Vibrational Study of the Fast Reductive and the Slow Oxidative Desorptions of a Nonanethiol Self-Assembled Monolayer from a Au(111) Single Crystal Electrode

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We present in-situ vibrational measurements of the reductive and the oxidative removals of a self-assembled nonanethiol monolayer from a Au(111) single crystal electrode in an alkaline aqueous solution. Immersion in an alkaline solution causes a disordering of the thiol layer which involves a significant tilt of the aliphatic chain toward the surface. The combined electrochemical/vibrational data show that the nonanethiols are reductively removed as thiolates via a one-electron process. The reductively desorbed thiolates display intense CH stretching bands after their desorption which, we suggest, is due to the formation of micelles of nonanethiolates. The oxidative removal of the nonanethiol layer is found to be a slow multiple-step process in which the carbon−sulfur bond can be broken and up to 11 electrons can be involved in the oxidation of a single chemisorbed thiol. In contrast to the reductive process, the oxidatively desorbed molecules have very weak CH stretching bands. We believe this is due to the slow oxidation of the thiols that leads to the desorption of individual molecules from the surface.

Introduction

Organic monolayers deposited on solid substrates are raising a lot of interest because of their possible applications.[1] In many devices such as electrochemical sensors or organic semiconductors, the organic layer is terminated by functional groups that are in contact with a solution, water vapor, or atmospheric contaminants. The environment in which the terminal group is immersed, or in contact with, influences the particular properties of the film.[2−5] Understanding the nature of the interactions between a chemisorbed organic layer and a solution is therefore relevant to the proper design of the organic layer. A well-suited model system for the study of the interactions between an organic layer and a solution is the thiol-terminated aliphatic chain adsorbed on Au(111) where relatively ordered monolayers are formed.[6] Several studies[2−5,7−9] of thiol monolayers in contact with different solvents have reported structural changes at the solvent/organic interface. However, fewer studies[4,5,7,8] have been carried out under electrochemical conditions which constitute an important area of applications for thin organic films.

Vibrational spectroscopy is a useful probe of the effects of the environment (solvent and ions) and of the electrode potential on the orientation and reactivity of molecules adsorbed at the surface of electrodes. Different spectroscopic approaches have been used in vibrational/electrochemical studies of self-assembled monolayers. Raman,[9] polarization modulation FTIR,[4] sum frequency generation,[7] and differential FTIR[5] studies of long-chain (18 carbons) thiol layers deposited on polycrystalline gold substrates have been reported. These results reveal that thiols deposited on smooth gold substrates do not undergo substantial potential-induced spectral changes in the double-layer region[5,7] whereas on rough gold substrates potential-induced spectral changes are seen.[4,8] Clearly these observations show that the quality of the substrate affects the electrochemical behavior of the deposited thiol layer. Almost all of the previous in-situ vibrational studies of self-assembled monolayers were concerned with the changes occurring in the double-layer region[4,5,7] and not with the mechanism of the electrochemical removal of the layer.[8]

In this paper, we present an in-situ vibrational/electrochemical study of the reductive and oxidative removal processes of a nonanethiol monolayer from a Au(111) single crystal electrode in an alkaline solution. This system presents some advantages over the formerly studied longer chain thiols. First, we found in a previous voltammetric study[10] that a nonanethiol monolayer deposited on a single crystal Au(111) electrode forms a compact monolayer with a small double-layer capacitance. In alkaline solution the nonanethiol layer is reductively removed from the surface in a single narrow peak. We also found that the fraction of the nonanethiol monolayer that can be oxidatively redeposited after its reductive removal depends strongly on the pH of the electrolyte solution. We suggested that the nonanethiols remain close to the surface after their reductive desorption because of their low solubility in water. The complete oxidative removal of the nonanethiol layer is possible in a single voltammetric scan although it occurs at a much slower rate than the reductive removal process. To explore the nature of the reductively and oxidatively desorbed thiols, we have used polarized infrared spectroscopy to detect the solution species. Second, because we are using a short-chain thiol, the vibrational changes will be easier to detect. In this study we report changes occurring in the vibrational spectrum upon immersion of the thiol-coated gold electrode in an alkaline solution. Also, using polarized infrared measurements, we found that different chemical species are formed in the reductive and oxidative removal processes. On the basis of these new results we will discuss possible mechanisms for these reactions.

Experimental Section

The Au(111) single crystal was prepared and cleaned as described previously.[10] All the solutions were made from Milli-Q water, and the KOH was from Aldrich (semiconductor grade). The electrochemistry was performed using a three-electrode system. The working electrode was the Au(111) single crystal, and the counter electrode was either a platinum gauze

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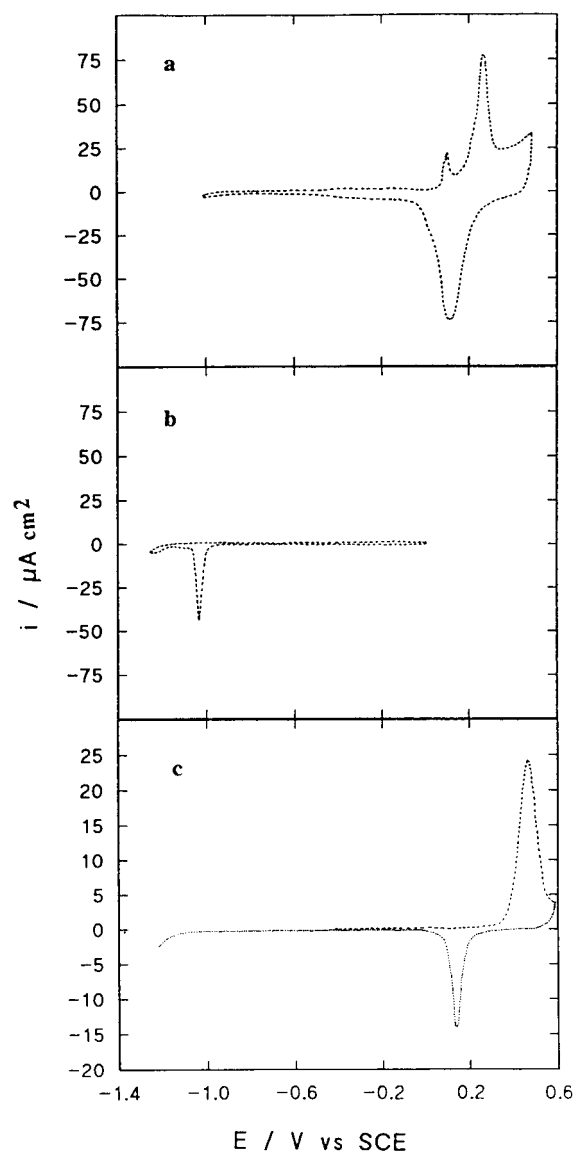

Figure 1. Cyclic voltammograms of (a) the bare Au(111) electrode in 0.1 M KOH solution at a scan rate of 20 mV/s, (b) the reductive removal of a nonanethiol monolayer from a Au(111) electrode in 0.1 M KOH solution at a scan rate of 20 mV/s, and (c) the oxidative removal of a nonanethiol monolayer from a Au(111) electrode in 0.1 M KOH solution at a scan rate of 2 mV/s.

