Selective Cleavage of the Nitro Group from a Nitrophenyl Monolayer by Synchrotron Soft X-ray[†]

Joong Ho Moon,[‡] Ki-Jeong Kim,[§] Tai-Hee Kang,[§] Bongsoo Kim,[§] Heon Kang,[‡] and Joon Won Park*,[‡]

Department of Chemistry, Center for Biofunctional Molecules, and Pohang Accelerator Laboratory, Pohang University of Science and Technology, San 31 Hyoja-dong, Pohang 790-784, Korea

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A synchrotron radiation source was utilized for X-ray photoelectron spectroscopic analysis of a nitrobenzaldimine-formed monolayer. The N(1s) peak intensity for the nitro group becomes reduced upon X-ray irradiation, while C(1s) and O(1s) peaks are invariant. This observation indicates that the nitro group is cleaved selectively, leaving the phenyl ring intact in the layer. The cleavage rate is measured as a function of photon energy and normalized with the photon flux. The cleavage is first-order to the concentration of the nitro group. The rate constant is independent of the incident photon energy, suggesting that the cleavage is not associated with a direct photoexcitation of atomic core electrons. Electrons ejected by the X-ray are proposed as the most viable cause for the bond cleavage. The molecules remaining on the irradiated surface were analyzed with gas chromatography–mass spectrometry coupled with the solid-phase microextraction method after hydrolyzing the imine bond. It is found that the amount of nitrobenzaldehyde is reduced upon the irradiation, but the expected products, benzaldehyde and hydroxybenzaldehyde, are not produced.

While X-ray photoelectron spectroscopy (XPS) has been widely used for the analysis of thin molecular films,[1] investigators have started to notice damage caused by the X-ray.[2] In particular, X-ray induced cleavage of CF_3CO_2- and CF_3CONH-terminated monolayers has been investigated, showing that photoelectrons ejected from the surface are largely responsible for the damage.[3] Very recently, the damage to the hydrocarbon chains was probed by a XPS–FTIR method.[4] Were the damages either by photoelectrons or by X-rays selective to a surface functional group, then it would transform the functional group into new ones. Such a transformation will change the surface properties with a resolution of X-ray lithography.[5] Herein, we report the *selective* cleavage of the nitro group from a nitrobenzaldimine monolayer upon X-ray irradiation. The rate constant and the cross section for the cleavage have been measured in order to unveil its mechanism.

The aminosilylated[6] layer was prepared by allowing silicon wafers to react with (3-aminopropyl)diethoxymethylsilane (APDMS) in toluene, and a subsequent condensation with *p*-nitrobenzaldehyde gave a nitroben-
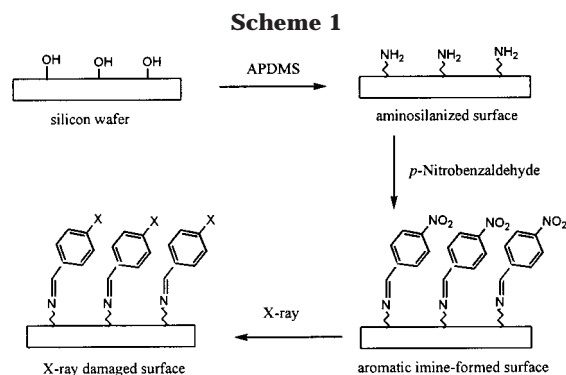
Scheme 1

zaldimine monolayer (Scheme 1).[7] The thickness and the surface density of thus prepared imine layer were typically 10 Å and 4 imines/100 Å^2, respectively. The average tilt angle of the aromatic chromophore from the surface normal was 29 ± 4°.

A synchrotron radiation source (Pohang Accelerator Laboratory, Korea)[8] was utilized for photocleavage and XPS analysis of the layer. N(1s), C(1s), and O(1s) binding energy regions were scrutinized to elucidate the involved chemical transformation of the molecular layer. In particular, X-rays of energies between 300 and 800 eV

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* To whom correspondence may be addressed: E-mail: jwpark@vision.postech.ac.kr.

[‡] Department of Chemistry, Center for Biofunctional Molecules.
[§] Pohang Accelerator Laboratory.

