Near-Edge X-ray Absorption Fine Structure Spectra and Site-Selective Dissociation of Phenol

Yi-Shiue Lin,† Kun-Ta Lu,‡ Yuan T. Lee,‡ Chien-Ming Tseng,§ Chi-Kung Ni,‡,‖ and Chen-Lin Liu*†

†Scientific Research Division, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
‡Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan
§Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan
‖Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

ABSTRACT: A time-of-flight mass spectrometer with orthogonal acceleration and soft X-rays from synchrotron radiation were utilized to measure near-edge X-ray absorption fine structure (NEXAFS) spectra of carbon and oxygen in phenol and the corresponding ionic fragments following core excitation. The photon energies were in the range of 284–298 eV for the carbon K-edge and 529.5–554.5 eV for the oxygen K-edge. The total ion yield, ion intensity for each ionic fragment, and ion intensity ratio, defined as ion intensity divided by total ion yield, were measured as a function of photon energy. Possible mechanisms of dissociation are proposed and enhancements of specific products of dissociation are reported. In general, the enhancement of these specific products is small in the carbon K-edge region but is clear for some products at the oxygen K-edge. In particular, elimination of the H atom from the hydroxyl group was observed only at the oxygen K-edge. One remarkable result is that an excitation of a core-level electron of oxygen greatly enhanced the cleavage of specific C–C bonds.

INTRODUCTION

In the early 1920s the wavelengths of X-ray absorption edges were discovered to depend on the chemical environment of atoms of a particular element.1,2 Near-edge X-ray absorption fine structure (NEXAFS) spectra soon proved to provide a sensitive technique to determine accurately the electronic structure of matter and for chemical analysis.3–8 The range of shifts of soft X-ray absorption spectra for a given element due to varied chemical environments is from a few hundred millielectronvolts to several electronvolts. For instance, the C 1s → π* excitation for a carbonate is blue-shifted as much as 4 eV relative to that of an aldehyde.9

When molecules are irradiated with X-rays, one core electron is excited to a valence orbital or directly ionized, forming a hole in the inner shell of the atom. The excited molecules then undergo Auger decay or photon emission. Auger decay is the major channel because fluorescence yields for carbon and oxygen atoms are typically small (0.2575% and 0.6909%, respectively).10 After emission of one or two electrons following Auger decay, the resulting molecular ions are mostly unstable and dissociate into charged and neutral fragments. Eberhardt and co-workers first observed a site-specific fragmentation upon core excitation.11,12 Selective bond breaking on excitation of inner-shell electrons of a chosen atom has received increasing attention,13–16 in part due to the availability of a third-generation synchrotron light source.17–22 Site-selective fragmentation using core–electron excitation has been observed for several molecules in gaseous samples as well as on surfaces.23–31 Two instances of site-specific dissociation of a gaseous sample are CF3CH3 and CF2CH2 reported by Klaus and co-workers;32 ions containing fluorine atoms (CF3+, CF2H+, and CF2+) are dominant products when the core of carbon connected to hydrogen atoms is excited. These observed phenomena demonstrate that chemical bonds near the excited atom have a greater probability of cleavage. Poly(methyl methacrylate) (PMMA) is an example of site-specific dissociation on a surface. When a core electron of oxygen is excited to σ*(O–CH3), cleavage of the O–CH3 bond is enhanced, but the C–OCH3 bond is more likely to break when the core electron is excited to σ*(C–OCH3).21

Site-specific fragmentation of aromatic molecules has been found for 2-amino-3-methylpyridine,33 2-fluoropyridine,34 and pyrimidine derivatives35–38 following excitation of electrons from C 1s and N 1s orbitals. The dissociation of phenol is of great interest39–43 because phenol is the chromophore of amino acid tyrosine. Excitation of an electron from the O 1s orbital or C 1s orbital of a carbon atom attached to an oxygen atom in phenol is expected to show site-specific dissociation. In this work, we investigated NEXAFS spectra of carbon and oxygen in gaseous phenol and the dissociation channels following core excitation, focusing attention on ionic products from site-specific or bond-specific dissociation.