or a gold wire. The reference electrode was a saturated calomel electrode (SCE) housed in a separate compartment and linked to the main cell via a Luggin capillary. All the potential values given in this paper are relative to a SCE. Before depositing the layer, the cleanliness and quality of the Au(111) electrode were checked by recording a cyclic voltammogram in 0.1 M KOH. The voltammogram is shown in Figure 1a and is identical to previous reports.[11] The Au(111) surface roughness factor was estimated by the measurement of the charge due to the formation of the gold surface oxide in 0.1 M HClO$_4$ at a scan rate of 20 mV/s following a method described in ref 12. The calculated surface roughness factor of the Au(111) single crystals used in this study is 1.15 ($\pm$10%). The monolayer was prepared by immersing the Au(111) electrode in a 1 mM ethanolic solution of the nonanethiol (from Aldrich) for 30 min. The electrolyte solutions were degassed thoroughly with argon before each measurement. The cyclic voltammograms of the reductive and the oxidative desorptions of the nonanethiols from the Au(111) electrode in 0.1 M KOH are shown in Figure 1, b and c, respectively. The reductive removal of the thiols occurs in
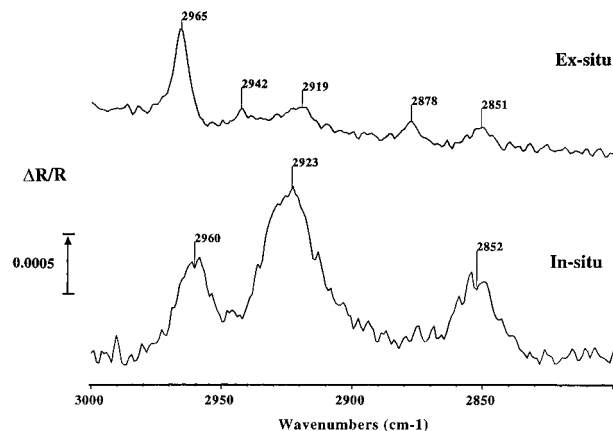

Figure 2. (a) Reflection–absorption infrared spectrum of a nonanethiol monolayer on Au(111) under a nitrogen atmosphere. The spectrum is obtained by referencing the reflectivity of nonanethiol-coated Au(111) surface to the reflectivity of a bare Au(111) surface. The spectrum was taken with p-polarized light and is an average of 1000 scans at 2 cm^{-1} resolution. (b) SNIFTIRS spectrum of a nonanethiol monolayer on a Au(111) electrode immersed in 0.1 M KOH solution. The potential was stepped from −0.50 V to +0.60 V. The spectrum was taken with p-polarized light and is an average of 200 scans at 2 cm^{-1} resolution.

a single narrow desorption peak, and no oxidative redeposition peak is found on the subsequent anodic (i.e., positive going) potential scan. The reductive desorption voltammogram has been discussed previously.[10] The oxidative removal shows a single oxidative peak at $\sim$0.50 V. On the cathodic (i.e., negative going) potential scan the gold oxide reduction peak is seen at 0.15 V. No reductive desorption peak at $\sim$−1.00 V is seen on the subsequent cathodic potential scan, indicating that all the thiols are oxidatively removed from the surface in a single slow anodic potential scan at 2 mV/s. The oxidative desorption voltammogram will be discussed in more detail later.

The vibrational measurements were made in an electrochemical cell having a 60° CaF$_2$ trapezoidal prism at the bottom. This design of the electrochemical cell allows the formation of a thin electrolyte layer of a few micrometers as well as electrochemical measurements with the hanging meniscus technique. The FTIR spectrometer was a Nicolet Magna 550. A ZnSe wire grid polarizer was used to obtain p-polarized or s-polarized light. The ex-situ and in-situ spectra were taken at similar angles of incidence (60 $\pm$ 5°) of the IR beam on the Au(111) surface and thus at similar surface sensitivity.[13] A differential technique[14] called SNIFTIRS which consists of recording a vibrational spectrum at a reference potential, R_0, and then stepping the potential to a different value and recording another spectrum, R, followed by a subtraction of these spectra ($R - R_0$) to give ΔR was used in this study. A subsequent division by R_0 is used to give the normalized differential reflectance (i.e., SNIFTIRS) spectra ($\Delta R/R_0$) shown in this work. The in-situ reference spectrum is that of a nonanethiol-coated Au(111) electrode at a potential of −0.500 V (i.e., in the double-layer region). For all the vibrational data reported in this paper, the reference spectrum was acquired first, and then a spectrum was recorded at another potential. In the normalized differential reflectance spectra, a negative peak indicates an increase of the intensity of the vibrational mode and a positive peak indicates a decrease of the intensity of the vibrational mode.

Results and Discussion

Effect of the Alkaline Solution on the IR Spectrum. In Figure 2 significant differences are found between the infrared spectrum, obtained with p-polarized light, of the nonanethiol-coated Au(111) immersed in a 0.1 M KOH solution and the

one taken under a nitrogen atmosphere. Using the same mode assignment as previously reported,[15] we see that under nitrogen atmosphere the in-plane asymmetric methyl CH stretching mode, r_a^-, dominates the spectrum and is located at 2965 cm^{-1}. The large intensity of the r_a^- band is in agreement with previous results.[16] The out-of-plane asymmetric mode r_b^- which should be located at 2956 cm^{-1} is absent. The methyl symmetric CH stretching mode is split by a Fermi resonance with low-frequency deformation modes into two peaks. The r^+ mode is at 2878 cm^{-1}, and the other mode, r^+(FR), is at 2942 cm^{-1}. The methylene asymmetric, d^-, and symmetric, d^+, CH stretching bands are weak and broad and located at 2919 and 2851 cm^{-1}, respectively. The CH stretching mode frequencies and relative intensities are similar to a previous report,[16] and the r_a^- band is relatively narrow (8 cm^{-1} fwhm). We interpret these observations as an indication that we can form an homogeneous (i.e., ordered) layer with our sample preparation. Our previous electrochemical estimation of the nonanethiol coverage[10] of 7.2 × 10^{-10} mol/cm^2 (±10%) is in agreement with the thiol coverage from diffraction studies[17] of 7.6 × 10^{-10} mol/cm^2. The determination of the exact orientation of the nonanethiol layer is beyond the scope of this paper, but on the basis of the ex-situ vibrational spectrum, we can assume that the terminal methyl group is almost parallel to the gold surface and the methylenes are mainly in a trans configuration with the molecular axis at an angle of ~30° from the surface normal.[18]

When the nonanethiol layer is immersed in the alkaline solution, the vibrational spectrum of the CH stretching region changes considerably as shown in Figure 2. The in-situ infrared spectrum in Figure 2 consists of the difference between a spectrum taken at −0.50 V (where we have a monolayer) and a spectrum taken at 0.60 V (where the nonanethiol layer is completely removed after a time sufficiently long so all the desorbed molecules have diffused away from the thin electrolyte region (see discussion below)). We observe in this spectrum an intense and broad (~30 cm^{-1} fwhm) band at 2960 cm^{-1}. The frequency of this band is between the frequencies of the r_a^- and r_b^- modes. We therefore believe that this band arises from both the r_a^- and r_b^- modes. The broadening and the red shift of the methyl asymmetric modes are in agreement with previous studies of a nonanethiol layer[7] and of longer chain thiol layers.[4,5] However, the most dramatic changes are the increases by more than 1 order of magnitude of the d^- band and by approximately a factor of 5 for the d^+ band relative to their values in the ex-situ spectrum. These bands are slightly blue-shifted to 2923 and 2852 cm^{-1}. The r^+(FR) and r^+ bands are not observed.

