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Specific fragmentation of the K-shell excited/ionized aniline molecule studied by electron impact

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ABSTRACT

Fragmentation of aniline upon K-shell excitation/ionization has been studied by the electron impact method. Ions detected as dominant fragments were $C_3H_3^+$, $CHNH^+/CNH_2^+$, $C_3H_2^+$, etc. The $C_3H_3^+$ ion was produced characteristically at the N 1s edge. We found from the mass spectra of aniline-2,3,4,5,6-d_5 that CD_3^+ is formed independent of excitation energy, suggesting that the aniline molecular cation isomerizes prior to dissociation. The mass spectra of the fragment ions by the direct dissociation of aniline were deduced by subtracting the contribution from the dissociation of the isomer, 4-methylpyridine. Enhancement of the $C_3H_3^+$, $CHNH^+/CNH_2^+$, and NH^+ yields at the N 1s edge shows that the cleavage of the C1—C2 bond of the initial benzene ring and the C—N bond fission are likely to take place by the N 1s excitation and ionization.

1. Introduction

Excitation of molecules at the K-shell level has attracted much attention for the last three decades, because site-specific fragmentation processes were observed in various molecular systems [1–15]. Inner-shell excited or ionized molecules dissociate into fragment ions following Auger electron emission. If the Auger decay process depends highly on the core-hole states, there is a high probability of producing fragment ions distinctive to the particular atomic site of excitation or ionization [16–18].

Recently, we have reported the site-specific fragmentation of the 2-, 3- and 4-methylpyridine molecules following the C 1s and N 1s excitation/ionization by electron impact [15]. Specific production of the C_2HN^+ and $C_5H_5^+/C_5H_6^+$ ions at the N K-edge reveals that the N—C2 and C4—C5/C5—C6 bond breakings of the pyridine ring is likely to occur following the N 1s excitation and ionization. *Ab initio* molecular orbital calculations indicate that the site specificity observed can be reasonably understood by the dissociation of the molecular dications in the most probable Auger final states.

This article reports the fragmentation of a structural isomer, aniline, with a nitrogen atom in the substituent group, induced by electron impact. Replacement of different positions in a target molecule with a heteroatom by changing molecules enables us to explore in more general the site-specific behavior of fragmentations of molecules. The main interest here lies in investigating if the site-specific fragmentations are observed in these molecular systems and whether the bonds dissociate around the excitation site.

To our knowledge, limited experimental studies have been reported on the spectroscopy of aniline in the K-shell region. Ohta and coworkers [19] observed the gas-phase X-ray photoelectron spectra of several mono-substituted derivatives of benzene including aniline. Oscillator strengths for the inner-shell excitation of aniline were reported by Hitchcock's group using inner-shell electron energy-loss spectroscopy (ISEELS) [20]. About a decade later, Duflot et al. [21] measured the spectra with higher resolution and gave a reliable assignment of the bands with the aid of *ab initio* configuration interaction calculations. The X-ray photoabsorption of condensed aniline was published by Luo et al. [22]. However, the mass spectrometric study on the fragmentation of aniline in the K-shell region has not been reported so far.

The article is organized as follows. Next section describes our experimental procedure. We then present the main results followed by the discussion. The mass spectra indicate that the $C_3H_3^+$ ion is produced characteristically at the N 1s edge, showing that the site-specific fragmentation occurs at this edge. The presence of the CD_3^+ peak for the aniline-2,3,4,5,6-d_5 sample suggests that the ring permutation leading to the 4-methylpyridine cation is involved in the dissociation of the aniline cation. Finally, we summarize the conclusions of this study.

2. Experimental

The experiments were performed in an electron-impact reaction chamber equipped with a quadrupole mass spectrometer (Hiden Analytical, HAL-4·EQS-300). Since the experimental setup and

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procedure have been described in detail previously [14], only a brief outline is given here. The electron beam for excitation was prepared by an electron gun (Yamamoto Shinku Lab., EG-50), which can emit electrons with the energy of 200–2000 eV. The energy resolution is stated as 0.7 eV. The electron beam current was monitored with a Faraday cup mounted downstream on the electron beam axis. An electrostatic potential of −50 V was applied at the extractor plate of the spectrometer in order to extract and detect fragment ions produced at the interaction region. The pressure in the chamber was kept at about 4×10^{-6} Torr (1 Torr = 133.2 Pa) during the measurements in which the effusive beam of sample gas was introduced. The measurements were also conducted for the sample where all the hydrogen atoms in the benzene ring have been replaced by deuterium (*i.e.*, aniline-2,3,4,5,6-d_5) in order to give unambiguous assignment among isobaric fragments for some mass-spectral peaks.

Mass spectra of ions produced by the K-shell excitation/ionization were acquired by a spectral difference method: 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 aniline and aniline-2,3,4,5,6-d_5 (minimum isotopic purity of 98% D) were obtained commercially (Aldrich Chemical Co., Inc.) and were carefully degassed under vacuum by repetitive freeze–pump–thaw cycles.

3. Results

Mass spectra of fragment ions of aniline and aniline-2,3,4,5,6-d_5 are displayed in Figs. 1 and 2, respectively. For each molecule the mass spectrum at the N 1s edge was obtained by subtracting the raw spectrum at 390 eV from the one at the 1000-eV electron energy, both of which had been normalized with electron beam intensities. On subtracting, efficiencies of ionization were taken into account by using the electron-impact ionization cross-sections. Since the cross-section data for aniline are not available, we assumed that they are approximated as those for benzene [23]. The spectrum at the C 1s edge was obtained in a similar way from the data at 390 eV and 270 eV. The spectrum for the valence ionization was acquired at the electron energy of 270 eV. The N 1s and C 1s ionization thresholds of aniline are 405.3 eV and 289.7–291.2 eV, respectively [19].