EXPERIMENTS

A new reflectron time-of-flight mass spectrometer with orthogonal acceleration (OA-R-TOF MS) was constructed in...
Taiwan Light Source, National Synchrotron Radiation Research Center. Figure 1 shows a schematic diagram of this apparatus that includes a source chamber, an ionization chamber, and a detection chamber. For clarity of depiction, this figure is not drawn to scale according to real instruments. An effusive molecular beam was generated in the source chamber. Molecules were ionized in the ionization chamber. Ions were accelerated by the electric field of the ion optics (collector) then collimated with the ion lenses in the ionization chamber. Masses were analyzed with a reflectron time-of-flight mass spectrometer with orthogonal acceleration in the detection chamber. The soft X-rays crossed the effusive molecular beam in the ionization chamber. The direction of propagation of the soft X-rays was perpendicular to the effusive molecular beam and perpendicular to the plane of the figure.

Figure 1. Schematic diagram of the apparatus. For clarity of depiction, this figure is not drawn to scale according to real instruments. An effusive molecular beam was generated in the source chamber. Molecules were ionized in the ionization chamber. Ions were accelerated by the electric field of the ion optics (collector) then collimated with the ion lenses in the ionization chamber. Masses were analyzed with a reflectron time-of-flight mass spectrometer with orthogonal acceleration in the detection chamber. The soft X-rays crossed the effusive molecular beam in the ionization chamber. The direction of propagation of the soft X-rays was perpendicular to the effusive molecular beam and perpendicular to the plane of the figure.

The effusive molecular beam of phenol was generated in the source chamber from a sample cell with an orifice of diameter 0.15 mm. The sample cell was kept at 308 K; the pressure of phenol inside the cell was estimated to be 0.8 Torr. The diffused molecular beam was collimated with a skimmer (2 mm diameter) located 8 mm downstream from the sample cell before it entered the ionization chamber. The skimmer separated the source chamber from ionization chamber and kept the pressure of ionization chamber low. During the experiment the pressures in the source chamber and ionization chamber were 2.7 × 10⁻⁶ and 1 × 10⁻⁶ Torr, respectively.

Soft X-rays from synchrotron radiation were directed into the ionization chamber with a pair of bendable refocusing Kirkpatrick–Baez mirrors coated with Au and were focused at the effusive molecular beam. The propagation direction of the soft X-rays was perpendicular to the effusive molecular beam. Soft X-rays crossed the diffusive molecular beam 20 mm downstream from the skimmer. The crossing point of the soft X-rays and effusive molecular beam was located inside an ion optics (collector). Molecules ionized with X-ray photons dissociated into ionic fragments when a large internal energy was left in the cations. Ions (parent ions or ionic fragments) generated with soft X-rays were accelerated by the electric field of the ion optics (collector) and pushed into the ion lens region; collimated with the ion lenses, they flew through a rectangular hole that separated the ionization chamber and detection chamber before entering the ion-acceleration region of a rectangular time-of-flight mass spectrometer with orthogonal acceleration in the detection chamber. The rectangular hole (8.8 × 40 mm²) was designed so that most collimated ions would pass through it, but it also kept the pressure in the detection chamber about one tenth that in the ionization chamber. During the experiment the pressure in the detection chamber was 4.3 × 10⁻⁶ Torr. Voltages applied on the ion optic (collector) and ion lenses were adjusted to optimize the mass resolution. Ion trajectories simulated with SIMION (version 8.1 by Scientific Instrument Services) showed that ions with kinetic energy less than 3 eV can be 100% collected and sent to the detection chamber. The collection efficiency decreased as the ion kinetic energy increased for ions with kinetic energy greater than 3 eV. Ions with kinetic energy greater than 3 eV and velocity nearly perpendicular to the axis of the ion lens were not collected.

When ions flew into the ion-acceleration region, a pulsed voltage was applied on the extraction plate and ions were accelerated along the axis perpendicular to their initial direction of motion. The repetition rate of the pulsed voltage was 50 kHz. Each voltage pulse generated a mass spectrum. The results were the accumulation of 1 × 10⁶ mass spectra in each step (50 meV/step) at the carbon K-edge and 4 × 10⁶ mass spectra in each step (150 meV/step) at the oxygen K-edge. All ions were accelerated to 15.8 keV before they reached the detector. Ions were detected with a chevron-configured microchannel-plate (MCP) detector (95 × 42 mm²). The large kinetic energy of ions ensured that the discrimination between various ions was minimized. Xe ions generated from X-rays, of which m/z ranged from 21 to 134 u for various Xe isotope ions with charges 1−6, served for mass calibration.