A simple explanation of the differences between the in-situ and ex-situ vibrational spectra is that, on average, there is an increase of the tilt of the aliphatic chain toward the surface. A quantitative interpretation of the changes between the in-situ and ex-situ spectra is difficult.[19] However, a simple qualitative interpretation is worthwhile since the observed spectral differences are large as shown in Figure 2. In our analysis we assume that the transition dipole moments remain the same in the alkaline solution as they are in air since the methyl and water molecules do not interact strongly.[20] We then use a geometrical model to predict the IR intensity of the modes.[18] As mentioned before, when the nonanethiol layer is under a nitrogen atmosphere, the terminal methyl group is almost parallel to the surface for a methylene chain in an all-trans configuration. This orientation gives a large intensity for the r_a^- mode and a weaker intensity for the r_b^- mode. Our ex-situ vibrational spectrum is in qualitative agreement with this geometry. Upon immersion of the layer in the aqueous alkaline solution, an intense and
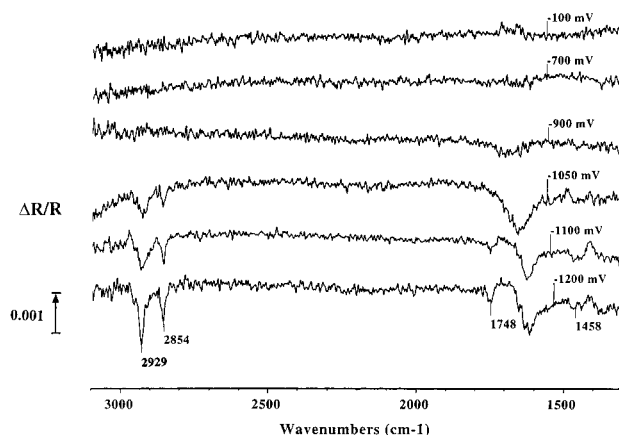

Figure 3. SNIFTIRS spectrum of the nonanethiol monolayer on a Au(111) electrode in a 0.1 M KOH solution as a function of the applied potentials. The reference potential is −0.50 V. The applied potentials are shown in the figure. All spectra were taken with p-polarized light and are averages of 64 scans at 4 cm^{-1} resolution.

broad band at 2960 cm^{-1} is observed. We have assigned this band to the unresolved r_a^- and r_b^- modes. The r_b^- band increases in intensity most likely because of a reorientation of the methyl group which becomes, on average, more perpendicular to the surface. The disorder caused by the reorganization of the methyl groups would evidently cause changes in the all-trans methylene chain. The increased intensities of the methylene stretching modes, their blue shift, and broadening support this suggestion. The large increase in the intensity of the methylene stretching modes requires an increased tilt of the methylene chain toward the surface so the transition dipole moment of the d^+ and d^- modes becomes more perpendicular to the surface.[18]

These results differ from those of previous in-situ infrared studies of 18 carbons chain thiols deposited on polycrystalline gold in neutral or acidic aqueous solution.[4,5] The large increase in the intensity of the methylene CH stretching modes was not observed in the case of longer chain thiols. These previous studies[4,5] reported a broadening of the r_a^- and the methylene CH stretching bands with a red shift of the r_a^- band and a blue shift of the methylene CH stretching bands relative to the spectrum observed in air. These changes were interpreted as a disorder of the terminal methyl groups and neighboring methylene groups. We also suggest that the spectral changes of the CH stretching modes in the case of the nonanethiol layer are caused by a disordering of the methyl groups. The reorganization of the thiol layer seen as an increase of the methylene CH stretching modes intensity is more easily detectable for a nonanethiol layer than in the case of the longer chain thiol layer because of the low intensity of the methylene CH stretching bands of a nonanethiol layer in air.

A simple geometrical interpretation of the observed vibrational intensities changes, specially for the terminal group which is in contact with the electrolyte solution, might not be totally appropriate. It was found that the environment in which the terminal group is immersed does cause noticeable changes of the methyl stretching modes.[15] Furthermore, the presence of an electric field might also cause spectral changes[21] which can be large in the case of a nonanethiol layer where a significant part (~30%) of the potential drop occurs across the aliphatic chain.[22]

There are no potential-induced changes over the double-layer region, between −0.100 and −0.900 V, as shown in Figure 3 by the in-situ infrared spectrum obtained with p-polarized light (i.e., p-polarized spectrum). This result agrees with the volta-

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mmetric data which indicate that the nonanethiols form a good blocking layer over this range of potentials with a constant capacitance of 2.5 μF/cm^2 ($\pm$10%). It also agrees with previous in-situ vibrational studies.[4,5,7] Furthermore, because of the stability of the thin electrolyte layer, we can say that there is no large amount of water moving in or out of the organic monolayer since no water vibrational peaks are detected. This result further shows that potential-induced effects are absent for the nonanethiol monolayer over the complete double-layer region. We can conclude that the differences between the ex-situ and in-situ vibrational spectra are caused by the immersion of the thiol-coated electrode in the electrolyte solution and that they are not potential induced.

The interaction of the hydrophobic aliphatic chain with the water molecules is known to cause disorder in the thiol monolayer.[4,5] Moreover, a recent study[23] suggests that, even in the absence of an electric field, there is a significant number of hydroxyl ions that accumulates at the organic/water interface because they form strong hydrogen bonds with the water molecules. Thus, is it possible that our observation of a disordered layer is partly caused by the accumulation of a large negative charge at the organic/water interface.

Reductive Desorption of the Nonanethiol Monolayer. Our vibrational data reflect the state of the thiol monolayer on a Au(111) surface. We see in Figure 3 that the onset of the spectral changes is sharp and located at the same potential (i.e., -1.050 V) where the reductive desorption starts in Figure 1b. This gives us confidence that the layer and the electrochemical processes are not significantly perturbed by the thin-layer scheme used in our vibrational measurements. The appearance of intense negative reflectance peaks in the CH stretching region for potentials more negative than -1.05 V indicates that the reduced molecules have intense CH stretching bands. This observation is surprising for the CH stretching bands since upon the desorption of thiols a decrease in the intensity (i.e., an increase in the reflectance) is expected because, in solution, the thiols would be quite disordered. We assign the two broad peaks at $\sim$2930 and $\sim$2855 cm^{-1} seen after a potential step to -1.05 V to the d$^-$ and d$^+$ methylene modes of desorbed molecules. It should be noted that in the p-polarized spectrum these modes are distorted due to the fact that the reference spectrum also contains CH stretching bands in this region. The negative reflectance peak at 1660 cm^{-1} is assigned to a water bending mode and is caused by the formation of a double layer at the gold surface upon the desorption of the hydrophobic thiols. At -1.10 V, a small positive band is observed at $\sim$2960 cm^{-1} which shows a decrease in the intensity of the methyl asymmetric stretching bands of the chemisorbed thiols. The methylene bands, d$^-$ and d$^+$, are increasing in intensity. The water bending mode shifts to 1630 cm^{-1}. Also, a small band at 1750 cm^{-1} begins to develop. A weak and broad negative reflectance peak is observed at 1458 cm^{-1}. We assign it to the methylene CH deformation modes of molecules in solution. A small positive reflectance peak is seen at 1410 cm^{-1}. We tentatively assign this mode to the methyl symmetric CH deformation mode blue-shifted from its ultrahigh-vacuum (UHV) value of 1383 cm^{-1} because of its interaction with the electrolyte solution. The thiol layer is completely desorbed from the electrode surface at -1.20 V since no further change in the vibrational spectrum occurs for more negative potential steps. We see that, for the potential step to -1.20 V, the CH stretching modes region consists of three negative reflectance peaks at 2955, 2930, and 2855 cm^{-1}. We assign the mode at 2955 cm^{-1} to the r$_b^-$ mode of desorbed molecules. The negative peak at 1750 cm^{-1} is slightly more intense. The water bending mode at 1630 cm^{-1}
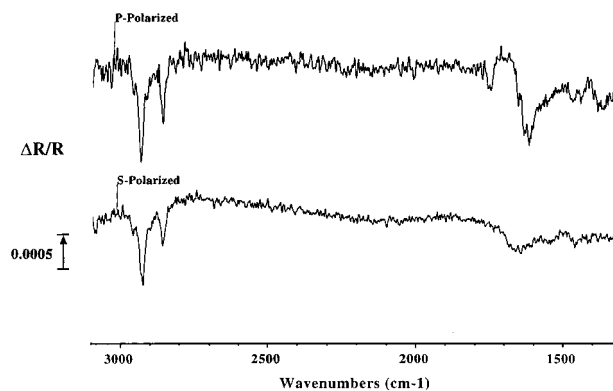

Figure 4. SNIFTIRS spectra of a nonanethiol monolayer on a Au(111) electrode in a 0.1 M KOH solution acquired using (a) p-polarized and (b) s-polarized light. The potential was stepped from -0.50 to -1.20 V. The spectra are averages of 64 scans at 4 cm^{-1} resolution.

is intense. A small negative peak at 1460 cm^{-1} and a small positive peak at 1410 cm^{-1} are also visible.