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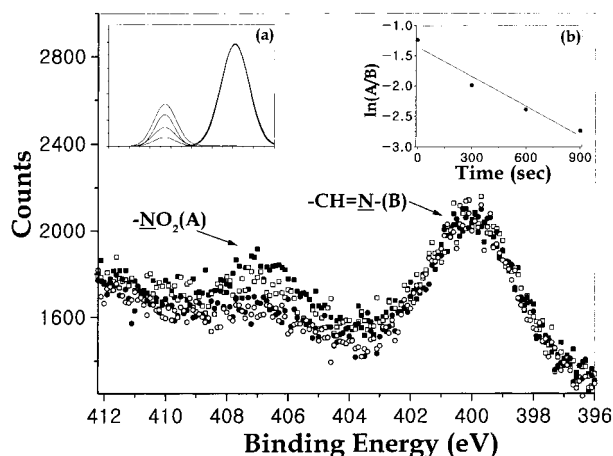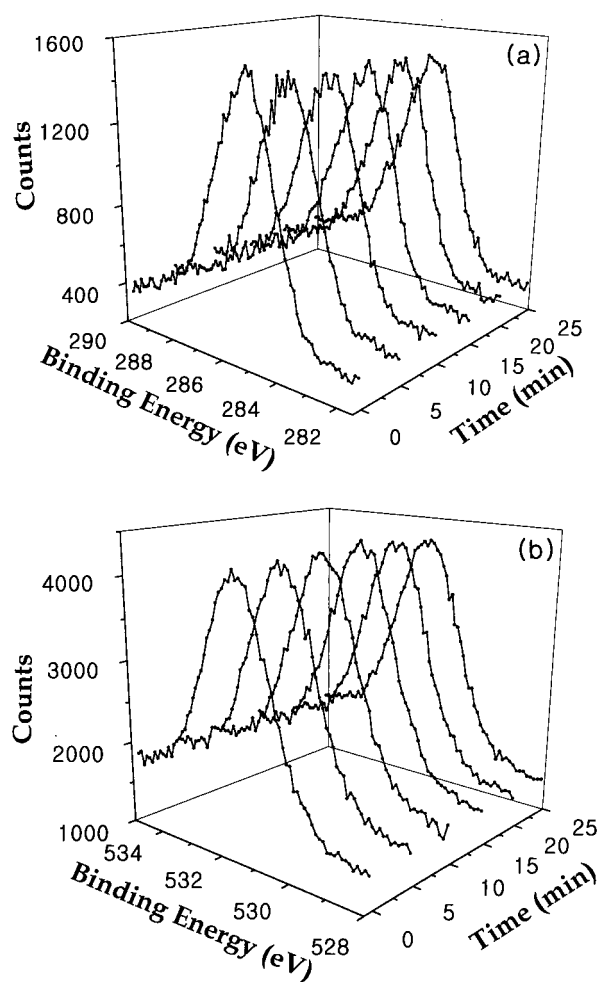
Figure 1. XPS spectra of a nitrobenzaldimine monolayer. Each spectrum was obtained after exposure to X-ray of 500 eV for 0 min (■), 5 min (□), 10 min (●), and 15 min (○). Inset: (a) Fitted curves of the raw data using a homemade program with Labview. (b) A kinetic plot to obtain the first-order rate constant for the cleavage.

were selected to see the effect of incident photon energy on the cleavage. The photoemission data were analyzed by a homemade software programmed with Labview.[9]

A survey scan for the aminosilylated film shows the peaks from O(1s), N(1s), C(1s), Si(2s), and Si(2p) levels, and the positions of these peaks coincide well with the literature values.[10] A new N(1s) peak at 407 eV that appeared after condensation reaction clearly indicates the presence of the nitro group in the layer (Figure 1).[11] The position of the imine peak (400 eV) is very close to that of amine, rendering them difficult to distinguish from each other.[12] However, it has been shown that the properly prepared aminosilylated layer is very close to the monolayer and that the surface amine group is transformed quantitatively into the imine.[7] Therefore, the peak at 400 eV should originate solely from the imine.

It is interesting to observe that the intensity for the N(1s) peak of the nitro group decreases as the irradiation continues. As evident in Figure 1, the peak intensity is significantly diminished after irradiation of 500 eV photons for 15 min. The filled squares (■) comprise a spectrum obtained right after a light-shutter was open. The scan period for this spectrum was 200 s, which was compromised between good signal-to-noise ratio and minimal photoinduced damage. The second (□), third (●), and fourth (○) spectra were taken with a time interval of 5 min under continuous X-ray irradiation at 500 eV. The fitted curves in inset (a) clearly show the decrease of the nitro group population. The rate of diminution is first-order to the concentration of the nitro group. The logarithm of the normalized peak area for the nitro group decreases linearly with increasing irradiation time (inset (b)). The slope of the line gives the rate constant for the diminution.

The peaks coming from the C(1s) and O(1s) levels were also examined as a function of irradiation time. The characteristic features and the intensity of the C(1s) and

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Figure 2. Three-dimensional plots for (a) C(1s) and (b) O(1s) peaks at a photon energy of 600 eV as a function of the irradiation time. No change of the characteristics by the irradiation is evident for both cases.

