

Adsorption Profiles of Chelating Aromatic Dithiols and Disulfides: Comparison to Those of Normal Alkanethiols and Disulfides

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This study provides a comparison of the rates of adsorption of the following thiols onto the surface of gold: 1,2-bis(mercaptomethyl)-4,5-dihexadecylbenzene (**1**), 1-mercaptomethyl-3,4-dihexadecylbenzene (**2**), hexadecanethiol (**4a**), and eicosanethiol (**4b**). This study also compares the rates of adsorption of these adsorbates to those obtained for the aromatic disulfide analogue of **1** (2,3-dithia-6,7-dihexadecyltetralin, **3**) and the normal dialkyl disulfide analogues of **4a** and **4b** (hexadecyl disulfide, **5a**, and eicosyl disulfide, **5b**, respectively). The adsorption behavior was monitored using ex situ ellipsometry and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). The adsorption profiles suggest that monolayer formation proceeds via two distinct kinetic regimes: (1) a fast initial adsorption, where ca. 80–90% of the monolayer forms during the first few minutes of immersion, followed by (2) a slower orientational ordering lasting several hours. Comparison of the rates of adsorption of the aromatic dithiols **1** to those of aromatic monothiol **2** and normal alkanethiols **4a** and **4b** reveals that the structure of the adsorbate plays a substantial role during the initial stages of thiol adsorption. The impact of structural and/or chemical variations is further illustrated by comparing the poor quality of the monolayer generated from the aromatic disulfide **3** to those of monolayers generated from **1**, **2**, **4**, and **5**.

Introduction

Self-assembled monolayers (SAMs) of alkanethiolates are formed by the spontaneous adsorption of organosulfur compounds onto the surface of metals such as Au, Ag, Pt, and Cu.^{1–3} Gold is typically the metal of choice because it forms no oxide coating and is inert to most common contaminants. The structural features of alkanethiolate SAMs on gold have been characterized extensively using a wide variety of techniques.² The intrinsic mechanisms of film formation, however, remain poorly understood. It is commonly believed that SAMs derived from either thiols or disulfides adsorb onto the surface of gold as alkanethiolates.^{4–6} Other studies have found, however, that the adsorbates exist as dimers (i.e., as disulfides) on the surface.^{7,8} To establish the optimum conditions for SAM formation, our research seeks to probe the nature of the adsorption process by varying the structures and binding properties of the adsorbates.

Previous studies of the adsorption process have utilized a variety of tools including spectral ellipsometry,⁹ contact angle goniometry,⁹ reflection/absorption infrared spectroscopy (RAIRS),¹⁰ scanning tunneling microscopy (STM),^{11–13} surface plasmon resonance spectroscopy

(SPRS),^{14,15} quartz crystal microbalance (QCM),^{16,17} second harmonic generation (SHG),¹⁸ and near-edge X-ray absorption fine structure (NEXAFS).¹⁹ The consensus opinion favors a two-regime kinetic model for film formation: a fast initial adsorption regime, where 80–90% of the monolayer is formed, followed by a slow adsorption regime, where the monolayer undergoes orientational ordering to achieve complete film formation. While most studies favor the two-regime model, the relative duration of the adsorption regimes remains controversial. Other studies, such as those by DeBono et al.,¹⁵ suggest three distinct kinetic adsorption regimes, while the studies by Bucher et al.¹¹ and Sondag-Huethorst et al.¹² favor a single adsorption regime. These differences can plausibly arise from several factors including differences in (1) the purities, concentrations, and/or chain lengths of the adsorbates, (2) the nature of the adsorption medium, and (3) the quality of the gold substrate.

While examining the kinetics of adsorption of normal alkanethiols on gold, previous studies have also examined the corresponding adsorption of dialkyl disulfides.^{9,20} While the quality of the films generated from normal alkanethiols and their corresponding disulfides are largely indistinguishable, competitive adsorption studies have revealed that the alkanethiols adsorb more rapidly from solution than their corresponding dialkyl disulfides. This difference

