

Specific Fragmentation of K-Shell Excited/Ionized Pyridine Derivatives Studied by Electron Impact: 2-Amino-3-methylpyridine and 3-Methylpyridine

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Fragmentation of 2-amino-3-methylpyridine has been investigated by electron impact in the carbon and nitrogen K-shell excitation regions with a comparison to that of 3-methylpyridine. Fragment ions were analyzed with a quadrupole mass spectrometer. Yields of the $NCNH_2^+$ and $C_5H_3^+/C_4HN^+$ fragment ions characteristically increase at the N 1s edge when compared to the C 1s excitation/ionization and valence ionization. This observation indicates that a valence electron forming the C–N bond in the pyridine ring is preferentially released through an Auger electron emission at the N 1s edge. The fragment ions produced via a hydrogen atom shift were observed as well.

Electron–molecule collisions drive many chemical processes relevant in various fields, such as planetary atmospheric physics,[1,2] plasma physics,[2,3] and radiation chemistry.[2] Importance of the processes is also recognized now in the rapidly advancing field of life sciences where damage of biomolecules can be caused by electrons as well as by radiation.[4,5] However, chemistry of the underlying processes is not yet fully understood. Various fragment ions can be produced by dissociative ionization of polyatomic molecules.

Fragmentation of molecules excited at the inner-shell levels has been the subject of great interest over the last two decades.[6] The localized nature of inner-shell electrons in a molecule enables the supply of energy into a specific site of the molecule. When an inner-shell electron is excited or ionized, the molecule dissociates into fragment ions through Auger decays. Since the valence electrons released in the Auger process originally lie in molecular orbitals partially overlapped with the inner-shell orbital, the main Auger process has also a local character. Much attention has been focused on the fragmentation process induced by the inner-shell excitation and ionization: An intriguing possibility is that the bonds around the excited atom are preferentially broken, i.e., site-specific fragmentation occurs.[6–14]

For the inner-shell excitation in gas phase site specificity is often found to be weak,[15] because the site-specific fragmentation occurs in competition with intramolecular flow of excess energy that is distributed within the molecule. The evidence was demonstrated in our previous studies on the inner-shell excitation of CF_3CN,[16,17] CF_3CCH,[18] $CH_3CO(CH_2)_nCN$ ($n =$ 0–3),[19] and CF_3COCH_3.[20] The extent of site specificity is correlated with the chain length of the molecules.[19,20]

In this paper we report the fragmentation processes of a heterocyclic molecule, 2-amino-3-methylpyridine, following the C 1s and N 1s excitation/ionization by use of a newly commissioned electron-impact reaction apparatus. Increase in the yield of some fragment ions produced through specific fragmentation channels was observed at the N K-edge. Support for the proposed fragmentation scheme was obtained by a similar experiment with 3-methylpyridine. The inner-shell excitation of pyridine has been reported in an inner-shell electron energy loss spectroscopy (ISEELS) study by Horsley et al.[21] and later by Hannay et al.[22] A near edge X-ray absorption fine structure (NEXAFS) study by use of synchrotron radiation has also been published recently by Kolczewski et al.[23] Electron impact ionization of pyridine was reported recently at electron energies of 10–200 eV.[24] However, to the best of our knowledge, no studies are found reporting the fragmentation of the inner-shell excited/ionized pyridine compounds. Published studies on the dissociation mechanism of pyridines were those by Ni and coworkers in the valence region.[25,26] They studied dissociation of pyridine[25] and 4-methylpyridine[26] by 193-nm laser excitation, and discussed the dissociation channels from the neutral excited states.