The infrared spectrum obtained with s-polarized light (i.e., s-polarized spectrum) at -1.20 V shown in Figure 4 contains only the contributions from the solution species. This spectrum confirms that the CH stretching modes of the desorbed molecules are intense and located at the same frequencies as in the p-polarized spectrum. We can therefore assign the CH stretching bands at 2955 (r$_b^-$), 2930 (d$^-$), and 2855 cm^{-1} (d$^+$) to desorbed thiol molecules. The p-polarized spectrum of the CH stretching region is significantly more intense than the s-polarized spectrum, once the contributions of the chemisorbed thiols from the reference spectrum are taken into account. Therefore, some of the reduced thiols are still at the surface since if all the reduced thiols would be in the solution, we should observed a similar intensity in the p-polarized spectra and in the s-polarized spectra. The fact that the d$^+$ and d$^-$ modes are still intense and not too broad for the molecules in solution suggests that the nonanethiols are in an homogeneous environment. Most likely, the thiols are still interacting with one another after their desorption from the surface. The large intensity of CH stretching bands of the reductively desorbed thiols contrasts with the oxidative removal of the thiols where the intensity of the CH stretching bands is very weak (see Figure 8). This observation indicates that the oxidatively and reductively desorbed molecules are in different environments. Furthermore, the CH stretching region of the s-polarized spectrum in Figure 4 is quite similar to the vibrational spectrum of liquid thiols[19,24] in terms of the frequency and relative intensity of the CH stretching modes. This observation lends support to our earlier suggestion that the thiols form micelles after their desorption. It is likely that if micelles of nonanethiols are formed, they would have a narrower and more intense CH stretching spectrum than that of isolated molecules.[25,26]

Further information on the nature of the lower frequency bands that appear upon the reductive desorption of thiols is found from the comparison of the p- and s-polarized spectra. The peak at 1750 cm^{-1} is completely absent from the s-polarized spectrum, showing that it is a surface mode. The nature of this mode is unclear. The fact that the relative intensities of the CH stretching bands and the band at 1750 cm^{-1} are reproducible in all the experiments that we have done suggests that this band originates from the thiols. This observation makes it unlikely that the 1750 cm^{-1} band is due to a contamination. This band cannot be assigned to a water mode since it is at higher frequency than what is observed under UHV conditions for the bending mode of chemisorbed water molecules with or without

coadsorbed ions.[27] The 1750 cm^{-1} surface mode is close to the frequencies of gold hydrides[28] and of a dihydride species related to the hydrogen OPD on platinum.[29] There is some electrochemical evidence[30,31] that hydrogen adsorbs on specific sites during the hydrogen OPD on gold which occurs after the reductive removal of the thiol layer. Isotopic substitution experiments done by replacing H$_2$O by D$_2$O as the solvent reveal that the 1750 cm^{-1} band is not associated with the hydrogen evolution process since neither changes in frequency nor changes in intensity are observed. It is possible that a hydrogen−gold stretching mode would be observed in our experiment. However, the isotopic substitution results show that the hydrogen atoms would have to come from the thiols and not from the water molecules. Clearly, more experiments are required to assign the 1750 cm^{-1} mode. We also see in Figure 4 that the water bending mode at 1630 cm^{-1} is more intense in the p-polarized spectrum than in the s-polarized spectrum, indicating that when the thiol layer is removed from the surface, water molecules do interact with the surface. The weak methylene deformation mode at 1460 cm^{-1} is observed in both s- and p-polarized spectra, confirming that it originates from the solution species. This former observation agrees with the large intensity of the CH deformation modes of bulk alkanes[32] which would mask the weaker surface CH deformation modes.[33] Finally, the mode at 1410 cm^{-1} is absent from the s-polarized spectrum, thus giving support to our assignment of this mode to the methyl symmetric deformation mode of chemisorbed thiols.

We do not see any SH stretching band between 2500 and 2600 cm^{-1}. The absence of the SH stretching band from the s-polarized vibrational spectrum supports previous suggestions[10,22] that the reductively desorbed species are thiolates. These results show that there is probably no reprotonation of the thiolates since the pH is higher than the pK_a of thiols of ∼10.[34] Our previous electrochemical study[10] as well as others[22,35] that suggested a one-electron process for the reductive removal of the nonanethiol monolayer when combined with the identification of the reductively desorbed species provided by the in-situ vibrational measurements gives strong support to the following mechanism for the reductive removal of thiols from a Au(111) surface in alkaline solution:

$$RS-Au + e^- \rightarrow RS^- + Au \qquad (1)$$
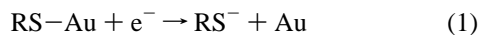
The good agreement between our electrochemical estimate[10] of the thiol coverage and those of diffraction studies[17] indicates that our data are representative of the reduction of a monolayer of nonanethiol. The narrow and well-resolved peaks in the nonanethiol ex-situ spectrum (see Figure 2) provide one more indication that the nonanethiols form a homogeneous monolayer.

The high homogeneity of the Au(111) surface might be responsible for the intense vibrational spectrum of the desorbed thiols. All the thiol molecules desorb over a narrow range of potentials in a few hundred milliseconds or less.[10] Thus, the solution concentration of thiolates close to the surface will be very large and would likely lead to the formation of micelles since the solubility of nonanethiol in aqueous solution is low.[36] This suggestion is based on the results of previous electrochemical studies[10,39] in which we found that the solubility of the thiol influences the extent of the oxidative redeposition of reduced thiols. A reduced long-chain (i.e., insoluble) thiol monolayer such as hexadecanethiol or octadecanethiol can be oxidatively redeposited quantitatively whereas reduced (soluble) butanethiols are not oxidatively redeposited. In the case of nonanethiols the extent of oxidative redeposition increases with the decrease of the pH. This behavior can be related to the decrease of the
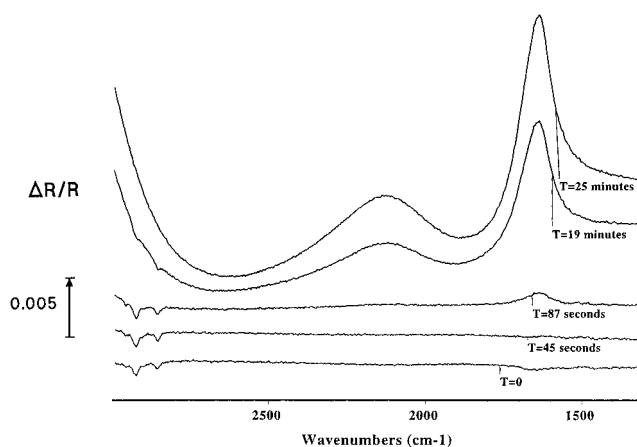