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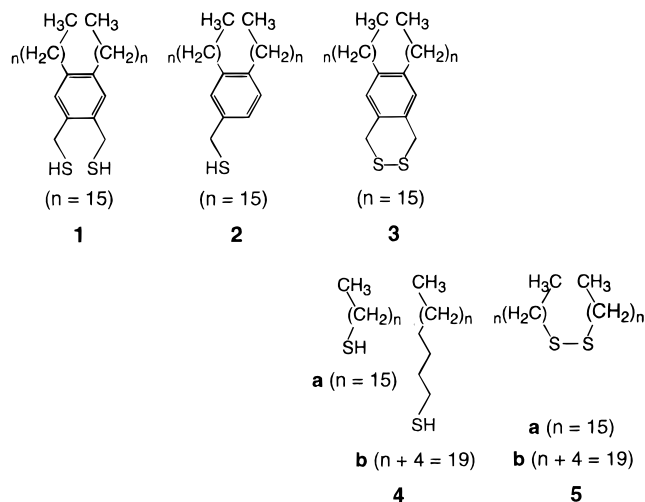


Figure 1. Structures of various aromatic-based and normal alkanethiols and disulfides used to generate SAMs on gold.

in rates can plausibly arise from a number of factors such as the relative rates of diffusion of the adsorbates to the metal surface,¹⁴ the relative abilities of the adsorbates to displace the solvent from the surface during adsorption,⁵ the relative magnitudes of steric hindrance posed by the adsorbates,²⁰ and the relative ease of reorganization of the organosulfur adsorbates and/or the surface atoms of the underlying gold substrate.²¹

Surprisingly few studies of SAMs on gold have explored the adsorption kinetics of species other than normal alkanethiols or dialkyl disulfides.^{22–26} Systematic studies of structurally distinct organosulfur adsorbates should permit a physical organic chemical probe of the adsorption mechanism(s). To this end, we report here studies of the kinetics of adsorption of aromatic alkanethiols **1** and **2** and compare the adsorption profiles of **1** and **2** to those obtained from the adsorption of the normal alkanethiols **4a** and **4b** (Figure 1).²⁷ We further compare these profiles to those obtained from the adsorption of the corresponding aromatic dialkyl disulfide **3** and the normal dialkyl disulfides **5a** and **5b**.

We chose to study the aromatic thiols **1** and **2** because we anticipated that these adsorbates would reveal key features of the adsorption process. For example, since the structures and binding properties of **1** and **2** are likely to differ from those of normal alkanethiols **4**, the relative contributions of structural variation and S–Au binding affinity could be directly assessed by comparing the adsorption profiles of **1** and **2** to those of **4**. Furthermore, since both methylene groups adjacent to the disulfide moiety in **3** are coplanar, while those in **5** are less conformationally restricted (preferred C–S–S–C dihedral angle $\sim 90^\circ$),²⁰ the latter species probably present greater steric bulk than **3** upon approach to the surface of gold. Consequently, we felt that a comparison of the adsorption profiles of **3** and **5** would permit us to assess the role of steric hindrance in the formation of SAMs on gold

(assuming insubstantial π -stacking and/or chelate effects for **3**). Moreover, we anticipated that a comparison of the adsorption profiles of the thiols (**1** and **4**) to those of the corresponding disulfides (**3** and **5**, respectively) would further clarify the chemical and structural parameters that govern SAM formation.

Experimental Section

Sources and/or Synthesis of Adsorbates. Hexadecanethiol (**4a**) was purchased from Aldrich Chemical Co., and eicosanethiol (**4b**) was prepared from eicosanol (Aldrich) using unexceptional methods. The preparation of 1,2-bis(mercaptomethyl)-4,5-dihexadecylbenzene (**1**) has been described elsewhere.^{27,28} During the course of the synthesis of **1**, the monobromomethyl precursor to 1-mercaptomethyl-3,4-dihexadecylbenzene (**2**) was obtained as a side product,²⁸ which was converted to **2** using standard transformations.²⁷ Analytical data for **2**: ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, 6 H, $J = 7$ Hz, CH₃), 1.24–1.54 (m, 56 H), 1.72 (t, 1 H, $J = 7$ Hz, SH), 2.55 (t, 4 H, $J = 8$ Hz, CH₂Ar), 3.68 (d, 2 H, $J = 8$ Hz, CH₂SH), 7.04–7.14 (m, 3 H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 13.2, 14.1, 22.7, 28.7, 29.4, 29.55, 29.63, 29.67, 29.71, 29.78, 29.83, 31.3, 31.9, 32.4, 32.7, 125.3, 128.7, 129.4, 138.3, 139.5, 141.0. Anal. Calcd for C₃₅H₇₂S: C, 81.82; H, 12.59. Found: C, 81.41; H, 12.30.

