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Selective Cleavage of Nitro Groups in Nitro-Substituted Aromatic Monolayers by Synchrotron Soft X-rays: Effect of Molecular Structure on Cleavage Rates

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Introduction

X-ray photoelectron spectroscopy (XPS) is one of the most powerful analytical tools for the study of organic thin films.[1] A number of earlier investigations have shown that X-ray-induced bond cleavage or film damage occurs during XPS analysis of the organic materials.[2−10] In particular, Whitesides and co-workers examined X-ray-promoted damage of CF_3CO_2- and CF_3CONH-terminated monolayers on gold and silicon substrates. These workers concluded that photoelectrons ejected from surfaces, rather than incident X-ray photons, are mainly responsible for the damage to the organic monolayers.[4] Sagiv and co-workers have also investigated damage to hydrocarbon monolayers, caused by using XPS, by using Fourier transform infrared (FTIR) spectroscopy.[5]

Monolayer damage caused by X-ray irradiation is likely to be selective to a particular functional group. If so, X-ray irradiation damage would be associated with specific chemical reactions, which transform functional groups into new ones.[11−13] Reactions of this type can be utilized to tailor surface properties with an X-ray lithographic level of resolution. Owing to this, it is important to carefully analyze damage processes that accompany exposure of monolayers to X-rays. The data obtained from these efforts should enable the design of new organic materials and new nanopattern-formatting methods.

Previously, we reported that carbon−nitrogen and carbon−halide bonds in the nitro- and halide-substituted benzaldimine monolayers are cleaved selectively by using X-ray irradiation.[14,15] In this paper, we describe the selective nitro group cleavage reactions of various nitro-substituted aromatic imine monolayers. Also, the rate constants and cross sections for the cleavage reactions have been measured in order to elucidate the effects of molecular structure on monolayer reactivity.

Experimental Section

General. The silane coupling agent, (3-aminopropyl)diethoxymethylsilane, was purchased from Gelest, Inc. 4-Nitrobenzaldehyde and 4-nitrocinnamaldehyde were purchased from Aldrich Chemical Co. and used as received. 4-[2-(4-Nitrophenyl)-vinyl]-benzaldehyde[15] and 4-(4-nitrophenyl-ethynyl)-benzaldehyde[16] were prepared by following literature methods, and 4-[2-(4-nitrophenyl)-ethyl]-benzaldehyde was synthesized through a procedure developed in this laboratory (see the Supporting Information). NMR spectra were recorded on a Bruker DPX300 (300 MHz) spectrometer, and elemental analysis was performed at Pohang University of Science and Technology (Elementar Vario-EL). UV grade fused silica plates were purchased from CVI Laser Co. Polished prime Si(100) wafers (dopant, phosphorus; resistivity, 1.5−2.1 Ω cm) were purchased from MEMC Electronic Materials, Inc. UV−vis spectra were recorded on a Hewlett-Packard diode-array 8453 spectrophotometer. Deionized water (18 MΩ cm) was obtained by passing distilled water through a Barnstead E-pure 3-Module system. The thickness of self-assembled thin films was measured with a variable angle spectroscopic ellipsometer (VASE) system (J. A. Woollam Co.). A synchrotron radiation source (Pohang Accelerator Laboratory, Korea)[17] was utilized for photocleavage reactions and XPS analysis of the aromatic imine monolayers. The photon energy was selected to give the most-enhanced photoemission intensity and/or the best-resolved spectra. Electron binding energies were calibrated against the Si(2p) emission at $E_b = 99.3$ eV.[1,2]

Preparation of Nitro-Substituted Aromatic Imine Monolayers. The aminosilylated substrates were immersed in anhydrous ethanol solutions (25 mL) containing the aromatic aldehydes (10 mg) under a nitrogen atmosphere at 50 °C for 6 h. The substrates were then sonicated for 1 min in ethanol, methanol, acetone, and dichloromethane sequentially. Finally, the substrates were dried under vacuum.

