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Comparison of Organic Monolayers on Polycrystalline Gold Spontaneously Assembled from Solutions Containing Dialkyl Disulfides or Alkanethiols[1]

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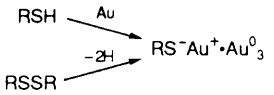
This paper compares the properties of self-assembled monolayers (SAMs) on polycrystalline gold formed at 24 °C from 1 to 1000 μM ethanolic solutions of dialkyl disulfides and of alkanethiols. The paper also describes an exploratory study of the kinetics of formation of these SAMs. The SAMs were characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), and wettability by water or hexadecane. SAMs derived from dialkyl disulfides or alkanethiols were indistinguishable when examined by ellipsometry and XPS; the contact angles of water or hexadecane were largely independent of the oxidation state—disulfide or thiol—of the organosulfur precursor. The rates of *formation* of SAMs from dialkyl disulfides or alkanethiols were indistinguishable. The rates of *replacement* of molecules from SAMs by thiols were much faster than by disulfides. This difference in the rates of replacement may account for the large preference for thiols in the competitive adsorption of disulfides and thiols on gold.

Introduction

Long-chain dialkyl disulfides or alkanethiols form self-assembled monolayers (SAMs) on gold.[3-8] These SAMs provide excellent model systems for studies involving the physical-organic chemistry of surfaces: Areas of interest include wettability,[9-11] monolayer structure,[12-18] adhesion,[19-23] tribology,[24-26] and interfacial chemical reactions.[27-32] In this paper we compare SAMs formed from solutions of disulfides or thiols.

In a previous paper,[33] we compared SAMs on polycrystalline gold derived from solutions of undecanethiol, diundecyl disulfide, 11-mercaptoundecanol, and bis(11-hydroxyundecyl) disulfide and from binary mixtures of these molecules. The wettability of the SAM was determined principally by the ratio of CH_2OH to CH_3 groups at the termini of the alkyl chains; it was largely unaffected by the oxidation state of the sulfur of the precursors used to form the SAM. SAMs formed on gold from ethanolic solutions containing 1:1 mixtures of dialkyl disulfides and alkanethiols of similar structure had a ~75:1 preference for inclusion in the SAM of groups derived from thiols over disulfides after 24 h of contact between the gold and these solutions. High-resolution XPS of the S(2p) peaks did not distinguish between SAMs formed from thiols or disulfides.[33-35] This observation suggested that both precursors form the same species on the surface (eq 1).



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The general experimental methods used to compare SAMs formed from disulfides or thiols were similar in the work described in this and in the previous paper:[33] We formed SAMs on gold from solutions of disulfides or thiols and characterized them by XPS, ellipsometry, and mea-

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surements of the contact angles. In the first part of this paper, we compare the properties of SAMs formed from dialkyl disulfides with those from alkanethiols; in the second part, we compare the kinetics of formation of SAMs from these two classes of precursors.

Experimental Section

General Information. Absolute ethanol (Quantum Chemical Corp.) was purged by N_2 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. Deuterated ethanol was used as purchased from MSD Isotopes.

Diethyl disulfide (Aldrich), dipropyl disulfide (Aldrich), dibutyl disulfide (Aldrich), and dihexyl disulfide (Fairfield) were purified by chromatography with hexane/ether (40:1) on Silica Gel 60 (Merck, 9 × $^3/_4$ in. column). A stock solution of $DS(CH_2)_{15}CH_3$ was prepared by dissolving 5 mg of $HS(CH_2)_{15}CH_3$ in 25 mL of EtOD, removal of the solvent at ~4 torr, and dilution of the residual thiol with EtOD to give 1 mM.

Synthesis of Disulfides from Thiols. The procedure that follows for dinonadecyl disulfide is an example of the method we used to form disulfides from thiols. Other dialkyl disulfides were prepared in a similar way.

Dinonadecyl Disulfide. A solution of nonadecanethiol (0.5 g, 1.7 mM) in 50 mL of ethanol was warmed to 50 °C and titrated to a persistent yellow endpoint with a 10 mM solution of I_2 in ethanol. The ethanol was removed on a rotary evaporator and the resulting yellow brown solid was dissolved in ether (50 mL), washed with distilled water (3 × 50 mL), and dried on $MgSO_4$. This suspension was filtered to remove the $MgSO_4$ and the ether was removed by rotary evaporator. The resultant white solid was dissolved in 5 mL of hexane/ethanol (1:1) and this mixture was chromatographed at ~40 °C with hexane/ether (40:1) on 150 g of Silica Gel 60 (Merck, 9 × $^3/_4$ in. column). Evaporation of the solvent left a white, crystalline solid that gave a negative test with Ellman's reagent, indicating the absence of thiols as impurities. ^1H NMR ($CDCl_3$) δ 2.65 (t, 2 H), 1.55 (m, 2 H), 1.2–1.4 (m, 32 H), 0.85 (t, 3 H). Anal. Calcd (found) for $C_{38}H_{78}S_2$: C, 76.18 (76.02); H 13.13 (12.97); S, 10.68 (10.88)

Didocosyl Disulfide. ^1H NMR ($CDCl_3$) δ 2.65 (t, 2 H), 1.55 (m, 2 H), 1.2–1.4 (m, 38 H), 0.85 (t, 3 H). Anal. Calcd (found) for $C_{44}H_{90}S_2$: C, 77.35 (77.27); H, 13.29 (13.37); S, 9.37 (9.61).