The synthesis of 2,3-dithia-6,7-dihexadecyltetralin (**3**), hexadecyl disulfide (**5a**), and eicosyl disulfide (**5b**) was accomplished using standard oxidation procedures;²⁹ complete analytical data are provided for the novel aromatic disulfide **3**: ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, 6 H, $J = 7$ Hz, CH₃), 1.24–1.56 (m, 56 H), 2.51 (t, 4 H, $J = 8$ Hz, CH₂Ar), 3.99 (s, 4 H, CH₂SS), 6.64 (s, 2 H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 14.1, 22.7, 29.37, 29.53, 29.60, 29.67, 29.70, 29.74, 29.78, 31.3, 31.9, 32.2, 34.2, 129.8, 130.6, 139.3. Anal. Calcd for C₂₀H₃₆S₂: C, 77.92; H, 11.69. Found: C, 77.96; H, 11.86.

Preparation and Analysis of SAMs. The methods used to prepare the SAMs and to measure their ellipsometric thicknesses and wettabilities have been described in a previous report.²⁷ The paragraphs below provide details of the IR spectroscopic analyses and the methods used to obtain the adsorption profiles.

Infrared Spectroscopy. A Nicolet MAGNA-IR 860 Fourier transform spectrometer was used to collect the polarization modulation infrared reflection absorption spectra (PM-IRRAS) for the SAMs generated from **1–5**. The mercury–cadmium–telluride (MCT) detector was cooled using liquid nitrogen. The infrared beam, which was incident at an angle of 80° , was polarized using a Hinds Instruments PEM-90 photoelastic modulator. The spectra were collected using 256 scans with a spectral resolution of 4 cm^{-1} .

Adsorption Studies. Data for the adsorption profiles were collected in the following manner. After immersing freshly evaporated gold-coated Si wafers ($\sim 1\text{ cm} \times 3\text{ cm}$) in solutions of the respective thiols or disulfides ($\sim 1\text{ mM}$ in isoctane), the wafers were removed at selected intervals of time, rinsed with ethanol, and blown dry with ultrapure nitrogen. Ellipsometric thicknesses, contact angle measurements, and PM-IRRAS spectra were collected immediately after the latter manipulation. Collection of adsorption profiles for at least two independent samples of each adsorbate afforded consistent trends in the relative rates of adsorption.

Results

Limiting Thicknesses, Wettabilities, and IR Spectra of SAMs Derived from 1–5. Table 1 shows the maximum ellipsometric thicknesses and hexadecane wettabilities of the SAMs derived from compounds **1–5**. These limiting values were obtained by soaking the gold substrates in ca. 1 mM solutions of the adsorbates in isoctane for 24 h.⁹ While the thicknesses of all SAMs are indistinguishably different, as are the wettabilities of the SAMs derived from **1**, **2**, **4**, and **5**, the hexadecane wettability of

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Table 1. Limiting Ellipsometric Thicknesses, Advancing and Receding Contact Angles of Hexadecane, and $\nu_a^{\text{CH}_2}$ Band Positions Derived from 1–5, Where $n = 15$

compd	thickness (\AA)	θ_a^{HD}	θ_r^{HD}	$\nu_a^{\text{CH}_2}$ (cm^{-1})
1	27	49°	35°	2922
2	26	50°	36°	2921
3	26	35°	15°	2925
4b	25	49°	36°	2919
5b	25	49°	35°	2919

^a Gold slides were immersed for at least 24 h in 1 mM solutions of the adsorbates in isoctane. The thicknesses were reproducible within $\pm 2 \text{ \AA}$, the average contact angles were reproducible within $\pm 2^\circ$, and the band frequencies were reproducible within $\pm 1 \text{ cm}^{-1}$.