Results and Discussion

The aromatic imine monolayers were prepared by reacting (3-aminopropyl)diethoxymethylsilane (APDES)-

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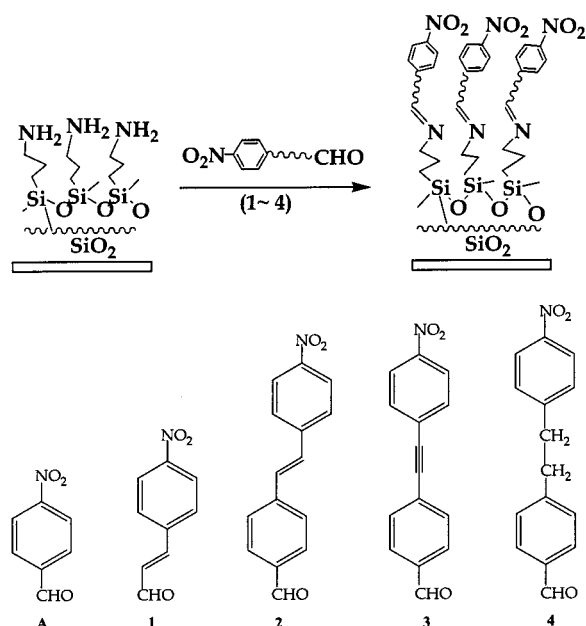
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Scheme 1

Table 1. Thickness of Aminosilyated and Imine-Formed Monolayers[a]

surface	thickness of employed APDES layer (in Å)	thickness of imine-formed layer (increment) (in Å)
1	8.0 ± 0.6	$15.1 \pm 0.7 \, (7.1 \pm 0.3)$
2	12.9 ± 0.4	$23.8 \pm 0.9 \, (11.1 \pm 0.7)$
3	7.7 ± 0.5	$26.7 \pm 0.6 \, (18.9 \pm 0.7)$
4	13.2 ± 0.4	$26.7 \pm 0.2 \, (14.2 \pm 0.6)$

[a] The thickness value is an average from the three independent samples.

treated silicon wafers with the following nitro-substituted aromatic aldehydes: 4-nitrocinnamaldehyde (**1**), 4-[2-(4-nitrophenyl)-vinyl]benzaldehyde (**2**), 4-(4-nitrophenyl-ethynyl)benzaldehyde (**3**), and 4-[2-(4-nitrophenyl)ethyl]-benzaldehyde (**4**) (Scheme 1).[14,18] Aldehydes **2** and **3** have more highly conjugated structures than those of 4-nitro-benzaldehyde[14a] or the nitrocinnamaldehyde **1**, and conjugation between the two aromatic rings is blocked in aldehyde **4**. The thicknesses of the imine monolayers, determined by ellipsometry, were found to be 8.0 ± 0.6, 12.9 ± 0.4, 7.7 ± 0.5, and 13.2 ± 0.4 Å for **1′**, **2′**, **3′**, and **4′**, respectively (Table 1). For aldehydes **1** and **3**, mono-layers were employed, and thicker films were used for the more reluctantly imine-forming aldehydes **2** and **4** (thicker films of higher amine density provide films of higher imine density). Atomic force microscopy (AFM) showed that all the aminosilane layers employed were smooth and did not feature any noticeable aggregation. It was also observed that longer aminosilylation time provided thicker films of higher density and rough surface due to the apparent aggregation.[19] The observed surface densities of the imine on the monolayers were consistently 3–4 imines/nm². The absolute densities of imines on the surface were determined by using the same method applied earlier for the 4-nitrobenzaldimine monolayer.[18]

The total thicknesses of the imine-formed layers were 15.1 ± 0.7, 23.8 ± 0.9, 26.7 ± 0.6, and 26.7 ± 0.2 Å for **1′**, **2′**, **3′**, and **4′**, respectively. Therefore, respective increments of the thickness involved in imine formation are 7.1 ± 0.3, 11.1 ± 0.7, 18.9 ± 0.7, and 14.2 ± 0.6 Å. Except for the monolayer derived from **3**, these values are in the range expected based on the molecular length of each of the aldehydes. The thickness of the monolayer derived from **3** is somewhat larger (18.9 ± 0.7 Å) than the expected value of ca. 12.5 Å. This might be due to the low tilt angle of the molecule against the surface owing to its linear skeleton and $\pi-\pi$ stacking effects. Also, use of isotropic parameters for the ellipsometric data fitting should contribute to the deviation.[20]

