-MS experiments using $[^2H_{12}]$cyclohexane proved that the mass shift is not ascribed to the elimination and intermolecular attachment of CH_2 (14u) in cyclohexane itself [Fig. 2(*a*)]. A similar result was obtained from the experiment using $[^2H_8]$THF [Fig. 2(*b*)]. We could not help but consider that this shift might be caused by a nitrogen atom at this point.

It is strongly suggested that the attached nitrogen atom comes from the nebulizing gas because no ion signals corresponding to the atomic nitrogen adducts were observed in the experiment using Ar as a nebulizing gas. Moreover, using $^{15}N_2$ as the nebulizing gas (99.7 atom% ^{15}N), a clear mass shift of 15u was observed based on the generation of the $[THF + {}^{15}N]^+$ ion [Fig. 3(*b*)]. The ions assigned as monomeric and dimeric THF were not interfered with. The $^{15}N_2$ experiments for cyclohexane, Et_2O and n-hexane are also shown in Fig. 3.

These results prove the formation of an atomic nitrogen adduct during the ESI process. How does it happen? Does the generation of atomic nitrogen species under atmospheric electric discharge[11] constantly occur? Although this behavior is

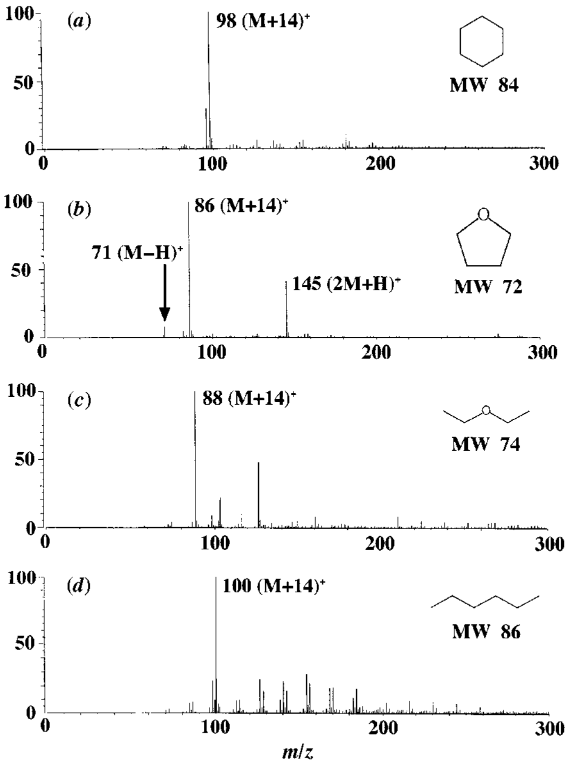


Fig. 1 Electrospray ionization mass spectra exhibiting mass shift of 14u; (*a*) cyclohexane, (*b*) THF, (*c*) Et_2O and (*d*) n-hexane

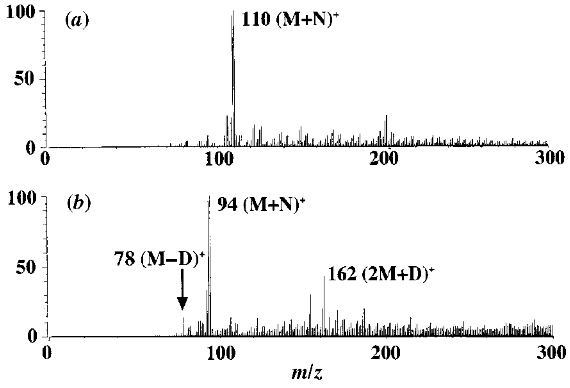


Fig. 2 Electrospray ionization mass spectum of (*a*) $[^2H_{12}]$cyclohexane and (*b*) $[^2H_8]$THF

