

Photooxidation of Thiols in Self-Assembled Monolayers on Gold

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We report here on the UV photooxidation of self-assembled monolayers (SAMs) of alkanethiols in air. Efficient photooxidation to form the alkanesulfonate (RSO_3^-) is observed for a variety of straight chain alkanethiols as well as thiophenols. Self-assembled monolayers have been studied extensively with a variety of experimental techniques.¹⁻¹⁵ As the result of such studies, details of the structure and chemical properties of SAMs have been revealed. Methods for the controlled chemical modification of SAMs are of great interest, particularly if there is potential for spatial resolution of the chemical modification, as would be the case for an optically induced modification.

In previous work¹⁴ we have shown that laser-induced desorption coupled with Fourier transform mass spectrometry (LID-FTMS) is a sensitive molecular probe of alkanethiol SAMs. In particular, short wavelength (193 nm) laser-induced desorption results in the direct desorption of the alkanethiolate negative ion (RS^-). The desorbed alkanethiolate negative ion is then easily detected and identified by standard FTMS methods. In our previous work we detected the existence of alkanesulfonate species (RSO_3^-) in the SAMs, made from straight-chain alkanethiols, due to long-term (several days) air exposure. The LID-FTMS technique is highly sensitive. However, in experiments in which ions are produced directly by the laser desorption event, quantification is often difficult. In spite of this, we were able to show that the concentration of sulfonate in our air-oxidized SAMs was quite low (below the detection limit of a few percent of a monolayer for X-ray photoelectron spectroscopy).¹⁴ The existence of sulfonates in air-exposed SAMs has recently been confirmed by Tarlov and Newman using negative-ion SIMS experiments.¹³ In contrast with our previous, nonphotolytic experiments, we report here the efficient photolytic conversion of a substantial fraction of the alkanethiols of a SAM to the corresponding sulfonates.

In the experiments described here, SAMs of alkanethiols or thiophenols are generated on evaporated gold films. Details of

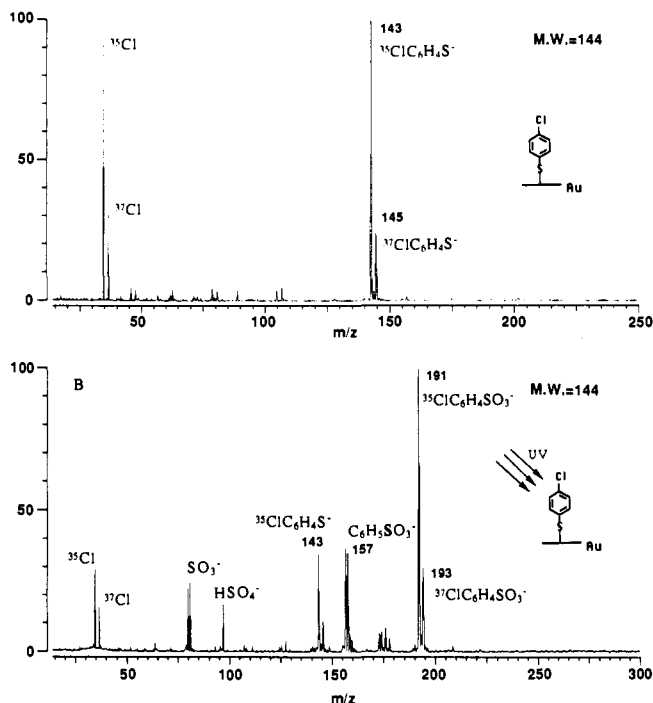


Figure 1. Negative ion mass spectra obtained by LID-FTMS from 4-chlorothiophenol self-assembled monolayers on gold. (a) Spectrum obtained from fresh SAM. (b) Spectrum obtained from SAM which has been irradiated with UV radiation for 25 min in air. The spectra were each obtained with a single laser pulse using a wavelength of 193 nm. Note that the mass scales in a and b are not the same.

our experimental setup and film preparation methods have been given in our previous paper.¹⁴ The films which were irradiated were exposed in air to radiation from a mercury lamp. A water filter with a 5-in. path length was placed in front of the lamp to eliminate infrared radiation thus reducing any complications from a thermally activated reaction. The ultraviolet radiation is focused by a lens such that the entire film surface is uniformly irradiated. The power density used was $\sim 0.16 \text{ W/cm}^2$. A typical exposure time was 25 min. The samples were put in the vacuum chamber of the FTMS system and analyzed immediately after the photolysis to avoid unnecessary air exposure. The laser-induced desorption was accomplished using 193-nm irradiation as in our previous experiments.¹⁴ Low laser pulse energies (well below the threshold for ablation of the gold substrate) were used. Samples were also analyzed before and after photolysis by X-ray photoelectron spectroscopy (XPS).