The output signal from the MCP was amplified with a preamplifier and recorded with a rapid time-of-flight multiscaler (FAST ComTec, model P7888) with 2 ns bin width. The probability of two ions of the same m/z arriving the detector at the same time was small (10⁻⁶) because of the small X-ray photon flux. A counting technique was utilized to accumulate the signal; a discrimination level was set to obtain an optimal signal-to-noise ratio.

As details of the synchrotron radiation beamline have been reported, only a brief description is provided here. This beamline delivers >10¹² photons/s with energy in the 60−1400 eV range. Energy resolution (ΔE/E) might be as great as 20,000, depending on the widths of open slits and the grating. In this experiment, energy resolutions were about 150 meV at the carbon K-edge region and 250 meV at the oxygen K-edge region. The size of the beam spot was 0.4 mm ×0.2 mm at the interaction with the diffusive molecular beam. The photon energy was calibrated with absorption spectra of CO₂ for both the carbon K-edge (290.77 eV) and the oxygen K-edge (535.4 eV).³¹,⁴⁹−⁵⁴

Phenol (Sigma Aldrich, 99%) was purified with three freeze−thaw cycles to remove the impurities in the sample cell.

RESULTS

Carbon K-edge. The total ion yield (TY) of phenol NEXAFS spectra at the carbon K-edge from 284 to 298 eV is shown in Figure 2. To assign the spectra, we compared the reported spectra of benzene,³⁵−³⁸ aniline,⁵⁶,⁶⁰ and phenol.⁵⁶,⁶¹ Duflot and co-workers analyzed a high-resolution NEXAFS spectrum of benzene utilizing electron energy loss.⁵⁵,⁶²−⁶⁶ The first intense absorption of benzene at 285.2 eV is assigned as the transition 1s → π⁰. A small absorption at 287.24 eV is attributed to the transition 1s → 3σ in which the latter MO is composed mostly of a₁(C→H). The major feature at 289.09 eV is assigned to arise from an excitation to Rydberg states. The following lines (290.6 and 293.8 eV) are assigned as excitation of a core electron to σ⁰, Rydberg states, or a mixture of both;
the core ionization threshold was found to be 290.3 eV.\textsuperscript{55,62–69} When one hydrogen atom of benzene was replaced by an amino group or a hydroxyl group, the absorption signal of the carbon atom beside the nitrogen or oxygen atom was blue-shifted by 1.5 or 1.8 eV, respectively.\textsuperscript{56} On comparison with the spectra of benzene, aniline, and phenol previously investigated, the two major absorption lines of phenol centered at 285.4 and 287.1 eV were assigned as 1s $\rightarrow$ $\pi^*$ of C$_2$–C$_6$ and a mixture of 1s $\rightarrow$ $\pi^*$ of C$_1$ and 1s $\rightarrow$ 3s$\sigma^*$ of C$_2$–C$_6$, respectively. C$_n$ (n = 1–6) denotes the position of carbon atoms in phenol, as shown in Figure 2. The broad line at 288.9 eV is composed of transitions from a core level to Rydberg states and $\sigma^*$ orbitals. Beyond 290.4 and 292 eV, C$_2$–C$_6$ and C$_1$, respectively,\textsuperscript{56} were directly ionized. These assignments are listed in table 1.

Figure 3 shows the mass spectra of product ions from phenol excited at various photon energies at the absorption signals in our NEXAFS spectrum. The major product ions are similar, although the relative intensities vary with the photon energy. Of the ion intensities as a function of photon energy for several major product ions in Figure 4, most show large intensities at 285.4 and 287.1 eV attributed to the resonant excitation shown as the lines in the NEXAFS spectrum at these two energies. A small signal centered at 288.9 eV in Figure 2 can also be observed for some ions.

To reveal the phenomena of specific dissociation following core excitation, the ion intensity ratios, defined as ion intensity for each ion in Figure 4 divided by the total ion intensity in Figure 2, are shown in Figure 5 for major product ions. In the following paragraphs, we propose possible compositions of ions and mechanisms of dissociation.

Two lines located at 285.4 and 287.1 eV, observed for parent ion (with m/z = 94 u), represent a large probability of no cracking and no second ejection of an electron after ionization.