Preparation of Substates. Gold substrates were prepared by electron-beam evaporation of 2000 Å of gold (Materials Research Corp., 99.999%) onto 1 mm thick, single-crystal silicon-(100) test wafers (Monsanto, MEMC, and Silicon Sense) precoated with 100 Å of Cr (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. The silicon wafers were cut into ~1 cm × 3 cm slides with a diamond-tipped stylus, rinsed with ethanol, and dried with a stream of N_2 before their addition to solutions.

Instrumentation. Ellipsometric measurements were performed on a Rudolf Research ellipsometer (Type 43603-200E) equipped with a He–Ne laser (λ = 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.[36] following an algorithm by F. L. McCrackin and co-workers; in the calculation, we used a refractive index of 1.45 for the SAMs.

Contact angles of water or hexadecane on these SAMs were measured using a motorized pipette (Electropipette, Matrix Technology) mounted on a precision *z* axis translator.[37] For each substrate and each liquid, the contact angle of the liquid with the surface was measured in at least three different locations.

X-ray photoelectron spectra were obtained on an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays. The area of illumination by X-rays was ~1 mm²; an analyzer pass energy of 50 eV was used for measurements of C(1s) and Au(4f); these spectra were acquired for 20 and 3 min, respectively.

Formation of SAMs. Adsorptions were carried out in 25-mL glass weighing bottles that had been cleaned with "piranha solution" (7:3 concentrated H_2SO_4/ 30% H_2O_2) at 90 °C for 24 h, and rinsed with copious amounts of distilled 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 (probably when mixed with significant quantities of an oxidizable organic material), it has detonated unexpectedly.**[38] 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 24 h.

Kinetic Studies. Solutions of adsorbate of the desired concentration were prepared in deoxygenated solvent by serial dilution of 1 mM stock solutions. The disulfide concentration was counted at twice its nominal value because each molecule contributes two RS moieties to the monolayer. All experiments were done at 23 ± 2 °C. Solutions (20 mL) used to form the SAM were stirred at ~10 Hz with an egg-shaped magnetic stir bar with dimensions of $^3/_{16}$ in. × $^1/_8$ in.

Freshly evaporated gold substrates were washed with ethanol (~15 mL), blown dry with a stream of N_2, and examined by ellipsometry. A substrate was placed in a stirred solution of the adsorbate and a stopwatch was used to time its immersion. At the designated time, it was quickly (~0.5 s) removed from solution and immediately (~1 s) washed with ethanol (~15 mL). The substrate was dried with a stream of N_2, and its optical constants were determined by ellipsometry. The contact angle of hexadecane was measured on the resultant film. The substrate was washed with ethanol (~15 mL) and dried with N_2 and reimmersed in the solution containing the adsorbate until the next time interval had passed. Each experiment was repeated twice.

We were concerned that this method of monitoring the formation of SAMs on a single slide might not reflect the true kinetics of adsorption for thiols or disulfides because of repeated handling of the substrate. We tested this possibility by preparing 11 degassed, 1.4 μM solutions of $HS(CH_2)_{15}CH_3$. Into each vial, a gold substrate was immersed for a set period of time; the substrate was taken out of solution, washed with ethanol (~15 mL), and dried with N_2. These 11 slides, each with a different time of immersion and therefore representing different stages of SAM completion, were analyzed by XPS.

In carrying out the XPS analysis, we acquired the Au($4f_{7/2}$) and S(2p) signals using a pass energy of 100 eV; the area illuminated by the X-rays was ~1 mm². We collected the Au(4f) signal for 3 min and the S(2p) signal for 50 min. We calculated the thickness of the overlayer on the gold substrate using the following relation where (Au) is the intensity of gold photoelectrons attenuated by an overlayer of thickness *d* (Å), $(Au)_0$ is the intensity of photoelectrons of gold from a substrate cleaned of hydrocarbon by argon sputtering under UHV, λ is the inelastic mean free path of the photoelectron (Å), and γ is the angle between the surface parallel and the analyzer axis.[39]

$$(Au) = (Au)_0 \exp(-d/\lambda \sin \gamma) \qquad (2)$$

We used a value of 42 Å for λ_{Au}, calculated by using eq 2 from data in this paper, to estimate the thickness of the overlayer on the gold substrate as a function of time.[39] We assumed the SAM was complete after 3 × 10^5 s in the thiol-containing solution (Figure 1a). Data for the rate of formation of the SAM derived from measurements of the intensity of photoelectrons on different gold substrates were in good agreement with the rate of formation of a SAM measured by ellipsometry on a single gold substrate.