Figure 1 shows LID-FTMS spectra before (1a) and after (1b) photolysis obtained from a SAM made from 4-chlorothiophenol. The spectra obtained from the fresh sample (Figure 1a) shows strong signals from the parent negative ion (RS^-), and little or no sulfonate signal is detected. Figure 1b shows spectra obtained from SAMs made with the same chlorothiophenol solution but which were irradiated in air with UV light as described above for 25 min. Strong signals from the sulfonate ($\text{ClC}_6\text{H}_4\text{SO}_3^-$, $m/z = 291$) dominate the spectrum. We also observe the photolytic loss of chlorine followed by hydrogen abstraction ($\text{C}_6\text{H}_5\text{SO}_3^-$, $m/z = 157$); note that the lack of the characteristic $^{35}\text{Cl}/^{37}\text{Cl}$ isotope pattern is a clear indication of the lack of chlorine in this species). Details about the formation of this species and the general photochemistry of halogen-substituted thiophenol SAMs will be discussed in a separate paper. We have obtained results similar to those just described for alkanethiols with a variety of chain lengths and a number of halogen-substituted thiophenols as well as thiophenol itself.

Figure 2 shows the sulfur 2p region of the XPS spectra of the fresh and photolyzed chlorothiophenol SAM. The spectrum of

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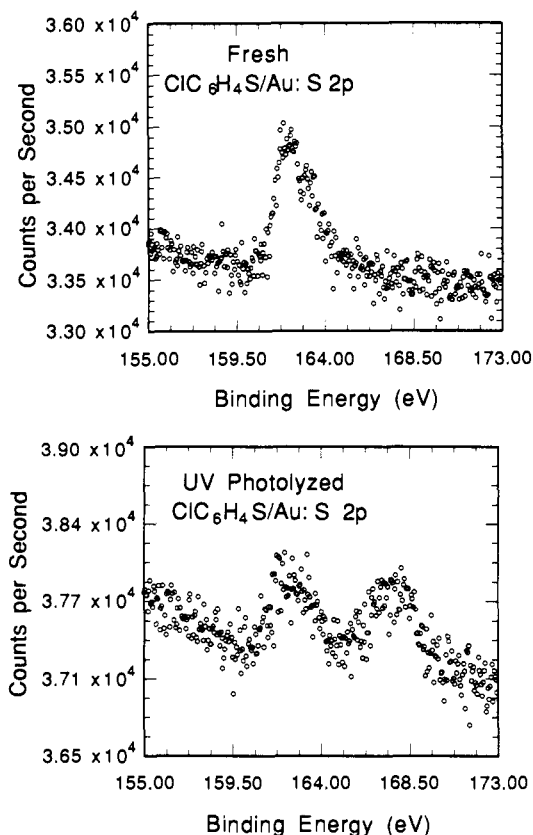


Figure 2. S 2p region of the X-ray photoelectron spectra of 4-chlorothiophenol self-assembled monolayers on gold. (a) Spectrum obtained from fresh SAM showing only one peak with a binding energy of 162.8 eV. (b) Spectrum obtained from SAM which has been irradiated with UV radiation for 25 min in air. The binding energies of the two peaks are 162.8 and 167.5 eV, respectively.

the fresh sample, shown in Figure 2a, shows only one type of S with a 2p binding energy of 162.8 eV, which is characteristic of the RS species on gold. In contrast, the spectrum of the SAM

photolyzed in air shows two S2p peaks; the RS species at 162.8 eV and a new peak at 167.5 eV, characteristic of a sulfonate species.¹⁶ Quantitative analysis of the spectra in Figure 2 show that no sulfur is removed from the surface during photolysis and that photolysis of this film has resulted in 60% conversion of the chlorothiophenol to the corresponding sulfonate. The ability to cleanly convert a substantial fraction of the thiolate to sulfonate by photolysis in air can be used to spatially modify films. The details of this more applied aspect of this work will be reported elsewhere.

The efficient oxidation of thiol solutions on exposure to air is well known, as is the sensitivity of this reaction to metal ions (M^+) and UV irradiation.¹⁷ Indeed the relative stability of alkanethiol SAMs to air oxidation is likely due to the covalent nature of the S–Au bond. It is likely that the photooxidation of SAMs occurs via UV excitation of electrons in the metal substrate. Transfer of the “hot” electron from the metal to either the RS species or to coadsorbed O_2 can then be followed by the oxidation of the thiolate species. Hot electron mechanisms are now well documented in the photochemistry of adsorbed species on metal substrates.¹⁸

The LID-FTMS technique has allowed us to directly determine the molecular identity of the photooxidation product in these experiments. This is one example of the potential use of this technique to follow chemical reactions in self-assembled monolayers. XPS on the other hand, while providing less definitive molecular identification, is more easily quantified.

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