Interchange between Monolayers on Gold Formed from Unsymmetrical Disulfides and Solutions of Thiols: Evidence for Sulfur–Sulfur Bond Cleavage by Gold Metal

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Reaction of an unsymmetrical disulfide, HO(CH_2)_sSS(CH_2)_sCF_6, with a gold surface yields a self-assembled monolayer containing approximately equal proportions of the two different thiolate groups. The S(CH_2)_sCF_6 group in these mixed monolayers is replaced by S(CH_2)_6CN on exposure to a solution of HS(CH_2)_6CN in ethanol about 10^3 times more rapidly than the S(CH_2)_sOH group, although approximately 70–80% of the latter group is eventually replaced. These observations support the conclusion that disulfides adsorb on the surface of gold with cleavage of their sulfur–sulfur bond to form a new species (a gold thiolate). The two thiolates formed from a single disulfide behave as independent entities in their subsequent reactions.

Introduction

Chemisorption of alkanethiols, RSH, or dialkyl disulfides, RSSR, on gold gives ordered monolayers. SAMs (self-assembled monolayers) formed from either precursor are believed to comprise the same species on the gold surface—gold(I) alkyl thiolate (RS-Au^+_3) and gold(I) dialkyl disulfide (RSSR-Au^+_4)—on these pre-dominantly Au(111) surfaces—but the only direct experimental evidence supporting this belief is the observation of indistinguishable S(2p) binding energies for both systems. The objective of the work described in this paper was to differentiate supporting this belief is the observation of indistinguishable S(2p) binding energies for both systems.

Neither the products released from the surface in these interchange reactions nor the mechanism(s) of the interchange reactions have been established, although data characterizing the kinetics of interchange for a few different SAMs are known. Our studies therefore had pre-dominantly an exploratory function and a descriptive character.

Background

Nuzzo et al. examined the XPS spectrum of SAMs prepared from dialkyl disulfides and alkanethiols chemisorbed on gold from solution or from the vapor phase under high vacuum. They observed that the S(2p) binding energy measured by XPS for chemisorbed species derived from dimethyl disulfide was ~1.5 eV lower than the binding energy for physisorbed multilayers of this disulfide on gold. They argued that the lower binding energy of the chemisorbed species supported the hypothesis that the organosulfur compound coordinates to the surface as an alkyl thiolate. We showed that properties (measured by ellipsometry, XPS and wetting) of SAMs formed on gold...
Interchange between Monolayers on Gold

Figure 1. Two possible outcomes for the replacement of species in a SAM formed on gold from \( \text{HO(CH}_2\text{)}_{n}\text{SS(Ch}_2\text{)}_{2}\text{CF}_3 \) by \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \). (A) The \( \text{S(Ch}_2\text{)}_{2}\text{CF}_3 \) half of the unsymmetrical disulfide is displaced selectively from the gold surface, resulting, for short times of exposure to \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \), in a monolayer comprising a ~1:1 mixture of species derived from \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \), in a monolayer derived from either dialkyl disulfides or alkane thiols in solution. (B) \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \) nonselectively displaces molecules from the SAM resulting in a correlated loss of species derived from both halves of \( \text{HO(CH}_2\text{)}_{n}\text{SS(Ch}_2\text{)}_{2}\text{CF}_3 \). The synthesis of 1 followed a literature procedure.

Table I. Properties of SAMs formed on Gold from Different Precursors of \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>( n = 16 )</th>
<th>( n = 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = \text{OH} )</td>
<td>( \theta_{\text{H}_2\text{O}} ^{\circ} )</td>
<td>78 ± 2</td>
</tr>
<tr>
<td>( \theta_{\text{N}_2} ^{\circ} )</td>
<td>51 ± 10°</td>
<td>118 ± 10°</td>
</tr>
<tr>
<td>( \theta_{\text{HD}} ^{\circ} )</td>
<td>18 ± 10°</td>
<td>75 ± 10°</td>
</tr>
<tr>
<td>( \theta_{\text{HD}} ^{\circ} )</td>
<td>&lt;10°</td>
<td>&lt;10°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>normalised signal ( ^{d} )</th>
<th>normalised signal ( ^{d} )</th>
<th>oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluorine</td>
<td>( 0.47 \pm 0.08^{e} )</td>
<td>&lt;0.03</td>
<td>1.00 ± 0.05</td>
</tr>
<tr>
<td>oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Thickness determined by ellipsometry. * Contact angle in degrees. * Values of the contact angles less than 10° cannot be determined with any accuracy by the methods used here. These values represent upper limits. * Normalized intensity of the specified element in the SAM measured by XPS. * This value is corrected for attenuation of the signal by an overlayer of 6 Å of carbon atoms.

Reaction at the surface of the metal generally decreases with increasing chain length of the alkyl thiolate in the SAM.