Table 1. Assignments of Absorption Lines and Ionization Energies of Core Excitation\textsuperscript{a}

<table>
<thead>
<tr>
<th>Carbon K-edge</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>285.4 eV</td>
<td>1s $\rightarrow$ $\pi^*$ of C$_2$–C$_6$</td>
</tr>
<tr>
<td>287.1 eV</td>
<td>1s $\rightarrow$ $\pi^<em>$ of C$_1$ and 1s $\rightarrow$ 3s$\sigma^</em>$ of C$_2$–C$_6$</td>
</tr>
<tr>
<td>288.9 eV</td>
<td>1s $\rightarrow$ 3s$\sigma^*$ of C$_2$–C$_6$ and 1s $\rightarrow$ Rydberg states of C$_2$–C$_6$</td>
</tr>
<tr>
<td>290.5 eV</td>
<td>1s $\rightarrow$ Rydberg states and $\sigma^*$</td>
</tr>
<tr>
<td>290.4 eV</td>
<td>IP of C$_2$–C$_6$\textsuperscript{56}</td>
</tr>
<tr>
<td>292 eV</td>
<td>IP of C$_1$\textsuperscript{56}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxygen K-edge</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>535.52 eV</td>
<td>1s $\rightarrow$ $\sigma^*$</td>
</tr>
<tr>
<td>537.98 eV</td>
<td>1s $\rightarrow$ $\sigma^<em>$ and 1s $\rightarrow$ $\sigma^</em>$ of C$_1$–H\textsuperscript{61}</td>
</tr>
<tr>
<td>540 eV</td>
<td>1s $\rightarrow$ $\sigma^*$ or Rydberg states$^{61,67}$.</td>
</tr>
<tr>
<td>538.90 eV</td>
<td>IP$^{67}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The locations of the lines were the positions of maximum absorption. The uncertainty due to energy resolution of the light source, overlap of some transitions, and initial and final vibrational states were estimated to be slightly greater than the energy resolution of the light source (150 meV for the carbon K-edge and 250 meV for the oxygen K-edge).
The intensity of the second line is slightly smaller than that of the first line. The first line represents excitation \(1s \rightarrow \pi^*\) of C2–C6, followed by ejection of an Auger electron that takes away most energy. The energy left for some phenol cations is so small that their dissociation does not occur, resulting in parent ions. The second line represents an excitation of a mixture of \(1s \rightarrow \pi^*\) of C1 and \(1s \rightarrow 3s\sigma^*\) of C2–C6. For the excitation to a \(\pi^*\) unoccupied orbital, an Auger electron might also remove most energy, resulting in the production of parent ions. Molecules excited to a \(\sigma^*\) orbital might, in contrast, dissociate rapidly into fragments because of the antibonding character of the \(\sigma^*\) orbital. As a result, the intensity of the second line in Figure 5, at 287.1 eV, is smaller than the intensity of the first line, at 285.4 eV. The intensity of the parent ion becomes small when the photon energy exceeds the core ionization threshold because most ions either become doubly charged cations and appear at \(m/z = 47\) u or dissociate into two cations.

An ion with \(m/z = 47\) u represents the doubly charged parent ion \((C_6H_5OH^{2+})\) that is the only possible composition. The ion intensity ratio, illustrated in Figure 5, shows that the generation of doubly charged parent ions is greatly enhanced for a photon energy greater than the core ionization threshold (290.4 eV). This observation is rationalized from the fact that direct core ionization followed by ejection of an Auger electron (normal Auger decay) can readily generate doubly charged ions. The presence of such doubly charged parent ions indicates that some Auger electron takes away most energy such that some doubly charged ions are stabilized. Although spectator or participant Auger decay was the dominant process for photon energy less than the ionization energy (290.4 eV) whereby singly charged parent ions were typically formed, we observed doubly charged parent ions (with \(m/z = 47\) u) also for photon energy less than the ionization energy, 290.4 eV, likely because of autoionization following Auger decay.

A fragment ion with \(m/z = 77\) u \((C_6H_5^+)\) resulted from cleavage of the C–O bond through OH elimination, and fragment ions with \(m/z = 72–76\) u represented elimination of additional H atoms following cleavage of that C–O bond. The possible compositions are listed in Table 2. A possible dissociation channel is shown in Figure 6a. Among these fragments, enhancement phenomena were observed only for those with \(m/z = 74\) and \(75\) u \((C_6H_4^+\) and \(C_6H_3^+)\); the signal of \(C_6H_2^{2+}\) had the largest intensity. Although it is expected that the excitation of a C1 core electron at 287.1 eV has a larger probability to break the C–O bond, no enhancement of this fragment ion was observed in this region. A small broad line centered about 289.5 eV was observed, but no line with a large intensity ratio was found for this fragment in Figure 5. The broad line is near the excitations C2–C6 C1s \(\rightarrow\) Rydberg states, C1 C1s \(\rightarrow 3s\sigma^*\), and another transition to \(\sigma^*\) orbitals, but no clear site-specific dissociation is assignable.