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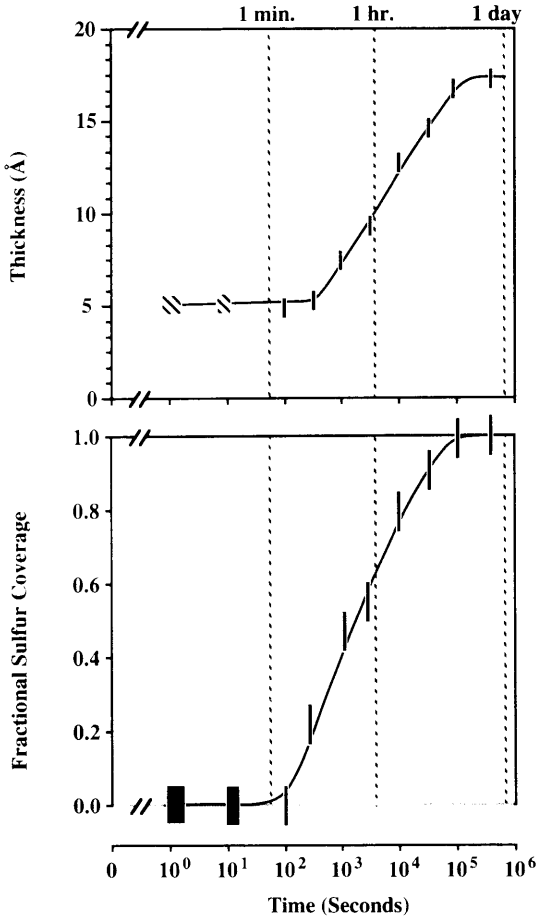

Figure 1. Thickness of organic films on polycrystalline gold after exposure to 1.4 μM solutions of $HS(CH_2)_{15}CH_3$ in ethanol was followed by XPS (upper figure). The change in the intensity of sulfur signals, measured by XPS and corrected for the thickness of the hydrocarbon layer (eq 4), matched the change in thickness of these films (lower figure). The lines through the data are provided as guides to the eye. Dashed boxes (at low times) indicate signals probably associated with physisorbed hydrocarbon present on "bare gold" substrates caused by exposure of these substrates to the laboratory environment. Gold sputtered clean by 3-keV argon cations under high vacuum in the XPS was the reference signal for all measurements. The logarithm of time is used to allow the data to be viewed conveniently.

We concluded that repeated washings of the gold substrate at intermediate stages of formation of the monolayer did not affect the measured kinetics in these studies.

Although Figure 1a established that the mass on the surface increased with time, we wanted to demonstrate a causal relationship between the increase in the thickness of the overlayer on gold and the molecules from which the SAM was formed. We measured, therefore, the concentration of sulfur in this overlayer.

Assuming the escape depth of a photoelectron is proportional to its kinetic energy, we estimated the escape depth, λ_s, of an S(2p) photoelectron from the known value of λ_{Au} using eq 3.[39]

$$\frac{\lambda_S}{\lambda_{Au}} = \frac{KE_S}{KE_{Au}} \tag{3}$$

Here KE_S and KE_{Au} are the kinetic energies of photoelectrons of sulfur and gold, respectively. This expression, although approximate, is valid because of the small difference in energy of the photoelectron of $Au(4f_{7/2})$ and $S(2p)$. Assuming the overlayer of carbon was uniform on the gold surface and using λ_S = 39 Å, the fraction, F_S, of the surface covered by sulfur is given by eq 4 where S_t is the intensity of the S(2p) signal at time

$$S_t = S_\infty F_S \exp(-d/\lambda_s \sin \gamma) \tag{4}$$

t, and S_∞ is the intensity of the S(2p) signal, corrected for attenuation by a 20 Å overlayer of carbon, for a completely formed monolayer, and d is the thickness of the monolayer calculated from eq 2. Figure 1b plots these data; we assumed monolayer formation was complete ($S_t \cong S_\infty$) at 3×10^5 s.

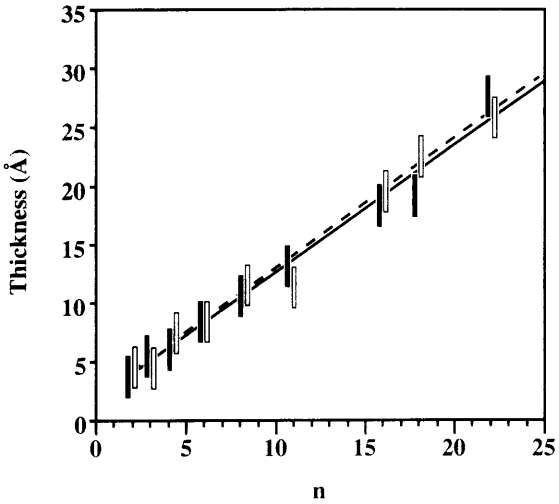

Figure 2. Thickness, measured by ellipsometry, of SAMs formed on polycrystalline gold from dialkyl disulfides (filled bars) or alkanethiols (open bars) increased linearly with the number of carbons in the alkyl chain of the precursor, HSC_nH_{2n+1} or $(SC_nH_{2n+1})_2$. The slope of the solid line fit to data for SAMs derived from dialkyl disulfides is 1.07 ± 0.1 Å/n. The slope of the dashed line fit to data for SAMs derived from alkanethiols is 1.08 Å/n. SAMs were formed by immersion of gold substrates for 24 h in 1 mM solutions of the precursor in ethanol. The size of the symbols shows our best estimates of the error in the measurement.

These data validated two hypotheses. First, the measured average thickness of these SAMs correlated, within experimental error, with the intensity of their S(2p) signals. This result confirmed that both sets of data reflected reaction of $HS(CH_2)_{15}CH_3$ with gold. Second, the kinetics of formation of SAMs measured by XPS agreed well with the kinetics of formation of SAMs measured by ellipsometry.