Experimental

The experiments were performed in an electron-impact reaction chamber equipped with a quadrupole mass spectrometer (Hiden Analytical, HAL-4•EQS-300). The electron beam for excitation was prepared by an electron gun (Yamamoto Shinku Lab., EG-50), which generates electrons with 200–2000 eV energy. The energy resolution is stated as 0.7 eV. The electron beam current was monitored with a Faraday cup placed downstream on the electron beam axis. The quadrupole mass spectrometer can be operated in a residual gas analysis, positive ion analysis, or negative ion analysis mode. We employed the positive ion analysis mode in order to extract and detect fragment ions produced at the interaction region in the chamber. The pressure in the spectrometer was about 2×10^{-9} Torr (1 Torr = 133.2 Pa) before measurements, which increased up to about 6×10^{-7} Torr when the effusive beam of sample gas was introduced into the reaction chamber. The sample gas is introduced through a leak valve and then a needle directs an effusive jet at an angle of 120° to the incoming electron beam. The axis of the spectrometer is orthogonal to both the needle and the electron beam.

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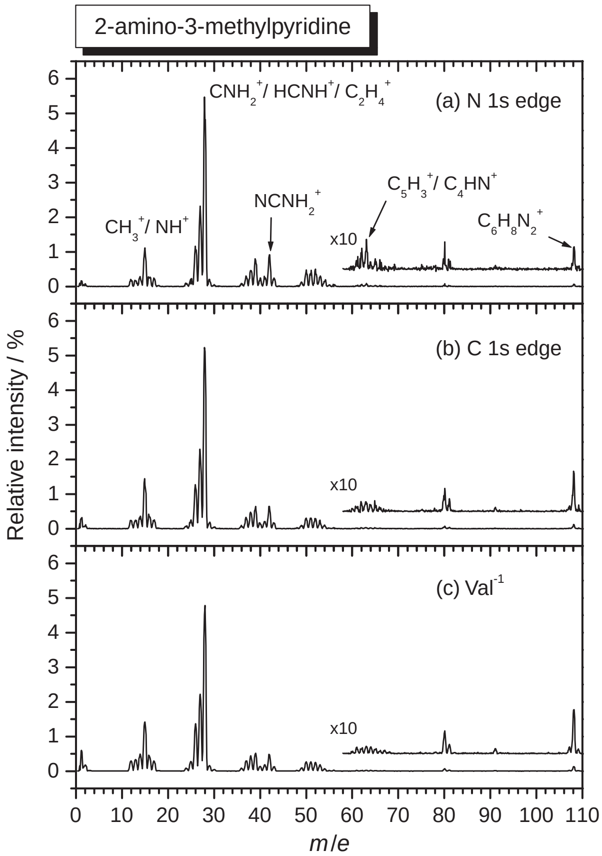


Figure 1. Mass spectra of 2-amino-3-methylpyridine obtained at the (a) N 1s and (b) C 1s edges, and at the (c) valence ionization. The spectra (a) and (b) were obtained by the difference between the above and below K-edges.