Fragment ions with \(m/z = 60\) \((C_6^+)\), \(61\) \((C_5H^+)\), \(62\) \((C_5H_2^+)\), and \(63\) u \((C_5H_3^+)\) resulting from the elimination of COH with additional H atoms require the cleavage of both C–C bonds connecting carbon atom C1 shown as in Figure 6b. The excitation of a C1 core electron at 287.1 eV is expected to have a larger probability to generate these fragments when a site-
specific dissociation occurs, but the enhancements are not limited to this photon energy. The enhancements were observed at 285.5, 287.6, and 289 eV for \(m/z = 63\) u (C\(_2\)H\(_2\)+). For those involving loss of more hydrogen atoms (\(m/z = 62, 61,\) and \(60\) u), the enhancements were not clear, but a broadened small enhancement centered at 290 eV was observed. The other fragment of this dissociation channel is COH, which might exhibit the same intensity and intensity ratio if the positive charge were equally located at each side of the fragment. The intensity ratio of the COH+ ion differs markedly, however, from that for \(m/z = 60–63\) u, as shown in Figure 4 and 5.

Fragment ions with \(m/z = 66\) (C\(_3\)H\(_2\)O+ or C\(_4\)H\(_5\)O+) and \(65\) u (C\(_3\)HO+ or C\(_4\)H\(_4\)O+) can result from the elimination of C\(_2\)H\(_2\) with an elimination of additional H atoms or from elimination of CO and COH, respectively. The corresponding possible bond cleavages involving loss of C\(_2\)H\(_2\) are shown in Figure 6c1,c2. The elimination of C\(_2\)H\(_2\) can include the cleavage of chemical bonds connected to C1 or exclude the cleavage of chemical bonds connecting to C1. Elimination of CO from a phenol cation has a small barrier,\(^70\) it was also observed in electron-impact ionization.\(^71\) Again, CO elimination requires the cleavage of both C–C bonds connected to C1. The feature of ion intensity ratios at \(m/z = 65\) and 66 u are similar: enhancement was not limited to the corresponding excitation (287.1 eV) but existed at both 285.4 and 287.1 eV. One possible explanation is that these fragment ions include at least C\(_2\)H\(_2\) elimination.

The dominant products are C\(_3\)H\(_3\)O+ (with \(m/z = 39\) u) and related fragments (C\(_4\)H\(_4\)+, C\(_5\)H\(_5\)+, and C\(_6\)H\(_6\)+) with \(m/z = 36–38\) u. To generate cation C\(_3\)H\(_3\)O+, cleavage of two C–C bonds is necessary; these bonds might be C1–C2 and C4–C5, or C2–C3 and C5–C6, as in Figure 6e. The former includes a chemical bond connecting atom C1, but the latter is unrelated to atom C1; as a result, enhancement is expected at both 285.4 and 287.1 eV. The enhancement is large for C\(_3\)H\(_3\)O+ at both 285.4 and 287.1 eV. The enhancement was small for C\(_4\)H\(_4\)+ and zero for C\(_5\)H\(_5\)+ and C\(_6\)H\(_6\)+. Almost no enhancement was observed for the other fragment of this channel, i.e., C\(_2\)H\(_2\)O+ (with \(m/z = 55\) u), indicating that the positive charge is not located equally on each side during dissociation.

For the other fragments, both the ion intensity and the enhancement from bond-specific dissociation are small; we accordingly omit discussion thereof.