The advantage of the XPS-based method was it gave absolute thicknesses of monolayers and had good signal to noise. Ellipsometry measures the relative change in the thickness of the overlayer on gold; the presence of physisorbed hydrocarbon, normally found in the lab atmosphere, decreased the signal to noise of this measurement relative to XPS and introduced systematic errors. Ellipsometry was, however, more convenient and required less time.

Results

Properties of SAMs Derived from Alkanethiols and Dialkyl Disulfides as a Function of the Number of Carbons in the Alkyl Chain of the Precursor. Static Measurements: Thickness and Contact Angle. We compared the thickness of SAMs on polycrystalline gold formed from a series of dialkyl disulfides or alkanethiols of different chain lengths (Figure 2). For each value of n, the thicknesses of monolayers formed from dialkyl disulfides and alkanethiols were indistinguishable.[4,5] The intensities of $Au(4f_{7/2})$ and C(1s) peaks in XPS for SAMs derived from corresponding thiols and disulfides were also indistinguishable (Figure 3).

In a previous study we remarked that the apparent binding energy of the C(1s) photoelectron shifted to higher energy and this peak broadened as the length of the alkyl chain increased.[5] SAMs from alkanethiols and dialkyl disulfides followed similar trends (Figure 3). These shifts were not caused by increased electrostatic charging as the thickness of the monolayer increased; similar shifts and broadenings were observed when surface charge was neutralized using a flood gun. The shifts observed in the peak position of the C(1s) peak probably arise from changes

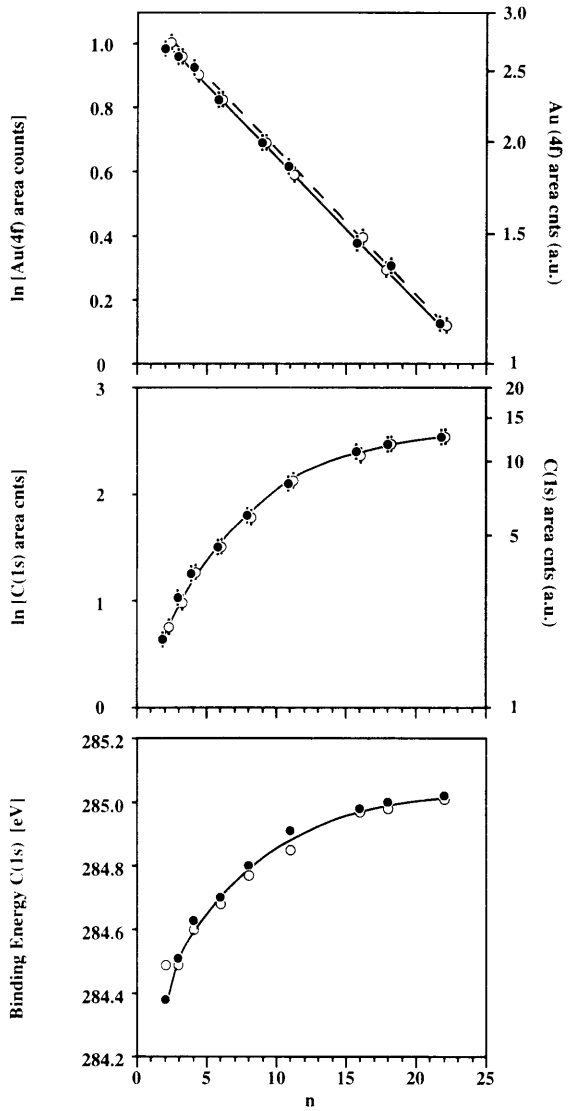

Figure 3. Logarithm of the intensity of photoelectrons of Au($4f_{7/2}$) for SAMs formed on polycrystalline gold from dialkyl disulfides (filled bars) or alkanethiols (open bars) decreased linearly with the number of carbons in the alkyl chain of the precursor, HSC_nH_{2n+1} or $(SC_nH_{2n+1})_2$. The slope of the sold line fit to data for SAMs derived from dialkyl disulfides results in a λ_{Au} of 42 ± 1 Å (eq. 2). The slope of the dashed line fit to the data for SAMs derived from alkanethiols results in a λ_{Au} of 42 ± 1 Å (eq 2). Part B (middle) plots the logarithm of the C(1s) signal as a function of *n* and part C (bottom) shows the energy of the C(1s) peak as a function of *n*. The lines in B and C are provided as guides to the eye. XPS data were accumulated using a pass energy of 50 eV and an X-ray spot size of ~0.018 mm². SAMs were formed by immersion of gold substrates for 24 h in 1 mM solutions of the precursor in ethanol. The size of the symbols shows our best estimates of the error in the measurement.

in the polarizability of the monolayers and not changes in its chemical state.[40-42]

Finally, we compared the contact angle of water or hexadecane (HD) on SAMs formed from dialkyl disulfides or alkanethiols (Figure 4). For $n > 10$, $\theta_a(H_2O)$ and θ_a-(HD) were 3–5° lower for a SAM derived from a dialkyl disulfide than for that formed from the corresponding alkanethiol; this difference was small but experimentally significant. Since a thiol and a disulfide adsorb onto gold and form a common species, probably a gold thiolate,[31,34,35,43,44] these small differences may reflect some difference in the organization of these monolayers.