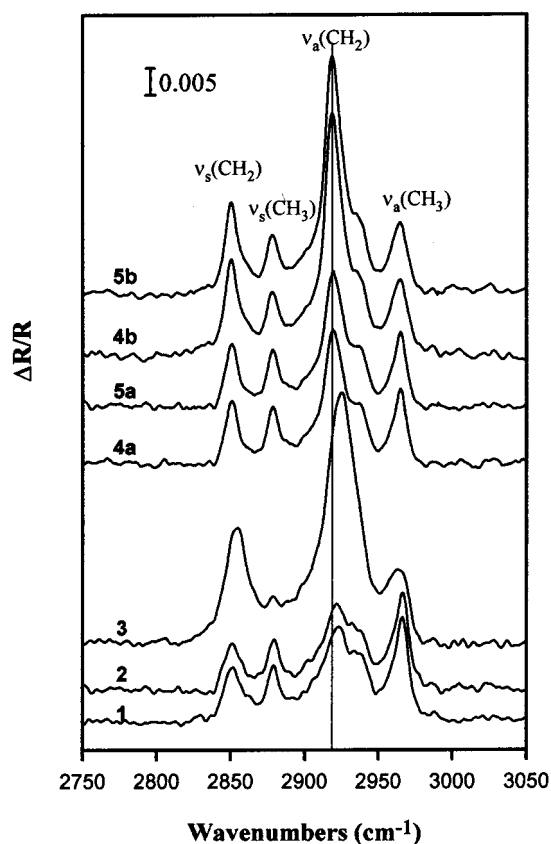


Figure 2. Infrared spectra (PM-IRRAS) of SAMs on gold generated by immersion in 1 mM solutions of 1–5 in isoctane.

the SAM derived from the chelating disulfide **3** is discernibly low, suggesting that **3** forms incomplete and/or disordered monolayers on gold.

We further characterized the fully formed SAMs by surface reflectance IR spectroscopy (specifically PM-IRRAS). For the purposes of comparison, we evaluated the frequency and bandwidth of the $\nu_a^{\text{CH}_2}$ band, which vary with the packing density and crystallinity of the monolayer.^{30,31} By comparing the IR spectra of these SAMs (Figure 2), the frequencies of the asymmetric methylene bands for the SAMs derived from **1** and **2** ($\nu_a^{\text{CH}_2} = 2921\text{--}2922 \text{ cm}^{-1}$) indicate slightly reduced crystallinity for these SAMs compared to those derived from the normal organosulfur adsorbates **4** and **5** ($\nu_a^{\text{CH}_2} = 2918\text{--}2919 \text{ cm}^{-1}$, irrespective of chain length). The lower crystallinity of the former SAMs might arise from two possible factors: interchain repulsive contacts arising from the relative

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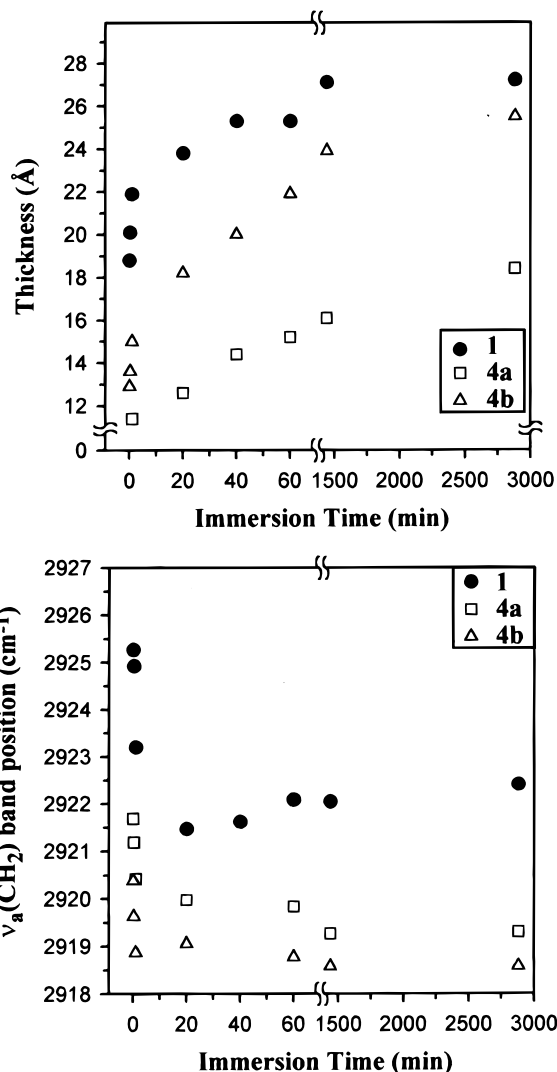