**Oxygen K-edge.** The total ion yield mode of the NEXFAS spectrum is shown in Figure 7. This spectrum comprises two lines at 353.52 and 337.98 eV and a broad line centered about 540 eV. The line at 353.52 eV was assigned as 1s → σ* of which the molecular orbital is significantly composed of a carbon 2p orbital.\(^67\) Although Francis and Hitchcock assigned this line as exciting to π*, there is also a contribution of 1s → σ*\(^{61,67}\). Prince and co-workers compared the spectra and theoretical calculation of tautomers of guanine; the structures of the two tautomers are similar to that of phenol. They assigned the first line to a transition between a core electron in oxygen and Rydberg states (3s orbital) coupled with an unoccupied π* molecular orbital.\(^4\) The line at 337.98 eV was assigned as 1s → π*\(^{61,67}\) or as excitation to Rydberg states.\(^4\) The broad line centered at 540 eV marks the transition to π* or Rydberg states as well as a continuum range beyond the ionization energy.\(^4,61,67\) Some small lines appeared about 545 eV, but no assignment was reported.\(^81,87\) The assignments and ionization energy of oxygen atom are listed in table 1.

Shown in Figure 8 are mass spectra of phenol excited at specific energies; these mass spectra are similar to those from the carbon K-edge excitation. One interesting difference is that fragment ion C\(_4\)H\(_2\)O+ (\(m/z = 93\) u), corresponding to the elimination of one H atom, was clearly observed only from excitation at the oxygen K-edge. Strong intensity of a fragment ion was observed also before the photon energy reached that of excitation of the oxygen core electron. This result is attributed
to an absorption tail of a core electron of a carbon atom, but the absorption cross section is about one tenth that at 290 eV.

Intensities and intensity ratios as a function of photon energy of major product ions are shown in Figure 7 and 9, respectively. Bond-specific dissociations observed from the ion intensity ratio in this region of photon energy are classified into three groups: one with enhancement at 535.5 eV, including ions with \( m/z = 93 \) (C₆H₅O⁺), 65 (C₅H₀⁺ or C₅H₂⁺), 63 (C₅H⁺), and 39 u (C₃H₃⁺), another with enhancement about the broad line from 536 to 541 eV, including \( m/z = 74 \) (C₆H₂⁺), 61 (C₅H⁺), and 50 u (C₄H₂⁺), and a third group with enhancement at both lines exhibited by ions \( m/z = 62 \) (C₅H₂⁺) and 38 u (C₃H₂⁺).

If a site-specific dissociation of a bond occurs on excitation of an oxygen core electron, fragments corresponding to cleavage of O–H and C–O bonds are expected to have large ion-intensity ratios (Figure 9). Fragments related to these bond cleavages are ions C₆H₅O⁺ (\( m/z = 93 \) u, O–H bond cleavage) and C₅H⁺ (\( m/z = 74 \) u, cleavage of C–O and a subsequent elimination of additional H atoms). Enhancements were found for these two fragment ions: C₆H₅O⁺ ions have a large enhancement at 535.5 eV and were clearly observed only from excitation at the oxygen K-edge. C₅H⁺ ions have enhancement from 537 to 545 eV. Although the other fragment ions have also a significantly enhanced ratio of ion intensities, for example, ions C₅H₂⁺, C₄H₂⁺, C₄H⁰⁺, and C₃H²⁺ at photon energy 535.5 eV, the mechanism of ion generation of these...
fragments excludes the chemical bond directly connecting the O atom.

**DISCUSSION**

Specific dissociations are generally separated into two types: element-specific and site-specific. This classification is attributed to the excitation of separate elements and varied chemical environments of the same elements, respectively. A possible mechanism leading to a specific dissociation is the localization of excitation and rapid dissociation following a core excitation and an Auger decay. If the final state after Auger decay is localized at one specific atom or chemical bond and the rate of dissociation is greater than that of energy redistribution, dissociation is more likely to occur around this excited atom. One example is the excitation to a σ* orbital of a specific chemical bond. If this electron stays in this antibonding orbital even after Auger decay, the antibonding characteristic results in rapid dissociation along this chemical bond. In contrast, if the redistribution of the intramolecular energy is more rapid than dissociation, excess energy is distributed to all degrees of freedom, which results in dissociation according to statistical predictions. The branching ratios among various dissociation channels are hence expected to vary slowly with the photon energy.