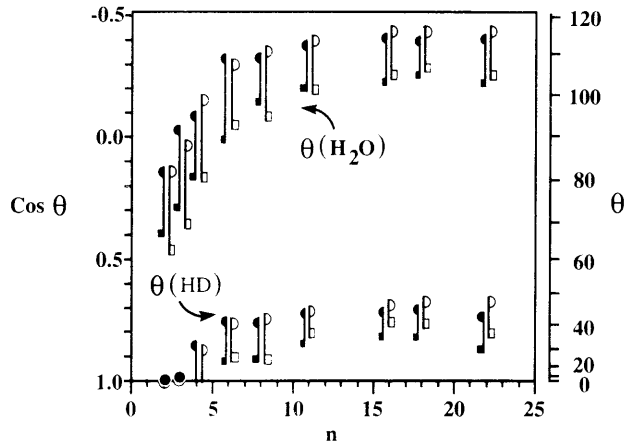

Figure 4. Contact angles of water or hexadecane on SAMs formed from dialkyl disulfides (filled symbols) or alkanethiols (open symbols) were similar. The maximum advancing angles (circles) and minimum receding angles (rectangles) are connected by a line to help organize the data visually and to indicate the hysteresis in the contact angle. SAMs were formed by immersion of gold substrates for 24 h in 1 mM solutions of the precursor in ethanol. The size of the symbols shows our best estimates of the error in the measurement.

When SAMs formed from dialkyl disulfides with $n > 10$ were reimmersed in a 1 mM solution of the corresponding alkanethiol in ethanol for 24 h, the contact angles of water or hexadecane on the resultant SAM were indistinguishable from those on SAMs derived directly from the alkanethiol. This result suggests the alkanethiol was able to complete the incomplete SAM formed from the disulfide. We emphasize that these small differences between SAMs formed from corresponding dialkyl disulfides or alkanethiols were evident only from the contact angles of liquids on these SAMs.

Kinetics of Formation of Monolayers. Measurement of Thickness and Wettability as a Function of Time of Exposure of the Gold Substrate to the Solution Containing the Organosulfur Compound. Our previous paper showed that the thiol component adsorbed preferentially from solutions containing a 1:1 mixture (in terms of RS groups) of dialkyl disulfide and an alkanethiol with the same length. After 24 h of contact with this solution, 99% of the RS moieties in the SAM were derived from the thiol (a 75:1 preference).[33] To determine how much of this preference for thiols was kinetic, we examined the rates of formation of SAMs on gold from solutions containing pure $(S(CH_2)_{15}CH_3)_2$ or $HS(CH_2)_{15}CH_3$ in ethanol. Figure 5 summarizes thicknesses and contact angles for these two systems. At two different concentrations, the rates of formation of SAMs from alkanethiol and dialkyl disulfide were indistinguishable when measured by thickness; using contact angles, rates were also very similar, but the ultimate contact angles measured using water or hexadecane on the SAMs formed from $(S(CH_2)_{15}CH_3)_2$ were slightly lower than those on SAMs formed from hexadecanethiol. This finding supports our inference that dialkyl disulfides are kinetically slow to complete monolayers. Again, this difference was evident only in the measurements of contact angles. Figure 6 shows the fit of these data, for low coverage of the gold, to a model that assumed the change in the thickness of the SAM was simply proportional to the number of

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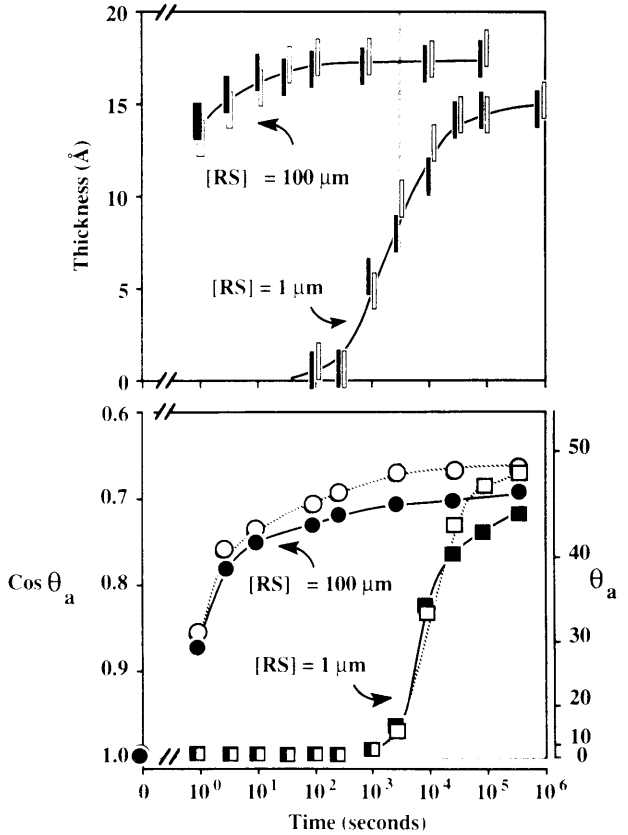


Figure 5. Rates of formation of SAMs on underivitized gold from solutions of $(S(CH_2)_{15}CH_3)_2$ (filled symbols) and $HS(CH_2)_{15}CH_3$ (open symbols) in ethanol at room temperature were indistinguishable. Part A (top) shows the thickness of SAMs, measured by ellipsometry, and part B (bottom) the θ_a of hexadecane after different times of exposure of underivitized gold substrates to solutions of the precursor. [RS] is the concentration in solution of alkyl thiolate equivalents used to form the monolayer. The logarithm of time is used to conveniently view the data. The lines through the data are provided as guides to the eye.