Spectra of the nitro-substituted aromatic imine mono-layers, obtained at 830 eV, exhibited bands corresponding to the O(1s), N(1s), C(1s), Si(2s), and Si(2p) levels. The positions of these bands coincide well with values reported in the literature.[2] The N(1s) binding energy region was carefully scrutinized in order to elucidate responsible chemical transformation. For this purpose, X-rays of 550 eV were used to cause enhanced sensitivity for N(1s). A new N(1s) peak at 407 eV was observed following all of the imine formation reactions. This is indicative of the presence of nitro groups in the product monolayers (Figure 1).[21] The position of the imine band at 400 eV is very close to that of an amine, rendering it difficult to distinguish these functional groups.[22] Since the surface amine groups are transformed nearly quantitatively in these reactions (based on imine surface density calculations) for **1** and **3**, the peaks at 400 eV should originate mainly from imine groups for these two cases.

Analysis of the spectra following X-ray irradiation of each of the nitro-arylimine monolayers shows that the nitro groups are selectively cleaved. As shown in Figure 1, the intensity of the N(1s) band for nitro groups decreases as the continuous X-ray irradiation time increases. In all cases, greater than 80% of the nitro groups are cleaved following irradiation for 30–40 min. The rate of cleavage shows a first-order dependence on the nitro group population. The logarithm of the peak areas of bands associated with the nitro groups decreases linearly with increasing irradiation time (Figure 1, inset), and the slopes of the lines yield observed rate constants for the cleavage reactions.

In Figure 2 are shown the C(1s) and O(1s) bands for the 4-nitrocinnamaldimine monolayer. More than three in-dependent locations on the sample surface were ex-amined to check reproducibility. The characteristic fea-tures and intensities of the C(1s) and O(1s) peaks were not altered by X-ray irradiation at 600 eV. This invari-ability, observed with the other aromatic imine mono-layers, indicates that the carbon skeleton (including the aromatic rings) is not affected by X-ray irradiation. The results convincingly demonstrate that, like in earlier examples,[14a] nitro group cleavage occurs selectively under these conditions.

The normalized rate constants and reaction cross sections[14] for the nitro group cleavage processes are given in Table 2. Because the cleavage reactions depend on the photon flux at the particular incident photon energy, the