Figure 5. Time-resolved SNIFTIRS spectra of the nonanethiol monolayer on a Au(111) electrode in a 0.1 M KOH solution with the potential of the electrode being stepped from −0.50 to −1.20 V. The reflectivity at −1.20 V was measured from the instant when the potential was jumped from −0.50 to −1.20 V ($T = 0$) and after the potential was held at −1.20 V for $T = 45$ s, 87 s, 19 min, and 25 min. The spectra were taken with s-polarized light and are averages of 64 scans at 4 cm^{-1} resolution.

solubility of nonanethiol with the pH.[36] These results suggest that the weakly soluble or insoluble thiols form hydrophobic structures after their reduction and remain close to the electrode surface such that they can be oxidatively redeposited. As mentioned before, micelles should display an intense vibrational spectrum relative to that of isolated molecules. The environment of the desorbed thiols does not change rapidly as shown by time evolution of the s-polarized spectrum in Figure 5. The CH stretching modes are still visible ∼20 min after their desorption, suggesting that if micelles are formed, they are stable for an extended period of time. Evidence of formation of micelles has also been reported after the electrochemical desorption of Langmuir−Blodgett films from Au(111) single crystal electrodes.[37] These observations raise the possibility that the formation of micelles upon the electrochemical desorption of an insoluble organic layer is common to many types of insoluble organic layers deposited on well-ordered solid substrates. We also see in Figure 5 that the water band at ∼1650 cm^{-1} first increases in intensity after the removal of the thiol layer and subsequently decreases. These intensity changes are related to the double-layer formation upon the removal of the thiols and the consumption of water molecules in the hydrogen evolution process.

Oxidative Desorption of the Nonanethiol Monolayer. The charge involved in the oxidative removal of the nonanethiol monolayer is much larger than in the reductive removal as is clearly shown in Figure 1b,c. The oxidative process is also much slower, and a potential scan rate of less than ∼3 mV/s is necessary for the complete oxidation of the thiol monolayer (see discussion below). At a scan rate of 2 mV/s we see in Figure 1c a large oxidation peak at ∼0.50 V on the first positive potential scan. On the subsequent negative potential scan, we observed the reduction of the gold surface oxide at 0.15 V. The position and the integrated charge of this peak are the same as those of the gold oxide reduction peak of a clean Au(111) surface. Therefore, the oxidation of the thiols does not leave a significant amount of byproducts that could block the formation of the surface oxide. There are no unoxidized thiols left on the surface as is found by scanning the potential to −1.20 V and observing no voltammetric features related to unoxidized thiols at ∼−1.00 V. Thus, the thiol monolayer is completely oxidized at a slow potential scan rate of 2 mV/s. Further proof that the thiol oxidation is complete was obtained by decreasing the
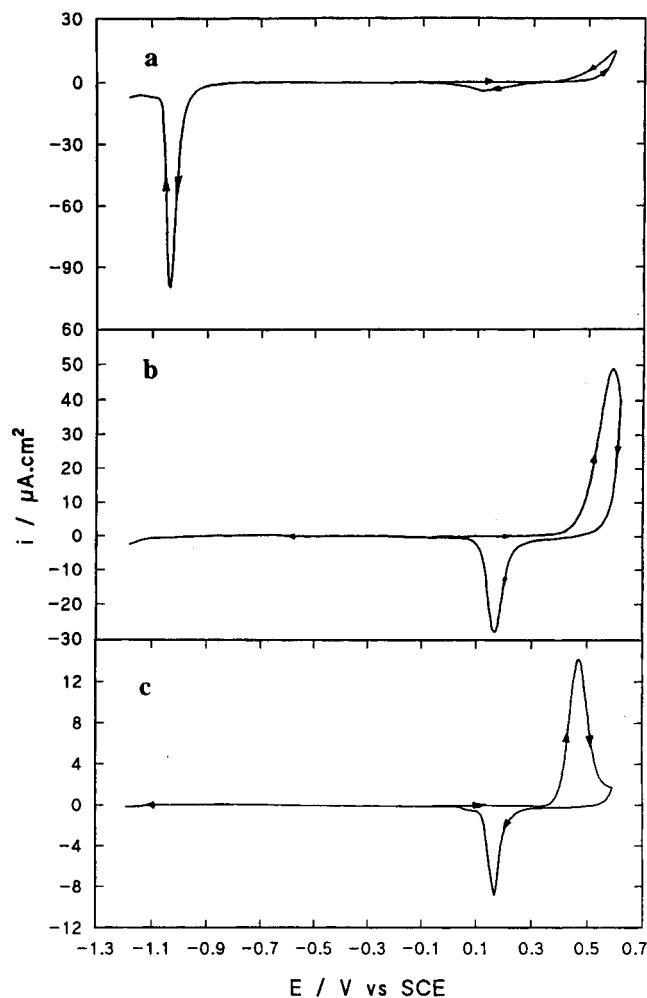
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Figure 6. Cyclic voltammograms of a nonanethiol layer on Au(111) in 0.1 M KOH at (a) 50, (b) 5, and (c) 1 mV/s. The potential is first scanned in the anodic direction and then in the cathodic direction.

potential scan rate to 0.5 mV/s and obtaining the same oxidation charge on the first anodic potential scan.

The results of a potential scan rate dependence of the nonanethiol oxidation are displayed in Figure 6. These results show that the oxidation of the thiols proceeds most probably via a series of consecutive reactions of which one of the first is the breaking of the gold−sulfur bond. At a scan rate of 1 mV/s a complete oxidative removal of the nonanethiol is observed. The integrated charge of the oxidation current peak at 0.46 V is identical (±10%) to the one measured at 2 mV/s. It is possible to completely remove the thiol monolayer at a scan rate of 5 mV/s with a total oxidation charge smaller by $\sim$30−70% compared to what is observed at a scan rate of 2 mV/s or lower. Although a smaller and variable oxidation charge is measured, there are no unoxidized thiols left at the surface as no thiol reduction peak is seen at $\sim$−1.00 V when the potential is scanned in the negative direction after the oxidation of the thiols. Also, the gold surface oxide reduction peak at 0.15 V indicates the formation of a full oxide layer at 5 mV/s. Hence, the gold−sulfur bond is broken at an early stage of the oxidation process, allowing the thiols to desorb from the surface. When the scan rate is increased to 50 mV/s, the oxidation current is very small on the anodic scan, and a small surface gold oxide is formed as shown by the reduction current peak at 0.1 V on the cathodic scan in Figure 6. The reductive current peak at −1.04 V (with an integrated charge of 95 μC/cm^2) shows that most of the nonanethiols were not oxidized. These results show that the oxidation of the nonanethiol layer is a slow process

and that extent of oxidation of the thiol depends on the potential scan rate. We suggest on the basis of these results that when fast potential scan rates are used, the thiols cannot be further oxidized and are thus dissolved in the electrolyte solution before their full oxidation.

We have estimated the charge associated with the oxidative desorption of the nonanethiol monolayer from the voltammetric data, at a potential scan rate of 2 mV/s. First, we remove the oxide formation contribution from the total oxidation charge. This is done by calculating the charge associated with the gold oxide reduction peak at 0.15 V on the first negative scan after the oxidation of the thiol monolayer and subtracting it from the total oxidation charge. We then normalized the charge by dividing it by the geometrical area of the Au(111) surface. The charge associated with the oxidative removal of the nonanethiol thus calculated is 820 μC/cm^2 (±5%). We did not subtract the capacitive charge from this value, but we expect this charge to be as small[38] as the uncertainty in our measurements. In a previous study[10] we found that the reductive desorption of a monolayer of nonanethiol requires a charge of $\sim$72 μC/cm^2 (±10%). Assuming that the reduction is a one-electron process as given in eq 1, we obtained a coverage of 7.2 × 10^{-10} mol/cm^2 (±10%), in agreement with the coverage estimates of 7.6 × 10^{-10} mol/cm^2 obtained from diffraction studies.[17] The ratio of the oxidative and reductive charges is therefore 11 (±1).