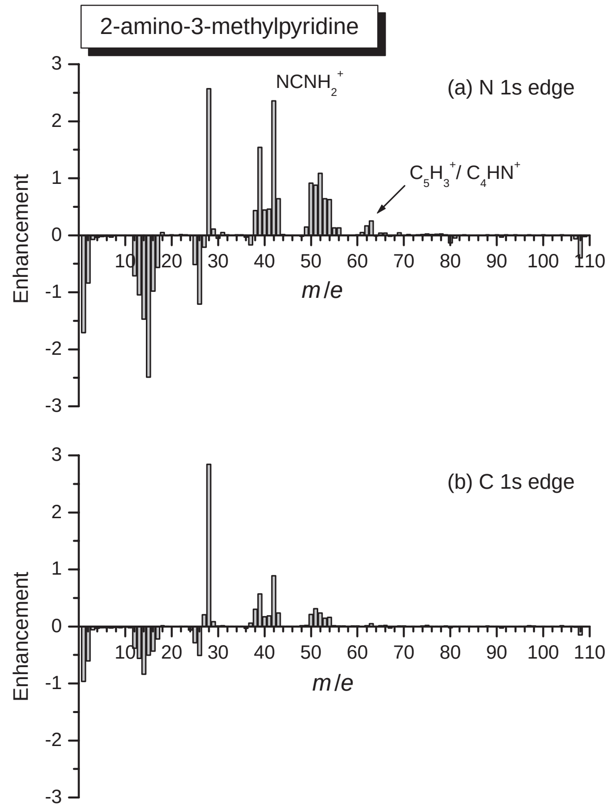


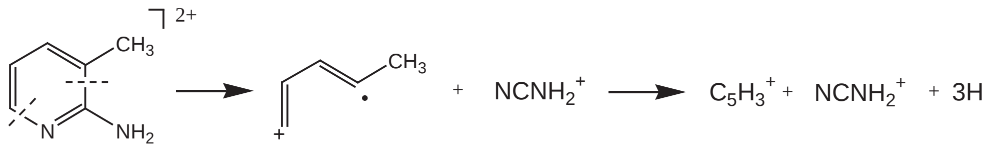
Figure 2. Enhancement of the yield of fragment ions produced by the (a) N 1s and (b) C 1s edges, relative to the yield of ions at the valence ionization. The enhancement is defined by the difference from the valence ionization spectrum and depicted as a bar chart.

Mass spectra of the ions produced by the K-shell excitation/ionization were acquired by a spectral difference method. That is, the mass spectra were first measured above the K-shell ionization threshold and then below the K-edge. Subtraction of the spectra between the above and below K-edges gives the mass spectrum of fragment ions produced at the energies of interest. The samples of 2-amino-3-methylpyridine and 3-methylpyridine were purchased from Wako Pure Chemical Industries, Ltd. and were carefully degassed under vacuum by repeated freeze–pump–thaw cycles.

Results

Figure 1 displays mass spectra of fragment ions of 2-amino-3-methylpyridine following the N 1s and C 1s excitation/ionization and valence ionization. The N 1s and C 1s ionization thresholds of 2-amino-3-methylpyridine have not been reported, but for pyridine they are 404.9 and 290.2–291.0 eV, respectively.[21,22] The mass spectrum at the N 1s edge was obtained by subtracting the raw spectrum at 390 eV from that at 408 eV, both of which had been normalized with electron beam intensities. The spectrum at the C 1s edge was obtained in a similar way from the data at 300 and 270 eV. The spectrum for the valence ionization was acquired at an electron energy of 200 eV. Prominent peaks observed were, in order of abundance, $m/e = 28$ ($CNH_2^+/HCNH^+/C_2H_4^+$), 27 ($HNC^+/HCN^+/C_2H_3^+$), 15 (CH_3^+/NH^+), 26 ($CN^+/C_2H_2^+$), 42 ($NCNH_2^+$), 39 ($C_3H_3^+/HC_2N^+$), etc. The assignment of the peak at $m/e = 42$ is discussed in the next section. The yields of ions with $m/e < 35$ are independent of excitation energy, while difference is found in the higher mass region: In particular, production of the ions corresponding to $m/e = 42$ ($NCNH_2^+$) and 63 ($C_5H_3^+$) is significant at the N 1s edge.

In order to get more insight into the effect of the inner-shell excitation/ionization, we plotted enhancement of the yield of the fragment ions produced by the N 1s and C 1s excitation/ionization, relative to the yield of ions at the valence ionization, in Figure 2. Enhancement is defined here by the difference of spectra between the K-shell excitation/ionization and valence ionization in Figure 1: For example, the spectrum of Figure 2a is the result of the subtraction of Figure 1c from Figure 1a. Positive and negative values mean an increase and decrease of the relative yields, respectively, compared with the yields at valence ionization energy. One can inspect a promotion effect by the inner-shell excitation/ionization on the fragmentation, with the mass spectrum at the valence ionization as a reference. Ion yields were calculated from the peak areas of the mass spectra, with totals normalized to 100. Peaks with higher m/e values increase, especially at the N 1s edge. The spectrum acquired in the C 1s edge region does not differ significantly from that at the valence ionization energy. This is due to almost equal probability of ionization of the C 1s electrons.



Scheme 1. Fragmentation of 2-amino-3-methylpyridine ion in Auger final states.