Experimental Design

We wished to have methods of characterizing the processes occurring on the surface that would yield as much information as possible, using relatively simple experiments. Our strategy for addressing the questions outlined in Scheme I was based on using the unsymmetrical disulfide \( \text{HO(CH}_2\text{)}_{n}\text{SS(Ch}_2\text{)}_{2}\text{CF}_3 \) (1) to form the monolayer and \( \text{HS(Ch}_2\text{)}_{2}\text{CN} \) (2) to carry out the replacement. These choices were based on five considerations. First, we wanted one of the two alkyl moieties of the disulfide to be significantly longer than the second. If the organosulfur species derived from the two halves of the disulfide were independent in the SAM, we expected their difference in length and stability to be reflected in a significant difference in the rates of replacement from the SAM by thiol in solution. If the sulfur–sulfur bond of the disulfide remained intact on the surface of gold, however, we expected nonselective replacement of species from the SAM (Figure 1). Second, changes in the composition of monolayers could be assayed by ellipsometry or XPS, using the thickness of the SAM as a measure of this change. Third, we wanted each half of the unsymmetrical disulfide to have a distinct element that could be observed using XPS. Fourth, we wanted an unsymmetrical disulfide that was easily distinguished (by NMR and chromatography) from symmetric disulfides corresponding to either half of the unsymmetrical disulfide. Fifth, we wished to follow incorporation of the thiolate derived from 2 into the SAM by XPS; the nitrogen atom in this compound made that analysis straightforward.

Results and Discussion

Synthesis and Characterization \( \text{HO(CH}_2\text{)}_{n}\text{SS(Ch}_2\text{)}_{2}\text{CF}_3 \). The synthesis of 1 followed a literature procedure of unsymmetrical disulfides by the oxidation of a 1:1 mixture of thiol corresponding to the two halves of 1 with \( \text{I}_2^{e} \). The unsymmetrical and symmetrical disulfides were easily separated, as determined by thin layer chromatography and NMR, by column chromatography.

SAMs of \( \text{HO(CH}_2\text{)}_{n}\text{SS(Ch}_2\text{)}_{2}\text{CF}_3 \) SAMSs were formed on gold substrates from 1 mM solutions of 1 in either isooctane or ethanol (see below). After 24 h of equilibration with this solution, the resultant SAM was characterized by XPS, ellipsometry, and its wettability by water and hexadecane. These data are summarized in Table I. The
Figure 2. Intensity of photoelectrons of F(1s), O(1s), N(1s), and Au(4f) measured by XPS for SAMs formed from HO(CH₂)₇SS-(CH₂)₇CF₃ change following exposure of these SAMs to 1 mM (A, left) or 10 mM (B, right) solutions of HS(CH₂)₁₆CN in ethanol. The nitrogen spectra in part A are offset to improve the clarity of the data.

F(1s) signal in SAMs of 1 was 36 ± 3% of the fluorine signal measured for SAMs formed from HS(CH₂)₇CF₃. Correction of the fluorine signal in SAMs of 1 for attenuation of the fluorine photoelectron through a disordered layer of 6 Å of methylene groups (due to the presence of species derived from HS(CH₂)₁₆OH in the
thickness of the monolayer and increasing conversion of the SAM. This decrease in the rate of replacement of species from thick monolayers probably results from two factors. First, sterically restricted access to the surface of gold by thiols or disulfides in solution, and increasing chain–chain interactions, decreases the rate of replacement in thick films. Second, the morphology of the surface of gold probably results in sites with high coordination numbers (>3) that bind thiolate better than sites with low coordination numbers (<3) and therefore reduce the rate of replacement of these thiolates. We found similar effects for the rates of replacement from SAMs of 1 by solutions of 2 in ethanol or isooctane.

Together these data suggest that species in SAMs formed from 1 behave as independent particles on the gold surface. This result supports the hypothesis that gold thiolates form on chemisorption of dialkyl disulfides on gold.

Conclusions

Reaction of an unsymmetrical disulfide HO(CH₂)₁₆SS(CH₂)₁₆CF₃ with a gold surface yields a SAM containing approximately equal proportions of the two possible thiolate groups. The -S(CH₂)₁₆OH group in these mixed monolayers is replaced by -S(CH₂)₁₆CN about 10⁶ times more rapidly than the -S(CH₂)₁₆OH group, although a large fraction (70–80%) of the latter group is eventually replaced. A fraction of the -S(CH₂)₁₆OH groups is not replaced, even after long exposure; the observation of a kinetically trapped population of thiolate groups is in agreement with work by Chidsey and Fox. These observations support the conclusion that disulfides adsorb on the surface of gold with cleavage of their sulfur–sulfur bond and form a new species (a gold thiolate). The two thiolates formed from a single disulfide behave as independent entities in their subsequent reactions.