Figure 3. Adsorption profiles as measured by ellipsometry (upper) and PM-IRRAS (lower) of aromatic dithiol **1** (filled circles) and normal alkanethiols **4a** (hollow squares) and **4b** (hollow triangles) in isoctane.

orientation of the benzylic carbon atoms of the alkyl chains (i.e., the benzylic carbon atoms are necessarily directed away from each other) and/or intermolecular repulsive contacts associated with the rigid aromatic moieties (i.e., the aromatic rings might prevent closest packing). Both effects might unfavorably influence the packing densities and thereby introduce gauche defects into the alkyl chains.

Analysis of the PM-IRRAS spectra of the SAM derived from the aromatic disulfide **3** suggests that this adsorbate yields liquidlike rather than crystalline films ($\nu_a^{\text{CH}_2} = 2925 \text{ cm}^{-1}$).^{30,31} As noted above, the hexadecane contact angle measurements also suggest that this adsorbate generates poorly ordered and/or poorly packed films (see Table 1). In light of the fact that the properties of the SAMs derived from **4** and **5** (i.e., normal alkanethiols and normal dialkyl disulfides, respectively) differ indistinguishably from one another, it is somewhat surprising that the properties of the SAMs derived from **1** and **3** (i.e., chelating aromatic dithiol and chelating aromatic disulfide, respectively) differ so drastically from one another. Because **1** and **3** are structurally identical except for the dithiol vs disulfide moieties, we believe that the differences in film quality arise from this chemical/structural difference.

Adsorption Profiles of Thiols 1, 2, and 4. Figure 3 shows the adsorption profiles of the aromatic dithiol **1**

and the normal alkanethiols **4a** and **4b**. Note that the chain lengths of the normal alkanethiols correspond exactly to those found in **1** when considering the number of methylene groups (**4a**) or the total number of carbon atoms per chain (**4b**). Both the ellipsometric thickness data and the PM-IRRAS data suggest two distinct adsorption regimes for all adsorbates: a fast initial adsorption lasting a few minutes, where 80–90% of the monolayer forms, followed by a slower adsorption lasting several hours, where the thicknesses of the monolayers and the frequencies of the $\nu_a^{\text{CH}_2}$ bands slowly approach their limiting values. The apparent differences in the ellipsometric values for **4a** vs those of **1** and **4b** arise from the shorter chain length of **4a**. Given the degree of error associated with the ellipsometric measurements (typically ± 2 Å) and the PM-IRRAS data (typically ± 1 cm^{-1}), we find that the adsorption profiles for the aromatic dithiol **1** differ insubstantially from those of the normal alkanethiols **4** (as long as one considers the characteristic limiting $\nu_a^{\text{CH}_2}$ values of the SAMs derived from **1** and **4** shown in Figure 2). Taken as a whole, these data therefore suggest that, under the adsorption conditions employed here, the structural rigidity associated with the benzene moiety in **1** fails to influence strongly the kinetics of monolayer formation.

Figure 4 shows that the rate of adsorption of **2** is slightly slower than that of **1**. We note in particular that the SAMs derived from **1** reach limiting crystallinity (as judged by the frequency of the $\nu_a^{\text{CH}_2}$ band) after only 20 min of immersion time, while those derived from **2** require ca. 40 min of immersion time. Because **1** and **2** are structurally identical except for the dithiol vs monothiol moieties, we believe that the differences in the rates of adsorption arise from this chemical/structural difference.

Adsorption Profiles of Thiols vs Disulfides. Many studies have compared the adsorptions of alkanethiols and dialkyl disulfides on gold.^{9–19} Of particular note are the early studies by Bain et al., which examined the competitive adsorption of specific mixtures of alkanethiol and corresponding dialkyl disulfide.^{8,32} These studies concluded that the thiols were preferentially adsorbed by a factor of $\sim 75:1$ and that the preference was kinetically controlled. In more recent studies involving adsorbate exchange,²⁰ Biebuyck et al. proposed that the kinetic preference arises from steric factors: the preferred 90°C-S-S-C dihedral angle of the disulfides leads to steric crowding of the sulfur atoms, which hinders the adsorption process. In the present work, the data in Figure 4 show that, over both kinetic regimes, the disulfide **3** adsorbs more slowly than either the dithiol **1** or the corresponding monothiol **2**. Since the steric factors are probably very similar for **1** and **3**, steric discrimination appears insufficient to rationalize their relative rates of adsorption.