The 11 electrons required for the oxidation of a single chemisorbed thiol molecule clearly illustrate the complexity of the oxidative desorption process. The large oxidation charge cannot be explained by a change in the oxidation state of the sulfur alone, further oxidation, i.e., bond breaking, must occur. Consequently, the extensive oxidation current seen in our study disagrees with a previous voltammetric study[22] which suggested that propanethiols and butanethiols are oxidized, in 0.5 M KOH, via a three-electron reaction to give sulfinic acid at a faster scan rate of 100 mV/s. However, our observation of a complete removal of the thiol monolayer with a smaller number of electrons (i.e., 3−7 electrons) per thiol at a scan rate of 5 mV/s shows that one of the initial steps in the oxidation of the thiols is the breaking of the gold−sulfur bond. We have measured the oxidative removal of a butanethiol monolayer from a Au(111) single crystal electrode in a 0.1 M KOH solution. We found that at a scan rate of 100 mV/s the thiol oxidative charge, estimated as described above, is 600 μC/cm^2 (±10%) This is significantly more than the butanethiol oxidative charge of 280 ± 35 μC/cm^2 on a Au/mica substrate reported previously[22] for the same potential scan rate. Our results show that the thiols are much more extensively oxidized on a Au(111) single crystal electrode. The differences between our results on Au(111) and those on Au/mica for the oxidation of butanethiols are probably due to a substrate effect.[10,39] Further confirmation of the potential scan rate effect on the slow oxidative removal of butanethiols is also found. When the potential scan rate is decreased to 5 mV/s, the oxidative charge increases to 800 μC/cm^2 (±5%), a value identical to the one obtained for a nonanethiol layer at a scan rate of 2 mV/s. This suggests that a charge of $\sim$800 μC/cm^2 is needed for the full oxidation of a thiol monolayer. Another important observation is that the length of the aliphatic chain (at least for these two thiols) does not influence the extent of oxidation if a slow potential scan rate is used. Notwithstanding the substrate differences, the observation of a three-electron oxidation process at high potential scan rates and of an 11-electron process at low potential scan rates raises the possibility that the oxidation of the thiols proceeds via at least two steps. A two-step oxidation process is not uncommon. It is observed in the electrooxidation of
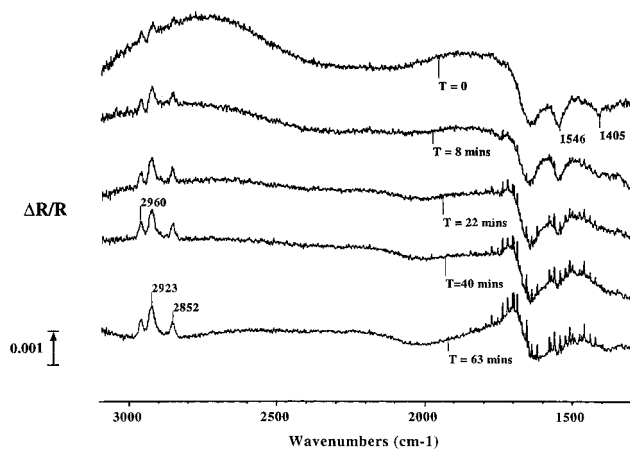
Figure 7. Time-resolved SNIFTIRS spectra of a nonanethiol monolayer on a Au(111) electrode in a 0.1 M KOH solution with the potentials of electrode being stepped from −0.50 to +0.60 V. The reflectivity at +0.60 V was measured from the instant when the potential was jumped from −0.50 to +0.60 V ($T = 0$) and after the potential was held at 0.60 V for $T = 8$, 22, 40, and 63 min. The spectra were taken with p-polarized light and are averages of 200 scans at 2 cm^{-1} resolution.
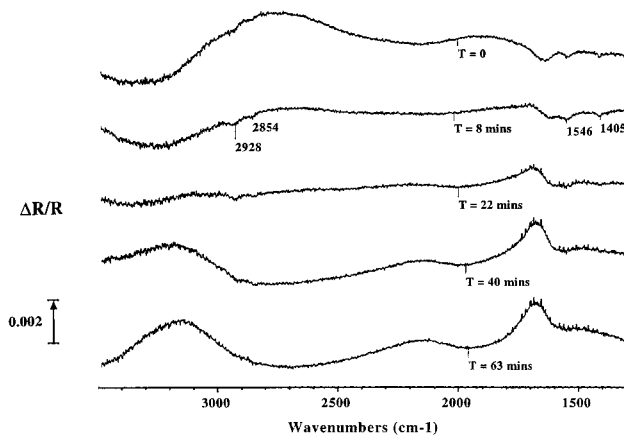

Figure 8. Time-resolved SNIFTIRS spectra of a nonanethiol monolayer on a Au(111) electrode in a 0.1 M KOH solution with the potentials of electrode being stepped from −0.50 to + 0.60 V. The reflectivity at + 0.60 V was measured at the instant when the potential was jumped from −0.50 to +0.60 V ($T = 0$) and after the potential was held at +0.6 V for $T = 8$, 22, 40, and 63 min. The spectra were taken with s-polarized light and are averages of 200 scans at 2 cm^{-1} resolution.

glucose[40] at gold electrodes in alkaline solution where at high concentration of glucose a two-electron process is measured and at lower glucose concentration an eight-electron oxidation occurs.

The in-situ vibrational measurements of the oxidative desorption of the nonanethiol monolayer in Figure 7 support our voltammetric data. The oxidative removal of the nonanethiol gives rise to an infrared spectrum obtained with p-polarized light (i.e., p-polarized spectrum) which differs considerably from the one observed upon the reductive removal of the thiol layer. Figure 7 presents the time evolution of a p-polarized spectrum after a potential step from −0.50 to +0.60 V which leads to the complete oxidative removal of the nonanethiol layer. The first spectrum represents the first ∼150 s after the oxidative potential step. It shows three peaks in the CH stretching region located at 2960, 2923, and 2852 cm^{-1} which are decreasing in intensity (i.e., positive reflectance peak). These bands are assigned to the overlapping r_a^-/r_b^- modes and the d^- and d^+ modes of chemisorbed thiols, respectively. The decrease in the intensity of the CH stretching bands in the oxidative removal contrasts with the reductive removal where an increase in the intensity of the CH stretching bands was observed. Clearly, the intensity of the CH stretching bands of the oxidatively desorbed molecules is much weaker than that of the reductively desorbed molecules. This is confirmed by the s-polarized spectrum of the oxidative removal of the nonanethiol in Figure 8 which shows a very weak increase in the intensities of the CH stretching modes due to the solution species. Only two bands at ∼2928 and 2854 cm^{-1} are seen in Figure 8, and we assign them to the methylene asymmetric and symmetric CH stretching modes of the solution species. In Figure 7 we also see an increase in the intensity of the water bending modes at ∼1660 cm^{-1} at longer time after the potential step. Finally, after ∼60 min there are no CH stretching modes visible in the s-polarized spectrum in Figure 8, indicating that the desorbed molecules have diffused away from the probed thin electrolyte layer. Thus, the p-polarized spectrum taken after ∼60 min is representative of the chemisorbed thiol layer. This in-situ p-polarized spectrum is displayed in Figure 2 and has been described and discussed above.