A major absorption line of phenol centered at 287.1 eV is assigned as a mixture of transitions 1s → π* of C1 and 1s → 3σ* of C2–C6. The transition 1s → 3σ* of C2–C6 can greatly enhance the cleavage of a chemical bond connecting carbon atoms C2–C6. We observed only a small enhancement of the ion intensity ratio at this photon energy for ions with m/z = 39 (C6H5O+), 50 (C6H4+), 63 (C6H3+, elimination of COH with additional H atoms elimination), and 65 u (C6H4+, elimination of COH). The generation of these ions is related to the cleavage of a chemical bond connecting carbon atoms C2–C6. The broad line at 288.9 eV is assigned as a mixture of an excitation to Rydberg states from a core electron of C2–C6. The transition 1s → 3σ* of C1 favors the cleavage of a chemical bond connecting C1. The cleavages of specific bonds at this photon energy involve fission of the C1–O bond generating an ionic fragment C6H5+ (m/z = 74 u) and fission of the C1–C2 bond resulting in an ion C6H4+ (m/z = 50 u). This enhancement is also small, but large enhancements were found for ions C6H3+, C6H4+, C6H5+, C6H4O+, and C6H5O+ at 285.4 eV (assigned as 1s → π* of C2–C6). The generations of these fragments are related to the cleavage of chemical bonds connecting carbon atoms C2–C6. Although no antibonding orbitals are involved directly in the core excitation, a large enhancement of the ion ratio at this photon energy indicates that the energy left after an Auger decay is localized around the initially excited atoms.

The spectrum at the oxygen K-edge comprises two lines at 535.52 and 537.98 eV and one broad line centered about 540 eV. The signal at 535.52 eV is assigned as 1s → π*. Enhancements of the ion intensity at this photon energy were found for C6H5O+ (H atom elimination), C4H5O+ or C4H5O+ (m/z = 65 u), C6H5+, C6H4+, and C6H3+. Only the fragment C6H5O+ is related to the cleavage of a chemical bond connecting the O atom. The line at 537.98 eV is assigned as 1s → π* or excitation to Rydberg states. The enhancement of the ion intensity at this photon energy involves ions C6H5+, C6H4+, and C6H3+. Only fragment C6H5+ (elimination of OH and additional elimination of three H atoms) is related to the chemical bond connecting the O atom.

Specific dissociation was defined also as the ion intensity difference between core excitation and ionization with electron impact at energy 70 eV. The major fragment ions of phenol obtained from such ionization include the parent ion and those with m/z = 39, 40, 65, and 66 u. Ions with m/z = 26, 27, 29, 37, 38, 47, 50, 51, 53, 55, 61–64, 67, and 74 u have small intensities. Compared to our result, many product ions (CHO+, C3H4+, CH2O+, C4H5OH+, C6H4+, C6H5+, C6H4+, C6H3+, C6H2+, C6H+, and C6H5O+) are enhanced through specific dissociation at both carbon and oxygen K-edges. In particular, an elimination of a H atom from the phenol cation (C6H5O+ with m/z = 93 u) was not observed from ionization with electron impact, but was observed following a core excitation of oxygen, which indicates that a core excitation of oxygen can specifically break the O–H bond.

Nguyen and co-workers measured the mass spectrum of ionized phenol following collisional activation (8 keV) in a nitrogen cell. The main product ions (with m/z = 26, 29, 39, 50, 55, 63, 65, 74 u) are similar to those from core excitation, although the corresponding intensities differ. The mass spectrum with the greatest abundance of an ionic product with m/z = 65 u and the next greatest abundance of an ion product with m/z = 39 u was found from collisional activation, indicating a distinct mechanism of ionization and dissociation.

The energy levels of ionized phenol and its isomers and the reaction mechanism of loss of CO have been explored with quantum chemical calculations. In the path with least energy, the elimination of CO begins from the migration of the hydrogen atom on the hydroxyl group to the β carbon (C2), followed by ring-opening, closure of a five-membered ring, and elimination of CO. In this mechanism of least energy, the energies of all transition species are less than that of the first step, hydrogen migration. CO elimination that has a small energy barrier is the major dissociation channel for phenol cations with small internal energy.

It is likely that energy greater than 10 eV was left in the phenol cation after excitation of a core electron to unoccupied orbitals and Auger decay. A similar large leaved in a cation was found in pyrimidine. Many electronic excited states might be involved during the dissociation because of a large energy left in a cation. The dissociation products also indicate that the dissociation paths must be complicated. The identification of the detailed dissociation paths with the current experimental and theoretical methods is difficult and is beyond the scope of this work.

**AUTHOR INFORMATION**

**Corresponding Author**

*Phone: +886-3-5780281, ext 7337. Fax: +886-3-5783813. E-mail: Liu.CL@nsrcc.org.tw.*

**Notes**

The authors declare no competing financial interest.

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