Experimental Section

Materials. Absolute ethanol (Quantum Chemical Corp.) was purified by N₂ or Ar prior to use. Hexadecane (Aldrich, 99%) was
percolated twice through activated, neutral alumina (EM Science). Water was deionized and distilled in a glass and Teflon apparatus (Pfaltz & Bauer) prior to use. 16-Mercaptohexadecane and 16-mercaptohexadecanol were available from previous studies. \(\text{CF}_2(\text{CH}_2)_{15}\text{SS}(\text{CH}_2)_{16}\text{OH}\) was synthesized according to a literature procedure.\(^6\) \(\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.62 (\(q\), 2H), \(\delta\) 2.70 (t, 2H), \(\delta\) 2.66 (t, 2H), \(\delta\) 1.96 (p, 2H), \(\delta\) 1.54 (p, 2H), \(\delta\) 1.4-1.2 (m, 24H). Anal. Calcd for C\(_{30}\)H\(_{75}\)F\(_3\)O\(_2\): C, 57.66; H, 9.44. Found: C, 57.41; H, 9.59.

Preparation of Substrate. Gold substrates were prepared by electron-beam evaporation of 2000 Å of gold (Materials Research Corp., 99.999%) onto 100 mm thick, single-crystal silicon (100) test wafers (Monsanto, MEMC, and Silicon Sense) that had been precoated with 100 Å of chromium (Johnson Mathey, 99.997%; Aldrich, >99.99%) as an adhesion layer between the silicon dioxide and the gold. The substrates were stored in wafer holders (Fluoroware) until used in experiments. Before being added to solutions, the silicon wafers were cut into \(-1\) cm \(\times\) 3 cm slides with a diamond-tipped stylus, rinsed with ethanol, and blown dry in a stream of nitrogen. The time between removal of the wafers from the evaporator and immersion in solutions containing thiols or disulfides was generally less than 4 h.

Instrumentation. Ellipsometric measurements were performed on a Rudolf Research Type 43903-200E ellipsometer equipped with a He–Ne laser (\(\lambda = 6328\) Å) at an incident angle of 70°. Samples were rinsed with ethanol and blown dry in a stream of nitrogen prior to characterization. Values of thickness were calculated using a program written by Wasserman\(^{15}\), following an algorithm by F. L. McCracken and co-workers; in the calculation, we used a refractive index of 1.45 for the SAMs. Contact angles of water and hexadecane were measured on a Ramé-Hart Model 100 goniometer at room temperature and ambient humidity. Advancing and receding contact angles were measured on at least three drops of each liquid per slide; contact angle data in the text represent the average of these measurements. A Micro-Electrapette syringe (Matrix Technologies) was used for dispensing and removing the liquids onto the SAMs (~1 μL/s). The method used for measuring the advancing and receding angles has been described previously.\(^4\)

X-ray photoelectron spectra were obtained on an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al K\(_\alpha\) X-rays. The spot size was 3 mm\(^2\) with an analyzer pass energy of 100 eV for measurements of N(1s), F(1s), and O(1s); spectra were accumulated for 30 min. A 1 mm\(^2\) spot and an analyzer pass energy of 50 eV were used for measurements of C(1s) and Au(4f); these spectra were acquired for 20 and 3 min, respectively. Spectra were fit using a 60% Gaussian/40% Lorentzian function in the computer system of the SSX-100.

Formation of SAMs. Adsorptions were carried out in 25-mL glass weighing bottles that had been cleaned with "piranha solution" (7:3 concentrated H\(_2\)SO\(_4\)/30% H\(_2\)O\(_2\)) at 90 °C for 1 h, and rinsed first with distilled water and then with copious amounts of deionized water. WARNING: Piranha solution should be handled with caution. It should not be allowed to contact significant quantities of oxidizable organic materials. In some circumstances (most probably when mixed with significant quantities of an oxidizable organic material), it has detonated unexpectedly.\(^{16}\) The weighing bottles were stored in an oven at approximately 100 °C until use. Adsorptions were carried out in 25 mL of ethanol or isooctane at a total concentration of sulfur of 1 mM. Adsorptions were performed at room temperature for 1 day.

Studies of Kinetics. Studies of rates of formation of SAMs were carried out in either 1 or 10 mM stirred (4 x 8 mm Teflon coated bar at ~5 revolutions per second) solutions of the thiol or disulfide. Samples were placed in solution and removed after a fixed period of time (~1 s) followed by immediate (within 1 s) washes with ethanol (10 mL) and hexane (10 mL). Samples were dried under a stream of nitrogen. Samples were split into two pieces. One piece was placed in a container made of polypropylene and transported to the XPS, where it was immediately (within 20 min) placed under high vacuum, <10\(^{-8}\) Torr. The thickness of the monolayer by ellipsometry and the contact angles of water and hexadecane were measured on the other piece. This procedure minimized contamination of the monolayer in the laboratory atmosphere.

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