One finds from the mass spectra of *normal* aniline (Fig. 1) that the dominant fragments are, in order of abundance, the ions with $m/e = 39$, 28, 38, 27, 26, etc. Closer look at the spectra reveals the increase of the peak at $m/e = 39$ at the N 1s edge (Fig. 1a) compared with the data for the valence ionization (Fig. 1c). The prominent peaks in the mass spectra of *deuterated* aniline (Fig. 2) are $m/e = 42$, 28, 40, 29, and 30.

Assignment of these peaks to fragment ions can be given from these spectral patterns. Let us begin with the peaks at $m/e = 38$ and 39. It is apparent that the trend in the increasing yield with m/e in 36–39 in Fig. 1 corresponds to that of $m/e = 36$, 38, 40, and 42 in Fig. 2. The peaks at $m/e = 38$ and 39 can thus be assigned mostly to $C_3H_2^+$ and $C_3H_3^+$, respectively. Assignment of the peaks in $m/e = 26$–28 is, however, not as obvious as that of the peaks at $m/e = 38$ and 39.

We employed a multiple linear regression (MLR) analysis [24] for the assignment of $m/e = 26$–28. Based on the fact that there are only trace amounts of CH^+ in the fragmentation of deuterated aniline (Fig. 2), virtually no H/D exchange is presumed to occur: for aniline-2,3,4,5,6-d_5 no D atoms make bonds with N throughout the process. We also assume that isotope effect is not crucial for the ion yields. For example, the peak at $m/e = 27$ in the mass spectra of normal aniline consists of CNH^+, CHN^+, and $C_2H_3^+$, where the notation $CH_mNH_n^+$ represents that there are m hydrogen atoms bonded with carbon and n hydrogen atoms bonded with a nitrogen atom. That is, the yields of CNH^+ are equivalent between normal and isotope-substituted anilines, and the intensity of CHN^+ for normal aniline is the same as the CDN^+ component for deuterated aniline. Such conditions formulate a set of simultaneous equations with the yields containing experimental errors. The solution for the N K-edge data indicates that $C_2H_2^+$ comprises 85% of the intensity at $m/e = 26$ and the peak $m/e = 28$ contains 66% $CHNH^+$ and 21% CNH_2^+. The intensity at $m/e = 27$ is not attributed to a particular fragment ion, consisting of CNH^+, CHN^+, and $C_2H_3^+$ in the ratio 34:25:41. Although the number of significant figures is one according to the statistical analysis, two digits are given here for the purpose of later discussion. Also, we are aware that the assumptions introduced above may bring errors in the MLR analysis due to the isomerization described in the next section, and such errors may be significant for the higher-mass peaks for which we did not employ the MLR analysis.

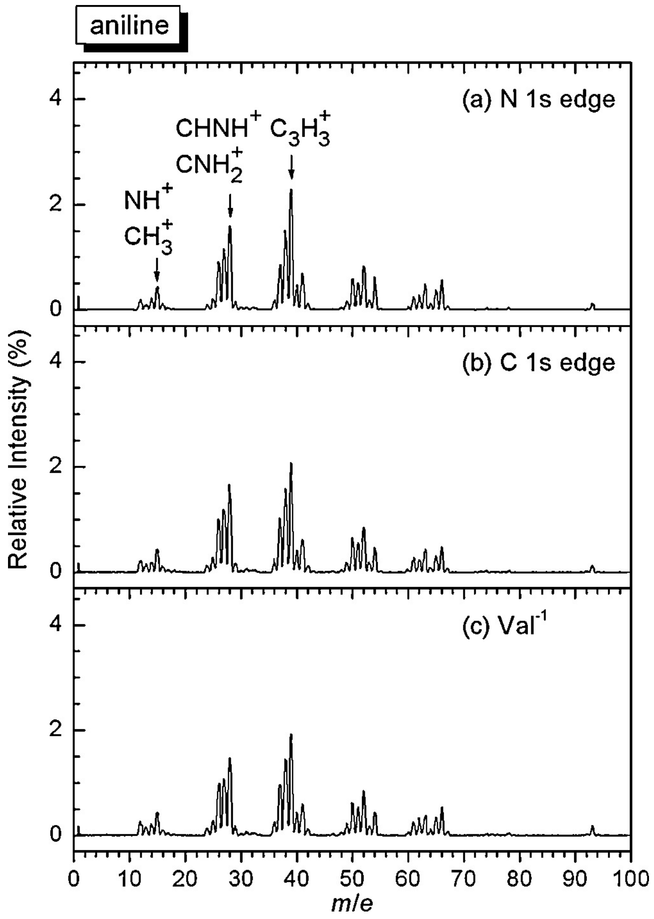

Fig. 1. Mass spectra of aniline acquired at the N 1s and C 1s edges (panels a and b), and at the valence ionization (panel c). The spectra (a) and (b) were obtained by the difference between the above and below K-edges.

The effect of the K-shell excitation/ionization on fragmentation can be clarified by an enhancement of the yield of the fragment ions relative to the mass spectral pattern obtained at the valence ionization. Enhancement of the yield of the fragment ions produced by the N 1s and C 1s excitation/ionization is shown in Fig. 3. The term "enhancement" here was defined in our previous studies [14,15]. That is, the spectrum of Fig. 3a is, for example, the result of the subtraction of Fig. 1c from Fig. 1a. Positive and negative values (as percentage points) mean an increase and decrease of the relative yields, respectively, compared with the yields for the valence