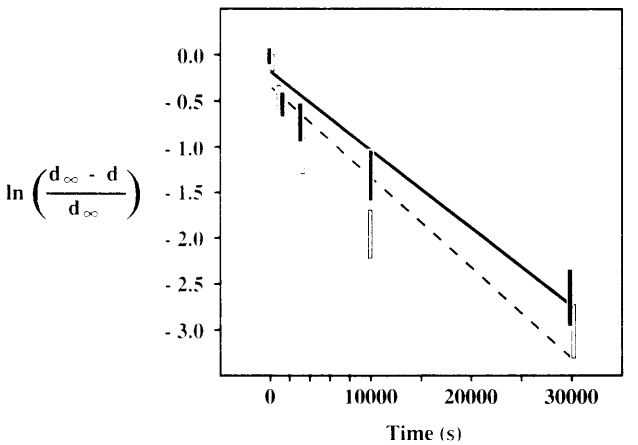


Figure 6. Adsorption of $(S(CH_2)_{15}CH_3)_2$ (filled symbols) and $HS(CH_2)_{15}CH_3$ (open symbols), at low coverages of the gold, fit a simple kinetic model where the change in the thickness of the SAM with time is proportional to the number of unoccupied sites on the gold (Langmuir adsorption). The slope of the solid line fit to data for SAMs derived from dialkyl disulfides is $(-8 \pm 3) \times 10^{-5}$ s^{-1}. The slope of the dashed line fit to the data for SAMs derived from alkanethiols is $(-9 \pm 3) \times 10^{-5}$ s^{-1}.

underivatized sites on gold (Langmuir adsorption). Although the fit to the data is not perfect, our results do not allow us to distinguish this simple kinetic model for adsorption of dialkyl disulfides or alkanethiols on gold from other, more complicated, models.

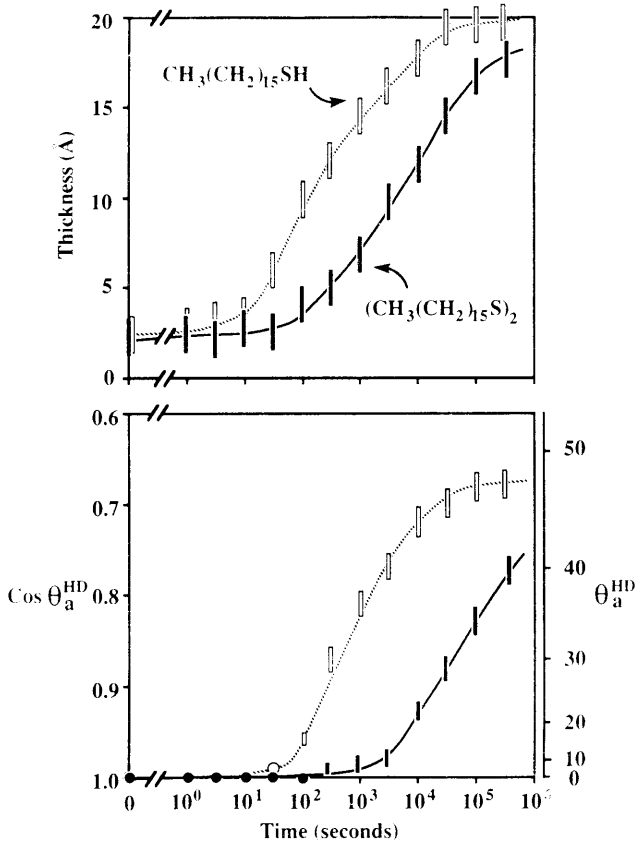


Figure 7. Replacement of SAMs of propanethiolate groups by $(S(CH_2)_{15}CH_3)_2$ is slower than replacement of SAMs of propanethiolate by $HS(CH_2)_{15}CH_3$. SAMs of propanethiolate groups were exposed to 1 mM solutions of $(S(CH_2)_{15}CH_3)_2$ (filled symbols) or $HS(CH_2)_{15}CH_3$ (open symbols) in ethanol at room temperature. The upper figure shows the thickness of the organic layer, measured by ellipsometry and (B, bottom) the θ_a of hexadecane after different times of exposure of gold derivitized by propanethiol to solutions of the precursor. The lines through the data are provided as guides to the eye. The logarithm of time is used to present the data conveniently.