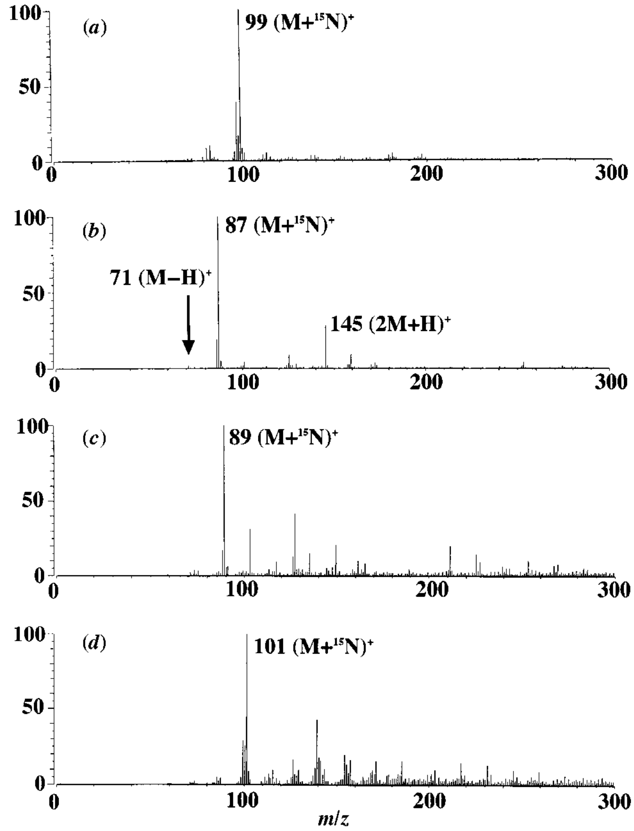
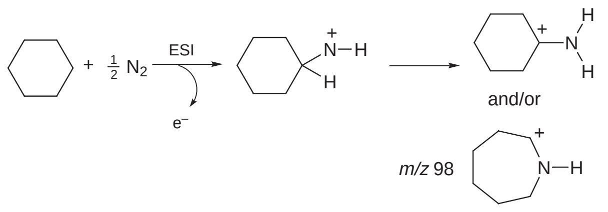


Fig. 3 Electrospray ionization mass spectra exhibiting mass shift of 15u using $^{15}N_2$; (*a*) cyclohexane, (*b*) THF, (*c*) Et_2O and (*d*) n-hexane

thought to be similar to that of the singlet nitrene,[12] a detailed mechanism and the structures of the products are unknown. A methoscopic cluster ion generated from an associative ionization is one of the possible adducts obtained from this process. However, this species is thought to contain a covalently bonded nitrogen because of the potent reactivity of absolute atomic nitrogen. Our result that atomic nitrogen attachment isn't observed in similar compounds that do not contain sp^3 carbons, such as furan and benzene, suggests particular reactivity of this species. In addition, we obtained an ESI mass spectrum of cyclohexylamine, which is identical to the spectrum of nitrogen-attached cyclohexane [Fig. 1(*a*)]. Thus, one of the probable structures of the nitrogen adduct in the case of cyclohexane is cyclohexylamine (Scheme 1).



Scheme 1

Detailed structure determination of this cation generated from the nitrogen attachment is our current task. We believe that the interpretation of various mass spectra displaying the unexpected mass shift of 14u will be made easier if the participation of atomic nitrogen attachment is taken into account.

In summary, atomic nitrogen attachment to sp^3 carbons in positive electrospray ionization mass spectrometry was observed. Experiments using $^{15}N_2$ and other evidence definitely suggest that the mass shift of 14u comes from an absolute nitrogen atom. This result points to a facile nitrogen fixation which will be useful in synthetic organic chemistry.[13]

Notes and References

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‡ The ion assigned as $[M - H]^+$ was observed together with $[2M + H]^+$. Constitution of a 14u shifted species was confirmed by exact mass measurements using these two peaks as the reference ions, *m/z* 86.0604 (C_4H_8NO requires 86.0606, $[THF + N]^+$).

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