The bands located below 1600 cm^{-1} provide the strongest evidence that the thiols are oxidized via an 11-electron process. Two intense bands at 1546 and 1405 cm^{-1} are observed

immediately after stepping the potential from −0.50 to +0.60 V (see Figure 7). These bands can be assigned to the asymmetric and symmetric CO stretching modes of an unprotonated carboxylate group.[32] This result implies that the carbon−sulfur bond is broken which, as will be discussed below, leads to further oxidation. These vibrational bands cannot not be assigned to SO stretching modes which are below 1400 cm^{-1}. Both bands are also observed in the s-polarized spectrum although they are slightly weaker. The carboxylate bands at 1546 and 1405 cm^{-1} and the CH stretching modes originate from the same chemical specie since their relative intensities remain constant in different experiments, and as the CH stretching bands decrease in intensity, at later times after the potential step, the two bands at 1546 and 1405 cm^{-1} decrease in intensity. The nature of the oxidized sulfur species has not been determined in this study. The cutoff of the CaF$_2$ window at ∼1100 cm^{-1} prevented the observation of the S−O modes which are between ∼1300 and 900 cm^{-1}. Experiments are in progress to probe the infrared region between 1300 and ∼800 cm^{-1} using ZnSe as the IR window of the electrochemical cell.

The weakness of the negative CH stretching bands in the s-polarized spectrum in Figure 8 of the oxidatively desorbed molecules contrasts with the intense negative bands seen in the reductive desorption of thiols. This observation can be related to the fact that the 11-electron oxidative process is sluggish as shown by the ∼0.1 V fwhm of the thiol oxidative peak at a scan rate of 2 mV/s and by the potential scan rate dependence of the cyclic voltammograms shown in Figure 6. If the thiol molecules are removed slowly from the surface, it is probable that individual, oxidized, molecules will be present in the solution. Isolated molecules will have a larger distribution of environment. This will give rise to a broad range of frequencies and thus a reduced infrared peak intensity. Furthermore, if most of the molecules are in the form of carboxylic acids and sulfate ions, they will be more soluble than the thiolates. Partially oxidized thiols in the form of sulfinic or sulfonic acids do not interact as strongly with the gold substrate as thiolates,[41−43] and thus they are not expected to readsorb on the surface as the potential is scanned negatively toward the double-layer region.

The formation of carboxylates and the 11 electrons involved in the oxidation of a single nonanethiol or butanethiol molecule are not compatible with the previously suggested three-electron mechanism for the oxidation of propanethiols and butanethiols.[22] However, in a recent in-situ FTIR study[8] the formation of CO$_2$

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was observed during the oxidation of a $NC(CH_2)_7SH$ layer on polycrystalline gold in a neutral electrolyte. This result also indicates that the C−S bond is broken. Both our and this previous IR study[8] show that the oxidative removal of thiols must either proceed further after the initial oxidation of the sulfur or via another mechanism. The fast potential scan rate used in the other study[22] is likely to have led to a partial oxidation of the thiols as we discussed before. However, others factors affect the thiol oxidation process. The length of the aliphatic chain influences the oxidation process by blocking the diffusion of the hydroxyls and water molecules to the gold surface. Therefore, the longer chain thiols are oxidatively desorbed at more positive potentials. However, the permeability of the layer does not modify the extent of the oxidation of the thiols at slow potential scan rate (∼2 mV/s) since the same oxidative charge is measured for both a butanethiol and a nonanethiol layer. The nature of the hydroxyl groups that react with the thiols is also important. We do not know whether the thiols react with the hydroxyls in solution or chemisorbed at the electrode surface. The high electrocatalytic activity of gold in alkaline medium toward the oxidation of organic compounds such as alcohols shows that the chemisorbed hydroxyls are efficient oxidants. Thus, it is possible that the thiols will react with the chemisorbed hydroxyls. In a recent review by Adzic,[44] it is shown that the different electrocatalytic activities of the low-index gold surfaces are related to the formation of the surface oxide in the case of aliphatic molecules that reacts on oxide covered gold. The formation of the surface oxide is more difficult on Au(111) than on stepped, vicinal, Au(111) surfaces.[44,45] On the basis of these observations, we should expect differences between the oxidative removal of the nonanethiol monolayer from a smooth Au(111) surface and from a stepped surface such as a gold film or a gold polycrystal. We cannot with our present set of results fully assess the relative importance of the chain length, the crystallographic orientation of the surface, and the scan rate in the electrooxidation of chemisorbed thiols. In-situ FTIR experiments with shorter chain thiols and on different crystallographic surfaces are under way.

Even in the absence of spectroscopic data regarding the nature of the oxidized sulfur species, the voltammetry can help us in suggesting a mechanism for the oxidation of the nonanethiol layer. The potential scan rate dependence which shows that the nonanethiol monolayer can be completely oxidatively removed with only ∼3−7 electrons per thiol suggests that the gold−sulfur bond is broken at the beginning of the oxidation process. The p-polarized spectrum in Figure 7 shows that the carboxylates are also formed early (i.e., in the first ∼150 s) after the potential step from −0.50 to +0.60 V. These results show that both the C−S and gold−sulfur bonds are broken early in the oxidation process. Because of the slow (i.e., seconds) time scale of the experiments, we cannot say whether these reactions are simultaneous or consecutive. It is, nevertheless, possible that sulfinic acid is one of the first intermediate formed as previously suggested.[22]

At slower potential scan rates or by holding the potential at 0.60 V, further oxidation of the chemisorbed thiols occurs as shown by the formation of carboxylates and an 11-electron oxidation process. These observations can only be explained if most of the C−S bonds are broken. Once the C−S bond is broken, the carbon would likely react with the hydroxyls at the surface or in the solution to first form an alcohol. Then this species will be further oxidized to a carboxylate probably via a four-electron process.[38] This process which consists of a reaction between the alcohol and the surface hydroxyl groups has often been reported in the electrooxidation of alcohols on

gold in alkaline medium. Interestingly, on Au(111) the oxidation of the alcohol stops at the carboxylate and does not proceed to the formation of carbon dioxide as it does on platinum electrodes.[38] As we mentioned before, the breaking of the C−S bonds was reported recently in an in-situ FTIR study[8] of the oxidation of $NC(CH_2)_7SH$ on polycrystalline gold in a neutral electrolyte. In this study[8] the oxidation of the thiols produces CO_2. These authors also suggested that the oxidation of the thiols occurs before the formation of a gold oxide. In our study we did not observe the formation of CO_2 (see Figure 8) which would form CO_3^{2-} in the alkaline medium we used. First, the number of electrons required for the formation of CO_2 is larger than the 11 electrons per oxidized thiol that we measured. Second, only one broad mode, the asymmetric CO stretching modes of CO_3^{2-} at ∼1450 cm^{-1}, would be observed[32] if CO_2 is formed instead of the two vibrational modes at 1546 and 1405 cm^{-1} that we observed. Lastly, in our study as well as in ref 22 the formation of a gold oxide is observed upon the oxidation of the thiol layer in alkaline solutions. Since different thiols, substrate, and electrolyte solution were used in ref 8 and that the number of electrons required for the oxidation of a $NC(CH_2)_7SH$ molecule is not known, further comparison with our results is unwarranted. Nevertheless, both studies show that the oxidation of thiols leads to the breaking of the C−S bond. We do not know the intermediate steps in the oxidation of the sulfur. However, at such a positive potential, in an alkaline solution, the final product of the sulfur oxidation is most probably a doubly negatively charged sulfate. According to a previous voltammetric study,[46] the oxidative removal of an atomic sulfur layer from a gold electrode, in 1 M NaOH, requires six electrons per sulfur atom.