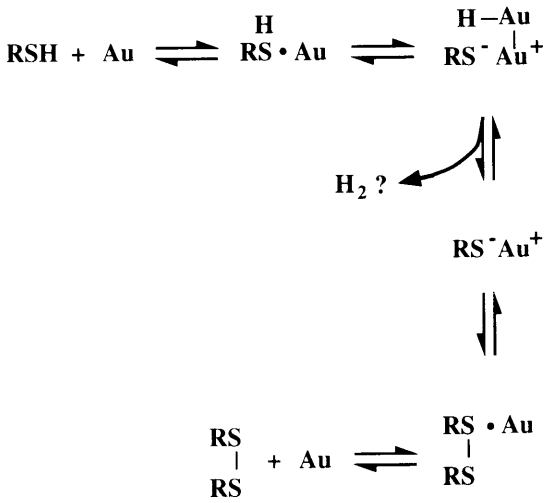
Kinetic Isotope Effects. We compared the rates of formation of SAMs from $HS(CH_2)_{15}CH_3$ (in EtOH) and $DS(CH_2)_{15}CH_3$ (in EtOD); these rates were indistinguishable. Breaking the S–H bond was not, therefore, rate-determining formation of SAMs from ethanolic solutions of alkanethiols.

Kinetics of Displacement of Alkanethiolates from a Preformed SAM by Alkanethiols and Dialkyl Disulfides. The data in Figure 5 define the *net* rate of formation of SAMs; they do not address interchange of RS moieties between the SAM, the precursor to the SAM, and solution. Thiols or disulfides in solution replace alkanethiolate moieties from preformed SAMs on polycrystalline gold: Long-chain thiols or disulfides readily replaced the species in SAMs formed from short-chain thiols or disulfides.[5,33,37,45-47] This rate of replacement from the SAM did *not* depend on the species used to form the SAM, evidence that further supported the hypothesis that alkanethiolates make up SAMs formed from disulfides or thiols.

Figure 7 shows data establishing that the rate of *displacement* of propylthiolate moieties from a SAM was ~50 times faster by $HS(CH_2)_{15}CH_3$ than $(S(CH_2)_{15}CH_3)_2$.

(45) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301–4306.
(46) Collard, D. M.; Fox, M. A. *Langmuir* **1991**, *7*, 1192–1197.
(47) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M.; Deutch, J. *J. Phys. Chem.* **1994**, *98*, 563–571.

Scheme 1. Possible Outcomes for the Reaction of a Dialkyl Disulfide or an Alkanethiol with Gold



Since the rates of *formation* of SAMs from thiols and disulfides were indistinguishable (Figure 5), we expect the observed preference for thiols over disulfides in SAMs formed from mixtures of the two reflects the difference in the ability of these molecules to replace chemisorbed species in SAMs. We offer the conjecture that this difference in rates of replacement arises from the larger steric bulk of disulfides.

Discussion

SAMs from alkanethiols and corresponding dialkyl disulfides are indistinguishable by many criteria: TEM,[18] XPS, thickness (as measured both by ellipsometry and XPS), and rate of formation. Small differences in contact angles using water and hexadecane suggest that the dialkyl disulfide-derived monolayers were slightly less ordered in their outer groups than those formed from alkanethiols under the conditions (24 °C, several hours contact of the gold film with the solution of organosulfur compound) commonly used in preparing these types of SAMs.

Alkanethiols and dialkyl disulfides differ, however, in their ability to replace thiolate groups present in previously formed SAMs. Dialkyl disulfides were slower to interchange between solution and the SAM than alkanethiol by a factor of ~50, in the single example studied carefully here: Replacement of propyl thiolate adsorbed on polycrystalline gold by $HS(CH_2)_{15}CH_3$ or $(S(CH_2)_{15}CH_3)_2$.

Combining the qualitative kinetic observations summarized in this paper with observations from previous work provides enough information to suggest a qualitative mechanism for formation of SAMs (Scheme 1). We summarize the key points supporting this scheme:

(1) Reaction of both alkanethiols and dialkyl disulfides with gold yield alkanethiolates RS^-Au^+ adsorbed epitaxially on a gold(0) surface as product. It is not presently clear where the hydrogen originally present on the thiol goes; we assume the product is H_2 but have not been able to detect it directly.

(2) The overall rate-limiting step in formation in surface alkanethiolates seems to be the same or very similar for both thiols and disulfides. This conclusion is based on the limited data summarized in Figure 5 and may not hold for other reactants or for other conditions. These results are the most surprising in this study in terms of mechanistic significance. The starting materials are clearly different although the product of the two reactions is the same so we anticipated different rates of transformation of starting material to product. At present there are three possible explanations for the unexpected similarity in rates of formation of SAMs from alkanethiols and dialkyl disulfides. First, the rate-limiting step might involve a process relatively weakly influenced by the composition of the organosulfur compound (oxidation of gold(0) to gold(I), for example). Second, the apparent similarity in rate may be an artifact. It might reflect the rate of replacement of impurities physisorbed on the gold surface by organosulfur compounds (a rate that might be similar for alkanethiols and for dialkyl disulfides).[48] Third, the rate-limiting step may involve organization of the alkanethiolates, or surface atoms on the underlying gold substrate.[48,49] We found, however, that the kinetics of formation of SAMs formed from hexadecanethiol on epitaxial films of gold were indistinguishable, by XPS and wettability, from these rates for SAMs formed on polycrystalline gold.[50]

(3) The surface species (RSH·Au or RSSR·Au) preceding the rate-limiting step are probably in equilibrium with the corresponding organosulfur species in solution.[47] This inference is based on the strong dependence of the rate of formation of SAMs on the concentration of organosulfur compounds in solution and on the relatively slow overall rate of formation of SAMs. This concentration dependence excludes a mechanism in which equilibrium between RSH or RSSR in solution and physisorbed on the gold surface lies far to the side of physisorbed species so the surface is always saturated with adsorbed alkanethiol or dialkyl disulfide. We expect no, or only weak, dependence on concentration of the organosulfur species in solution in this case. Because the reaction to form a complete SAM is certainly not mass transport limited (since $\tau_{1/2}$ = 100 s at (RS) = 1 μM), we infer the surface coverage of RSH·Au or RSSR·Au to be less than unity. The rapid rate of formation of SAMs at (RS) = 100 μM suggests that the coverage of the gold surface by physisorbed organosulfur compounds may, in fact, be close to unity at high concentrations of organosulfur compounds in solution.