Discussion

The production of the ions at $m/e = 42$ ($NCNH_2^+$) and 63 ($C_5H_3^+$) is characteristic of the N 1s excitation/ionization. The following dissociation reactions are considered to occur for this finding. The K-shell ionized molecule decays in general through a normal Auger process emitting two valence electrons. The K-shell excited molecule decays through a resonant Auger process emitting an electron. The present N 1s excitation/ionization is followed by the cleavage of the N–C6 bond at the 1- and 6-positions and the C2–C3 bond given in Scheme 1 to produce the fragment ions:

$$CH_3–C_5H_3N–NH_2^{2+/+} \rightarrow NC–NH_2^+ + C_4H_3–CH_3^{(+)} \quad (1a)$$

$$CH_3–C_5H_3N–NH_2^{2+/+} \rightarrow NC–NH_2^+ + C_4H_3–CH_3^{(+)}$$
$$\rightarrow NC–NH_2^+ + C_5H_3^{(+)} + 3H \quad (1b)$$

Therefore, K-shell excitation/ionization of the N atom on the ring most probably induces the effective scission of the N–C bond. The data supporting this interpretation were obtained by a similar experiment with 3-methylpyridine. In this case, the following reactions will take place at the N 1s edge:

$$3\text{-}CH_3–C_5H_4N^{2+/+} \rightarrow NC–H^+ + C_4H_3–CH_3^{(+)} \quad (2a)$$

$$3\text{-}CH_3–C_5H_4N^{2+/+} \rightarrow NC–H^+ + C_4H_3–CH_3^{(+)}$$
$$\rightarrow NC–H^+ + C_5H_3^{(+)} + 3H \quad (2b)$$

Peaks at $m/e = 63$, 66, and 27 are expected to increase. Figure 3 shows mass spectra of fragment ions of 3-methylpyridine produced by the N 1s and C 1s excitation/ionization and valence ionization. Typical fragment ions in this case were, in order of abundance, $m/e = 28$ ($HCNH^+/C_2H_4^+$), 39 ($C_3H_3^+/HC_2N^+$), 38 ($C_3H_2^+/C_2N^+$), 27 ($HCN^+/C_2H_3^+$), and 26 ($CN^+/C_2H_2^+$). Production of ions with $m/e = 63$ and 65 is significant at the N 1s edge. This result strongly supports the mechanism that we propose and the specific fragmentation occurring at the N 1s edge. In the case of 3-methylpyridine, these two peaks can be produced by the cleavage of the N–C2 and C5–C6 bonds, and will be discussed elsewhere.[27] But it is not a specific fragmentation at the K-edge at least for 2-amino-3-methylpyridine, judging from the $m/e = 80$ peak in Figure 2.

The peak at $m/e = 42$ in the mass spectra of 2-amino-3-methylpyridine (Figure 1) is assigned not to $C_3H_6^+/C_2H_4N^+$ originating from the ring skeleton, but to $NCNH_2^+$. This is because the peak does not appear in the spectra of 3-methylpyridine (Figure 3). Moreover, $C_3H_6^+$ should come from $CH_2=CH–CH_3^+$, which is unlikely to be produced due to the migration of two H atoms. Similarly, the production of $C_2H_4N^+$ requires at least two H-shifts.

Intramolecular H migration was observed in both molecules. The peak of $m/e = 43$ in Figure 1 corresponds to the $H–NC–NH_2^+$ fragment formed through a rearrangement of the atomic hydrogen from the 6- to the 1-position. The same type of rearrangement is seen in the 3-methylpyridine case (Figure 3), where the fragment with $m/e = 28$ is assigned to $H–NC–H^+$. Another rearrangement is observed in the peak at $m/e = 67$ assigned to $CH_3–CH=CH–CH=CH^+$, which is formed by the H atom shift from the 2- to the 3-position followed by the C2–C3 and C6–N bonds breakage. This fragmentation is enhanced at the N 1s edge. This type of rearrangement cannot occur in the 2-amino-3-methylpyridine since it has no hydrogen atom at the 2-position.