We suggest a new mechanism for the oxidative desorption of thiols based on the electrocatalytic properties of gold in alkaline medium and on our results. The mechanism consists of breaking the C−S bond, oxidizing the sulfur to SO_4^{2-}, and the formation of RCO_2^-. This process can be written as

$$RCH_2S-Au + 14OH^- \rightarrow$$
$$SO_4^{2-} + RCO_2^- + 8H_2O + 11e^- + Au \quad (2)$$
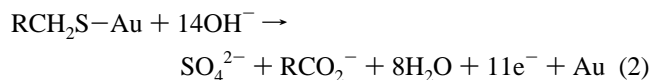
This mechanism is compatible with our voltammetric data since it requires 11 electrons per oxidized thiol molecule and with our spectroscopic data since carboxylates are formed. A more complete verification of the suggested mechanism for the oxidation of a nonanethiol monolayer requires the spectroscopic determination of the oxidized sulfur species. However, the 11-electron per oxidized thiol limits the types of oxidized sulfur species that can be formed.

Summary

The combined in-situ vibrational and electrochemical study of a nonanethiol self-assembled monolayer on a Au(111) single crystal electrode revealed several new aspects of the electrochemistry of this important type of thin organic layer. We found that when the nonanethiol monolayer deposited on a Au(111) single crystal is immersed in an alkaline solution, it undergoes a significant reorganization that involves an increases tilt of the aliphatic chain toward the surface. The reorganization of the organic layer is not potential dependent and is caused by the interaction of the hydrophobic aliphatic chain with the electrolyte solution. The vibrational measurements of the reductive desorption of the chemisorbed thiol monolayer are compatible with a one-electron process that leads to the formation of thiolates. The reductively desorbed molecules display an intense CH stretching modes spectrum, which we believe, indicative of the

formation of micelles of nonanethiolates. The oxidative desorption of the thiols is found to be a complex process. Spectroscopic and voltammetric data show that the carbon–sulfur bond can be broken and that carboxylates are formed in addition to the oxidation of the sulfur. This oxidation of both the sulfur and carbon requires as many as 11 electrons per thiol molecule.

Note Added in Proof. A recent study[47] shows that the oxidation of 2-mercaptoethanesulfonate on a Au(111) electrode requires 12 electrons per thiol.

References and Notes

(1) Ullman, A. *An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(2) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91,* 1281. Engquist, I.; Lundstrom, I.; Liedberg, B. *J. Phys. Chem.* **1995**, *99*, 12257.

(3) Nuzzo, R. G.; Zegarski, B. R.; Korenic, E. M.; Dubois, L. H. *J. Phys. Chem.* **1992**, *96*, 1355.

(4) Anderson, M. R.; Gatin, M. *Langmuir* **1994**, *10*, 1638.

(5) Popenoe, D. D.; Deinhammer, R. S.; Porter, M. D. *Langmuir* **1992,** *8*, 2521.

(6) Poirier, G. E.; Tarlov, M. J. *Langmuir* **1994**, *10*, 2853.

(7) Hines, M. A.; Todd, J. A.; Guyot-Sionnest, P. *Langmuir* **1995**, *11*, 493.

(8) Sato, Y.; Ye, S.; Haba, T.; Uosaki, K. *Langmuir* **1996**, *12*, 2726.

(9) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 3629.

(10) Yang, D.-F.; Wilde, C. P.; Morin, M *Langmuir*, in press.

(11) Hamelin, A.; Sottomayor, M. J.; Silva, F.; Chang, S.-C.; Weaver, M. J. *J. Electroanal. Chem.* **1990**, *295*, 291.

(12) Angerstein-Kozlowska, H.; Conway, B. E.; Hamelin, A.; Stoicoviciu, *J. Electroanal. Chem.* **1987**, *228*, 429.

(13) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.

(14) Ashley, K.; Pons, S. *Chem. Rev.* **1988**, *88*, 673.

(15) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

(16) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987,** *109*, 3559.

(17) Camillone, N. III; Chidsey, C. E. D.; Eisenberger, P.; Fenter, P.; Li, J.; Liang, K. S.; Liu, Y. G.; Scoles, G. *J. Chem. Phys.* **1993**, *99*, 744. Fenter, P.; Eberhardt, A.; Eisenberg, P. *Science* **1994**, *266*, 1216.

(18) Truong, K. D.; Rowntree, P. A. Manuscript in preparation.

(19) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.

(20) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1825. Nuzzo, R. G.; Zegarski, B. R.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1992**, *96*, 1355.

(21) Lambert, D. *Electrochim. Acta* **1996**, *41*, 623.

(22) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335.

(23) Marinova, K. G.; Alargova, R. G.; Denkov, N. D.; Velev, O. D.; Petsev, D. N.; Ivanov, I. B.; Borwankar, R. P. *Langmuir* **1996**, *12*, 2045.

(24) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45. Walczak, M. M.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2370.

(25) McPhail, R. A.; Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1982**, *77*, 1118. Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316.

(26) Cameron, D. G.; Hsi, S. H.; Umemura, J.; Mantsch, H. H. *Can. J. Chem.* **1981**, *59*, 1357.

(27) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211. Stuve, E. M.; Krasnopoler, A.; Sauer, D. E. *Surf. Sci.* **1995**, *335*, 177. Brosseau, R.; Ellis, T. H.; Morin, M. *J. Vac. Sci. Technol. A* **1990**, *8*, 2454.

(28) Ringstrom, U. *Nature* **1963**, *198*, 981.

(29) Peremans, A.; Tadjeddine, A. *J. Chem. Phys.* **1995**, *103*, 7197.

(30) Conway, B. E.; Bai, L. *Electrochim. Acta* **1986**, *31*, 1013.

(31) Hamelin, A.; Weaver, M. J. *J. Electroanal. Chem.* **1987**, *223*, 171.

(32) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Academic Press: New York, 1990.

(33) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *53/54*, 1143.

(34) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constant*, 3rd ed.; Chapman and Hall: New York, 1984.

(35) Walczak, M. M.; Aves, C. A.; Lamp, B. D.; Porter, M. D. *J. Electroanal. Chem.* **1995**, *396*, 103.

(36) Reid, E. E. *Organic Chemistry of Divalent Sulfur*; Chemical Publishing Co.: New York, 1958; Vol. 1.

(37) Bizzotto, D.; Lipkowski, J. *Prog. Surf. Sci.* **1995**, *50*, 237.

(38) Beden, B.; Leger, J. M.; Lamy, C. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M, Conway, B. E., White, R. E., Eds.; Plenum Press: New York, 1992; Vol. 22, Chapter 2.

(39) Yang, D.-F.; Wilde, C. P.; Morin, M. *Langmuir*, submitted.

(40) Larew, L.; Johnson, D. C. *J. Electroanal. Chem.* **1989**, *262*, 167.

(41) Garell, R. L.; Chadwick, J. E. *Colloids Surf. A* **1994**, *93*, 59.

(42) Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398.

(43) Li, Y.; Huang, J.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992,** *114*, 2428.

(44) Adzic, R. In *Modern Aspects of Electrochemistry*; White, R. E., Bockris, J. O'M, Conway, B. E., Eds.; Plenum Press: New York, 1990; Vol. 21, Chapter 5.

(45) Hamelin, A. In *Modern Aspects of Electrochemistry*; Conway, B. E., White, R. E., Bockris, J. O'M, Eds.; Plenum Press: New York, 1985; Vol. 16, Chapter 1.

(46) Wierse, D. G.; Lohrengel, M. M.; Scultze, J. W. *J. Electroanal. Chem.* **1978**, *92*, 121.

(47) Calvente, J. J.; Kovocova, Z.; Sanchez, M. D.; Andreu, R.; Fawcett, W. R. *Langmuir* **1996**, *12*, 5696.