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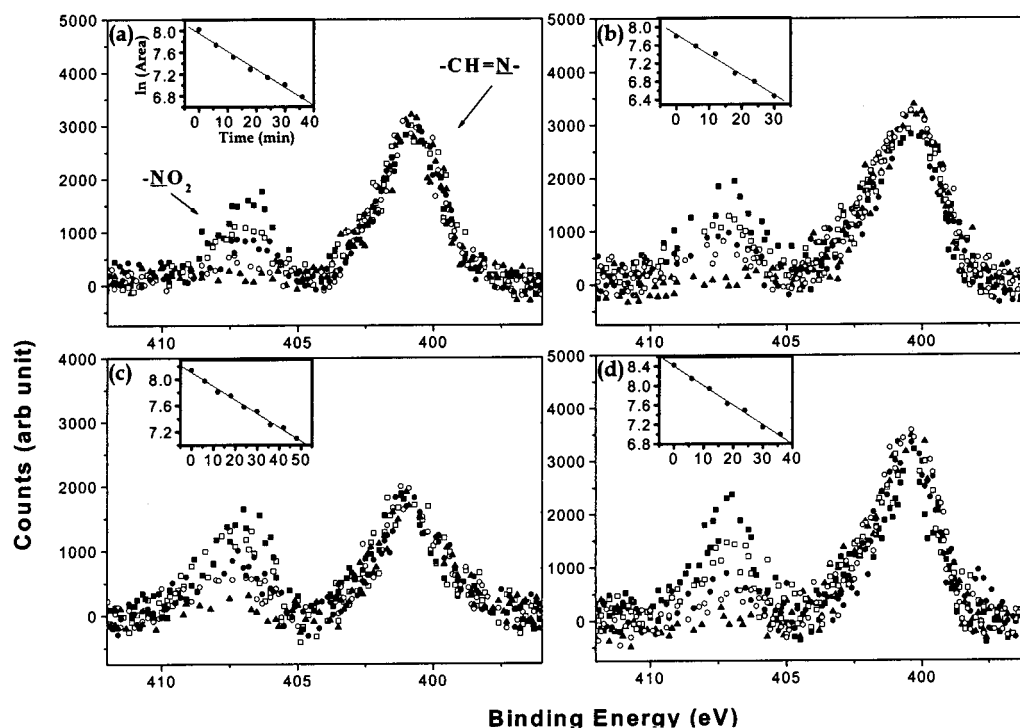
Figure 1. XPS spectra showing the N(1s) region for the nitro-substituted aromatic imine monolayers: (a) 4-nitrocinnamaldimine monolayer, (b) 4-[2-(4-nitrophenyl)-vinyl]-benzaldimine monolayer, (c) 4-(4-nitrophenyl-ethynyl)-benzaldimine monolayer, and (d) 4-[2-(4-nitrophenyl)-ethyl]-benzaldimine monolayer. Each spectrum was obtained after exposure to X-rays of 550 eV for 0 min (■), 12 min (□), 24 min (●), 36 min (○), and 48 min (▲). Insets: Kinetic plots as a function of the irradiation time.
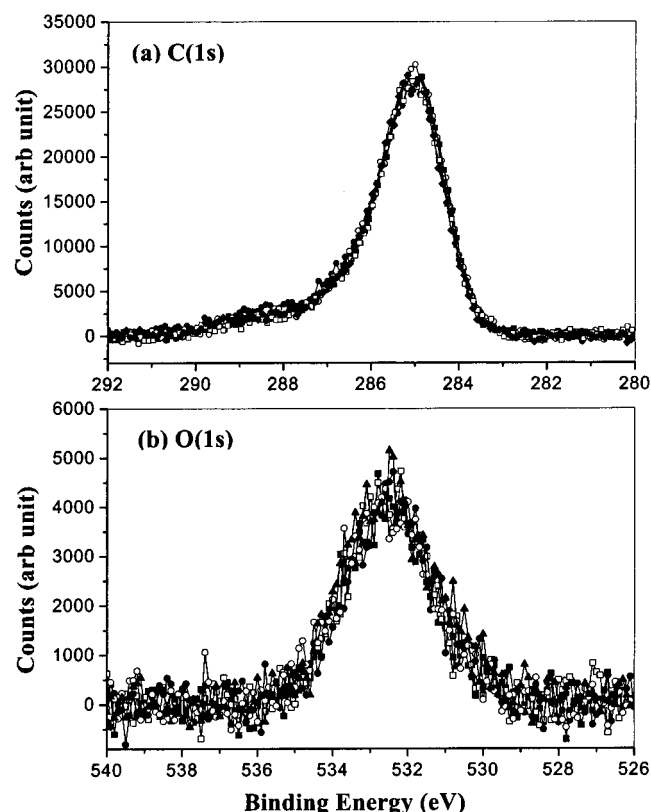

Figure 2. XPS spectra of (a) C(1s) and (b) O(1s) regions for the 4-nitrocinnamaldimine monolayer. Each spectrum was obtained after exposure to X-rays for 0 min (■), 12 min (□), 24 min (●), 36 min (○), and 48 min (▲).

rate constants are normalized to a particular photon flux (2.2 × 10¹¹ photon/(cm² s)) in order to make them more accurately reflect cleavage reaction efficiencies. Another