One might argue that the observed slow/poor adsorption of **3** arises from contamination of the cyclic disulfide with oligomeric or polymeric disulfides. To test for this possibility, we examined by high resolution ^1H NMR spectroscopy (600 MHz) a sample of **3** that had been stored neat at room temperature for >6 months. The spectrum showed no evidence of oligomeric or polymeric species, which would afford resonances corresponding to $\text{ArCH}_2\text{-SS-}$ at chemical shifts slightly less than δ 3.99.³³ Moreover, given the known equilibrium constant for the formation

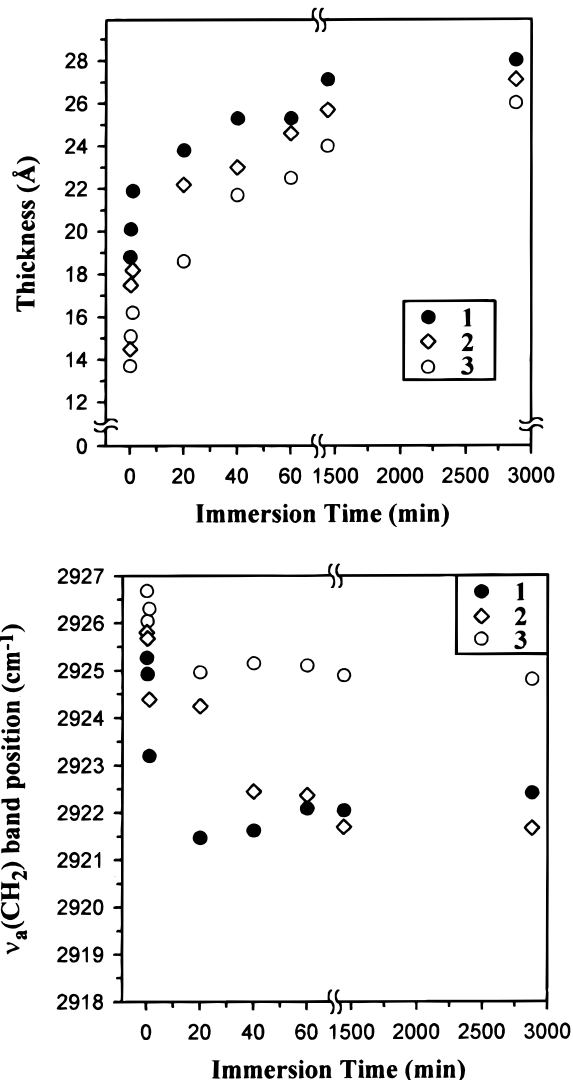


Figure 4. Adsorption profiles as measured by ellipsometry (upper) and PM-IRRAS (lower) of aromatic dithiol **1** (filled circles), aromatic monothiol **2** (hollow diamonds), and aromatic disulfide **3** (hollow circles) in isoctane.

of cyclic disulfides such as **3**,³⁴ one would predict a negligible fraction of oligomeric/polymeric species in neat samples of **3**.³⁵

The adsorption profiles of **4b** and **5b** are shown in Figure 5. The corresponding profiles for the shorter chain lengths (**4a** and **5a**, respectively) gave similar results (data not shown). While other methods have established that alkanethiols adsorb more rapidly than dialkyl disulfides,⁵ the ellipsometric data and the PM-IRRAS data obtained here fail to distinguish these kinetic differences. From the similarity in the adsorption profiles for **4** and **5**, we infer that the markedly slow adsorption of **3** relative to **1** probably originates from some factor(s) other than “chemically” slow oxidative addition of disulfide moieties to the surface of gold. If this type of “chemical” difference were responsible, then, in the absence of other factors, we would expect to observe differences in the rates of adsorption of **4** and **5** in a fashion similar to that in which we observe differences in the rates of adsorption of **1** and **3**.