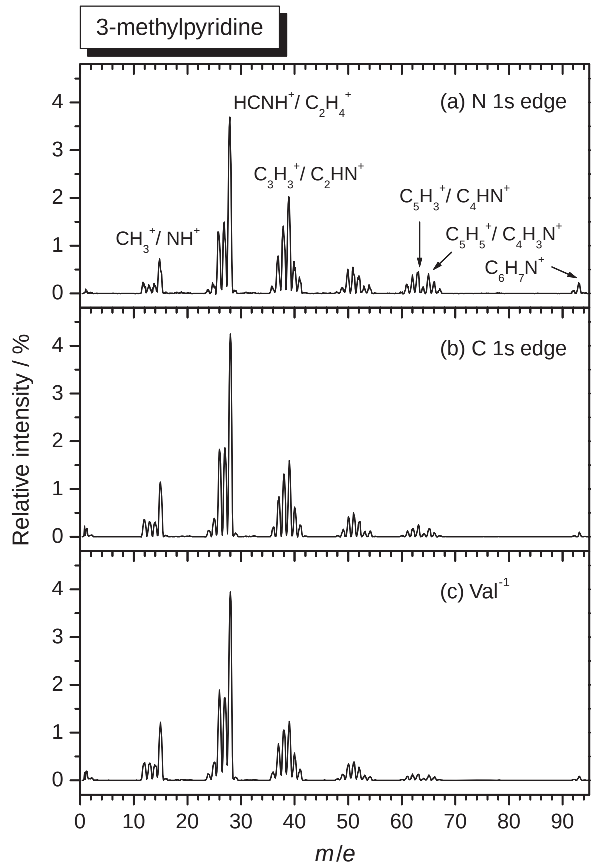


Figure 3. Mass spectra of 3-methylpyridine obtained at the (a) N 1s and (b) C 1s edges, and at the (c) valence ionization. The spectra (a) and (b) were obtained by the difference between the above and below K-edges.

The peak of $m/e = 39$ in the spectra of 2-amino-3-methylpyridine (Figure 1) is assigned to C_2HN^+ and/or $C_3H_3^+$. The peak increases at the N 1s edge. The C_2HN^+ fragment ion can be produced by the elimination of the amino group and the fission of the C2–C3 and C5–C6 bonds. The ion can also be formed by the fission of the N–C2 and C4–C5 bonds and the elimination of a hydrogen atom. The latter mechanism can exist in the fragmentation of 3-methylpyridine; the peak does appear in Figure 3. The $C_3H_3^+$ fragment also contributes to the peak, due to the presence of a series of peaks at $m/e = 36$–38.

A study on the dissociation of pyridine was reported by Lin et al., using a 193-nm laser.[25] They proposed rapid H-atom migration before dissociation in the photodissociation of deuterized pyridine. We think that fragmentation from ionized states of pyridine occurs through similar pathways, although in the present work we detected smaller ions formed by the fragmentation from the ions in Auger final states. Decay branching ratios to the Auger final states are presumed to be dependent on the inner-shell excited/ionized states. Bond cleavage around the N atom is induced through the Auger processes following the N 1s excitation/ionization, although site specificity is rather weak.

Summary

Fragmentation of 2-amino-3-methylpyridine has been studied at the N 1s and C 1s edges by electron impact. The fragment ions were analyzed with a quadrupole mass spectrometer. Increase in the yields of the $NCNH_2^+$ and $C_5H_3^+$ ions was characteristically observed at the N 1s edge. The excited/ionized molecule emits an Auger electron followed by breaking N–C6 and C2–C3 bonds to produce the fragment ions. The proposed mechanism is supported by the experiment with 3-methylpyridine. The spectrum acquired at the C 1s edge, on the other hand, does not differ significantly from that at the valence ionization energy. Bond cleavage around the N atom is induced through the Auger processes following the N 1s excitation/ionization, although site specificity is rather weak. Fragment ions formed through a hydrogen atom shift were observed as well.

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