Table 2. Normalized Rate Constants for the Selective Cleavage of the Nitro Groups

substrates	PE (eV)^a	k' (× 10³) (s⁻¹)^b	cross section (σ_r) (× 10¹⁵) (cm²/photon)^c
4-nitrobenzaldimine (**A**)^d	500	0.53	2.4
imine from **1**	550	0.97(3)	4.5(2)
imine from **2**	550	1.4(1)	6.2(6)
imine from **3**	550	0.75(4)	3.4(2)
imine from **4**	550	0.93(8)	4.2(3)

^{a} Photon energy used for the irradiation. ^{b} The rate constants were normalized using a particular photon flux (2.2 × 10¹¹ photons/(cm² s)). ^{c} The cross section can be obtained by dividing the rate constant with the incident photon flux. ^{d} From the previous result.

way to gain this information is to compare reaction cross sections (σ_r), calculated by dividing the rate constants by the incident photon flux. The latter values are 2.4 × 10⁻¹⁵, 4.5(2) × 10⁻¹⁵, 6.2(6) × 10⁻¹⁵, 3.4(2) × 10⁻¹⁵, and 4.2(3) × 10⁻¹⁵ cm²/photon for X-ray irradiation reactions of the imine monolayers obtained from 4-nitrobenzaldedehyde, **1**, **2**, **3**, and **4**, respectively.

The cross sections are dependent on the molecular structures and, in particular, the extent of conjugation of the nitro-arylimine groups in monolayers. The nitro groups in the imine derived from aldehyde **2** are more efficiently cleaved than those in the monolayer derived from **1**. Also, the cross section for the reaction of the monolayer derived from **1** is higher than that of the 4-nitrobenzalimine monolayer (**A**).[14] This trend parallels the molecular conjugation length of arylimine moieties in the monolayers (i.e., **2** > **1** > **A**). Especially noteworthy is the low rate of nitro group cleavage for the arylimine monolayer derived from aldehyde **4**, in which conjugation between the two aromatic rings is blocked. Therefore, it seems reasonable to conclude that the rate of nitro group cleavage is dependent upon the conjugation length of the aromatic

imine moiety. The imine monolayer derived from aldehyde **3** has a low cleavage efficiency although it contains a relatively highly conjugated aromatic grouping. Thus, it appears that conjugation length is not the only factor determining the rate of this process.

Previously, Whitesides and co-workers reported that X-ray-promoted damage to the self-assembled monolayers is the result of indirect, photoinduced dissociation processes. Our earlier findings are in complete accord with this conclusion.[4,10,14b] The photodissociation processes are commonly thought to occur via an electron-stimulated desorption (ESD) mechanism.[23] Since this mechanism involves the intermediacy of electronically excited states, the cross section of the reaction is not simply proportional to the strength of the bond(s) undergoing cleavage in the ground state. Thus, the energy and character of the lowest unoccupied molecular orbital (LUMO) for the cleaved bond(s) should be important in governing the reaction cross section. Accordingly, if an antibonding interaction exists in a particular bond in the LUMO of the reacting grouping, addition of an electron to the orbital could lead to cleavage of that bond. Also, proximity of the bond undergoing cleavage to the substrate is also an important factor in determining the reaction cross section since excitation energy quenching is faster when it occurs over a shorter distance.[23d] However, for the monolayer systems under current study, the last factor is apparently not important, and consequently the most important factors determining reaction cross sections are conjugation length and type.

Conclusion

The results described above show that selective cleavage of nitro groups in various nitro-substituted aromatic imine monolayers is promoted by soft X-ray irradiation. Cleavage rates were found to be dependent on molecular structure and, in particular, on the arylimine conjugation length as well as type. Quantitative analysis of kinetics of these processes shows that the imine monolayers, bearing more highly conjugated aromatic groupings, undergo cleavage more rapidly.

Supporting Information Available: The synthetic procedure of 4-[2-(4-nitrophenyl)-ethyl]-benzaldehyde, its spectral data for the full characterization, and survey spectra of nitro-substituted aromatic monolayers. This material is available free of charge via the Internet at http://pubs.acs.org.

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