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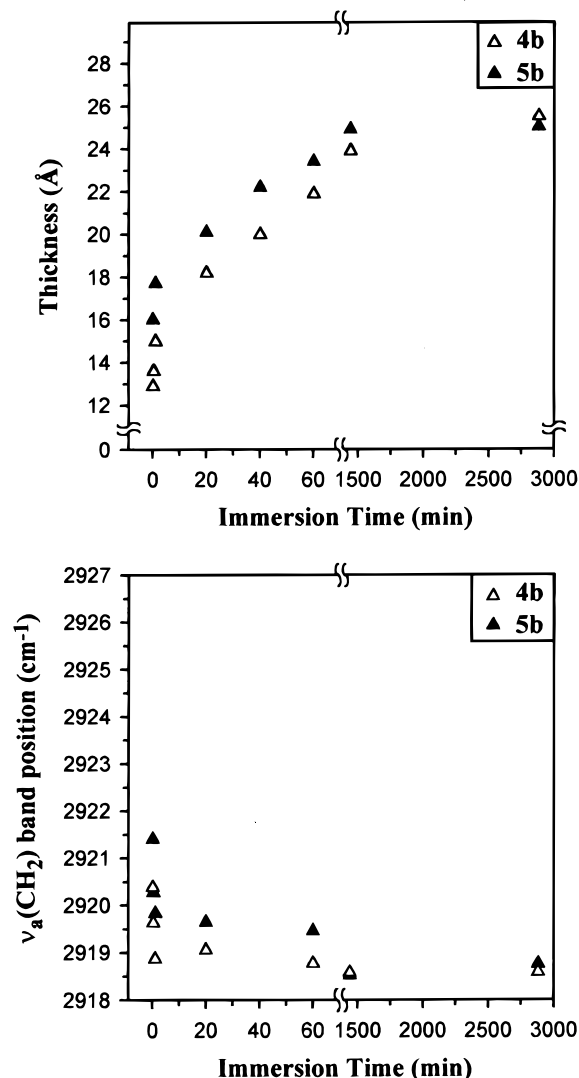
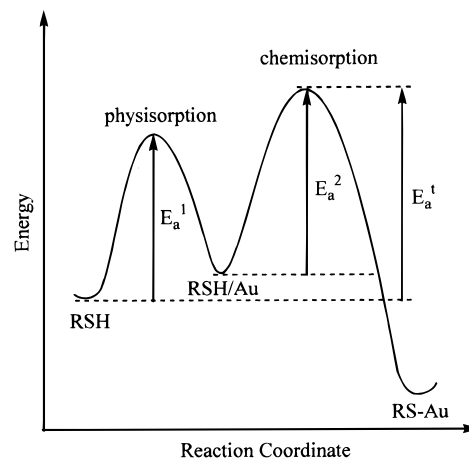


Figure 5. Adsorption profiles as measured by ellipsometry (upper) and PM-IRRAS (lower) of normal alkanethiol **4b** (hollow triangles) and normal dialkyl disulfide **5b** (filled triangles) in isooctane. The shorter chain length analogues **4a** and **5a** gave similar results; the data are omitted for clarity.

Discussion

Several UHV and solution-phase studies have examined the adsorption behavior of normal alkanethiols and dialkyl disulfides on gold.^{9–20,32,36–41} At least two recent reports provide evidence that the adsorption proceeds via initial physisorption followed by chemisorption, where the chemisorption occurs by formal oxidative addition of the S–H or S–S bond to the surface.^{37,38} In Scheme 1, we present a reaction coordinate diagram that illustrates this two-step process. While we have yet to directly observe a physisorbed (i.e., striped or lying-down)^{37–41} phase for the adsorption of **1–3**, we infer the existence of physisorbed intermediates based upon the observations, in particular, by Xu et al.³⁸ and by Yamada and Uosaki,^{40,41} where lying-

Scheme 1. Proposed Reaction Coordinate Diagram for the Adsorption of SAMs on Gold



down phases have been observed in situ during the adsorption of normal alkanethiols from solution. We further note that the previous studies used solvents (namely, 2-butanol and *n*-heptane, respectively) that were more likely to destabilize the physisorbed state than that used in the present study (isooctane). Given these considerations and the absence of other reliable adsorption models, we have chosen here to analyze the adsorption behaviors of **1–3** in the context of this two-step model (Scheme 1).⁴²

In Scheme 1, if we assume that the steady-state approximation holds for the initial physisorption, we can then evaluate the relative rates of adsorption of **1–5** on the basis of the physisorption preequilibrium and the subsequent barrier to chemisorption. In this model, we assume that the relative population of the physisorbed intermediate is influenced largely by the length of the alkyl chains of the adsorbates,³⁶ while the barrier to chemisorption is influenced by steric constraints, conformational constraints, and/or chemical factors.