O(1s) peaks were invariant under X-ray irradiation at 500 and 600 eV, as exemplified by the spectra taken by the photon energy of 600 eV (Figure 2). These spectra clearly show the dissimilar nature of the two peaks, their intensity, position, and shape being invariant with the irradiation. The invariant C(1s) intensity indicates that the carbon units are not destroyed, including the phenyl ring. From the sharply contrasting behavior of C(1s) and N(1s) peaks, we conclude that the cleavage of the nitro group occurs *selectively*. A decrease of the O(1s) intensity could be expected in concert with the nitro group cleavage, but the O(1s) peak did not show any appreciable change even in a low-angle XPS measurement. Two reasons can be incurred: (1) an oxygen from siloxane and silica layer overwhelms that of the nitro group; (2) the aromatic chromophore is not well aligned such that the O(1s) peak intensity comes mostly from the substrate oxygen, but not from the nitro group.

To unveil the mechanism, the dependence of the cleavage rate upon incident photon energy was measured. Figure 3 shows the normalized cleavage rate constants and photon fluxes obtained at photon energies of 300, 500, 600, and 800 eV. At least three independent measure-

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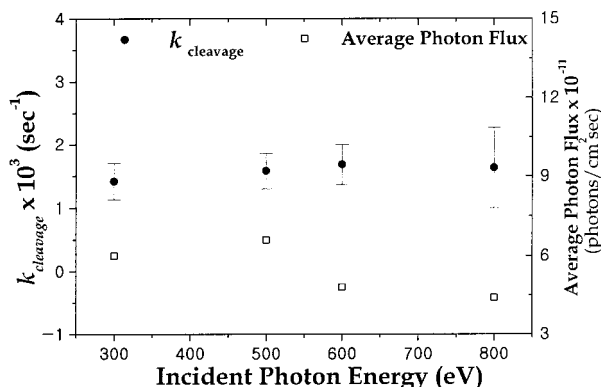
Figure 3. Plot of the normalized cleavage rate constant (●) as a function of the incident photon energy. The open square (□) represents the averaged photon flux measured at each energy. The rate constants were normalized using a particular photon flux (6.6×10^{11} photons/(cm^2 s)) observed at 500 eV. The cleavage efficiency is independent of the photon energy.

ments were executed at each energy, and their error bounds are shown by the bars. For example, the rate constant measured at 500 eV was 1.6×10^{-3} s^{-1} at photon flux of 6.6×10^{11} photons/(cm^2 s). The dissociation rate constant, when normalized to a particular photon flux (6.6×10^{11} photons/(cm^2 s)), was essentially invariant with photon energy within experimental error range. If the nitro cleavage were associated with excitation of the 1s core level, there should be an eminent optimal energy for the cleavage in the examined range. Therefore, the direct excitation of core electrons can be eliminated from possible dissociation mechanisms.

The rate constant can be expressed by the reaction cross-section (σ_r) times the incident photon flux (I). Thus the calculated σ_r value is 2.4×10^{-15} cm^2/photon. Because the area of a nitrobenzaldimine, or the molecular cross section (σ_m), is estimated to be 2.5×10^{-15} cm^2/molecule,[13] the ratio of σ_r/σ_m is 0.96 molecule/photon. This ratio is too large to be interpreted as a photocleavage reaction under nonresonant condition. The incident X-rays can also eject photoelectrons from the surface. The electron emission yield from a solid surface, including both Auger and secondary electrons, ranges $10-10^3$ electrons per X-ray photon.[14] With such a large number of photoelectrons being produced, they should be the most possible cause

for the cleavage of the nitro group. The electron-induced cleavage has previously been proposed for the decomposition of CF_3CO_2- and CF_3CO_2NH-terminated molecular layers under X-ray irradiation.[3]

In an attempt to identify the chemical state of the nitro-cleaved imine layer, the whole area of the substrate is irradiated. To ensure uniform exposure of the X-ray beam over the whole area (1 × 3 cm), the position of the beam (beam size = 1.5 × 3.0 mm) was moved after each irradiation of 30 min. Then, the irradiated sample was dipped into water for the hydrolysis of the imine bond. The final aqueous solution was analyzed with gas chromatography−mass spectrometry (GC−MS) coupled with the solid-phase microextraction (SPME) method.[15] It was found that the amount of nitrobenzaldehyde was reduced upon the X-ray irradiation, but the possible products resulting from the nitro group cleavage, benzaldehyde and hydroxybenzaldehyde, were not observed.[16] Therefore, it is most probable that the nitro group cleavage accompanies secondary reactions that transform the imine functionality to a nonhydrolyzable one.

In summary, while the nitro group of the nitrobenzaldimine monolayer is cleaved by the X-ray, the aromatic group of the layer is not destroyed. The constant cleavage efficiency over photon energy ranging from 300 to 800 eV and a very large cross section suggest that the cleavage process is not associated with the direct photoexcitation of the molecule. The cleavage reaction may also affect the imine functionality, transforming it into a nonhydrolyzable one.

Supporting Information Available: GC−MS spectra (4 pages). Ordering information is given on any current masthead page.

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