(4) The exchange of R′S in an existing SAM for RS moieties from soluble RSH or RSSR in solution is a replacement reaction, rather than a dissociation/association process.[5,47] SAMs on gold are stable for weeks in ethanol or isooctane.[5] Nuzzo reported, in contrast, that thermal dissociation in high vacuum of SAMs formed from either RSH or RSSR leads to the same product—RSSR.[34,35] Dissociation in the form of a reductive elimination is likely in this case (eq 3).

$$2RSAu \rightarrow RSSR + 2Au(0) \qquad (3)$$

In our studies, the interchange of species between the SAM and soluble organosulfur compounds in solution was slower for RSSR than for RSH. We think that this difference in rate has a contribution from steric hindrance. The CSSC dihedral angle of dialkyl disulfides is close to 90°, and the sulfur atom of a dialkyl disulfide is much more hindered sterically than that of an alkanethiol. We suggest that it will be sterically more difficult for a dialkyl disulfide to insert itself into a preformed SAM (perhaps at a structural defect in the SAM) than for an alkanethiol

(48) Some insight on the kinetics of monolayer formation has been provided recently with the following study: Hähner, G.; Wöll, C.; Buck, M.; Grunze, M. *Langmuir* **1993**, *9*, 1955–1958.

(49) Edinger, K.; Gölzhäuser, A.; Demota, K.; Wöll, C.; Grunze, M. *Langmuir* **1993**, *9*, 4–8.

(50) Epitaxial films of gold were fabricated by evaporation of Au onto mica substrates warmed to 350 °C in ultrahigh vacuum. The root mean square (RMS) roughness of these films, measured by tunneling microscopy, was ~3 Å, substantially smoother than polycrystalline gold substrates prepared at room temperature on Si substrates grown at room temperature (RMS roughness ~30 Å).

to do so. Electronic contributions from the oxidation state of the sulfur to this difference in rate may, of course, also be important. 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. The redox chemistry at these sites with thiols or disulfides is necessarily different and may account for the difference in rate of replacement of thiolates in SAMs by thiols.

Our studies limit, but do not define, the mechanism of the replacement reaction. We have not defined the products, although we would guess that the presence of RSH in solution results in generation of R′SH from SAMs of R′S on gold and that RSSR generates RSSR′ and R′SSR′ from SAMs of R′S on gold (Scheme 1). Displacement as gold thiolates may also contribute,[49] although we found that gold substrates were not dissolved after 1 month of refluxing these substrates in neat butanethiol in sealed vials.[51] The dependence of the rate of replacement on the concentration of soluble organosulfur species and on the structures of both soluble and gold-bound organosulfur species remains to be established.

(5) The form in which the hydrogen present in the thiol is lost remains to be determined. Plausible products are H_2 and H_2O (from adventitious oxidation of a reactive gold surface hydride). The formation of SAMs proceeds, however, in vacuum. Thus, it appears that the presence of oxidants is not required for reaction to take place and suggests H_2 as the most plausible product. Experiments to detect H_2 have, however, so far been unsuccessful.

The broad outline of the mechanism for formation of SAMs that emerges from these and other studies[5,34,37,43,47,49] is thus one in which RSH and RSSR react with the gold and reach similar final states by paths that are similar. SAMs derived from RSSR have slightly greater wettability than those from thiols. This difference may be due to residual disorder in the SAM[48] and probably reflects steric hindrance to approach of the dialkyl disulfide to the gold through the partially formed SAM. The composition of mixed monolayers, especially for gold films held in contact with the organosulfur-containing solution for long intervals of time, appears to be determined by a complex set of kinetic factors, including an inferred preequilibrium involving intact alkanethiols (and/or dialkyl disulfides), and a structure-sensitive replacement of components from the surface that is roughly competitive in rate with the rate of formation of the SAM. In particular, the preference for incorporation of thiols in competitive adsorptions involving mixtures of thiols and disulfides seems to be largely the result of this replacement reaction: at short times, RSH and R′SSR′ of the same length adsorbed competitively. As time increases, the disulfide component of the monolayer becomes progressively more dilute, as both RS and R′S components in the SAM are preferentially replaced by RS groups derived from the thiol.

Acknowledgment. We thank Dr. John Folkers and Dr. Paul Labinis for useful discussions of this work.

(51) 1 × 3 cm silicon substrates, coated with 50 Å of chromium and 1000 Å of gold on the front and back sides, were placed in a vial with 15 mL of butanethiol. The vial was sealed and placed in an oil bath at 90 °C. The vial was opened after 1 month and examined by optical and scanning electron microscopy. The substrates appeared similar to control substrates of gold not exposed to refluxing butanethiol.