Due to the structural similarities of **1** and **2**, we infer that the magnitude of physisorption is probably similar for both adsorbates, unless both sulfur atoms in **1** are physisorbed strongly to the surface.³⁶ Consequently, the differing rates of adsorption for **1** and **2** would be expected to arise from their relative rates of chemisorption. Moreover, we can rationalize the faster rate of adsorption of **1** relative to **2** by a simple statistical model of oxidative addition of the S–H bonds to the surface: if the degree of physisorption is the same for **1** and **2**, then **1** might chemisorb faster than **2** because it possesses two reactive thiol groups rather than one. In the context of Scheme 1, these results are consistent with a lower barrier to chemisorption for **1** relative to that for **2**.

The substantially faster rate of adsorption for **1** relative to **3** is, however, somewhat more difficult to rationalize.⁴³

(42) We acknowledge that the adsorbate concentrations employed by Xu et al.³⁸ and by Yamada and Uosaki^{40,41} were substantially lower than those employed in the present study. These differences in concentration might invalidate the adsorption model and corresponding analysis presented here. Future studies will explore concentration effects and will attempt to characterize any observable physisorbed intermediates.

(43) Recently, Jung et al.⁵ proposed that the rates of chemisorption of thiols and disulfides differ due to the different manner in which they displace solvent from the surface. The authors proposed that while thiols require only one site for chemisorption, disulfides simultaneously require two sites for chemisorption. Since, however, the dithiol **1** and the disulfide **3** both simultaneously require two adsorption sites and the rate of adsorption of **1** appears substantially faster than that of **3**, our data fail to support their proposal.

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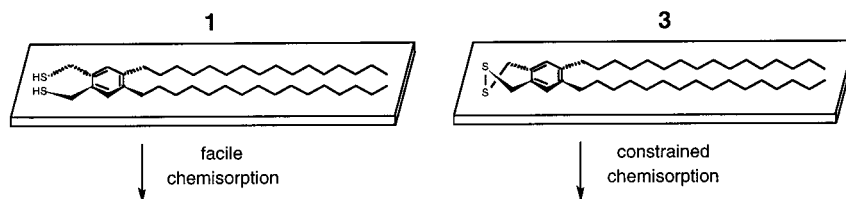
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Scheme 2. Proposed Structures for Physisorbed **1** and **3** on the Surface of Gold

Again, since both species are structurally similar, the degree of physisorption is probably similar for both adsorbates,³⁶ leaving chemisorption as the distinguishing step in the adsorption process. The differences between the rates of chemisorption of **1** and **3** can plausibly arise from at least two factors: (1) differing "chemical" rates of oxidative addition of the S–H bond in **1** and the S–S bond in **3** to the surface of gold or (2) differing conformational constraints of physisorbed **1** and **3** in a manner that deters attachment of the sulfur atoms to the surface of gold for **3** relative to **1**. Given that our analysis finds that the rates of adsorption of the thiols **4** and the disulfides **5** are indistinguishable, it appears that the difference in the rates of adsorption of **1** and **3** probably originates from some factor other than the "chemical" difference in the rates of oxidative addition of the S–H bond in **1** and the S–S bond in **3** to the surface of gold. Moreover, since the cyclic disulfide moiety in **3** is strained,⁴⁴ we would have predicted that relief of the strain in **3** upon adsorption would enhance its rate of adsorption relative to that of **1**, which is inconsistent with the experimental observations. We propose instead that the adsorption of **3** is hindered by conformational constraints imposed by both its cyclic nature and the conjoined rigid aromatic ring. These conformational constraints limit the degrees of freedom available to the disulfide moiety in physisorbed **3** and

thereby limit the rate at which **3** chemisorbs to the surface of gold (see Scheme 2).⁴⁵ In contrast, the conformationally accessible mercapto moieties in **1** permit facile chemisorption to the surface. In the context of Scheme 1, this proposal would be interpreted to indicate a higher barrier to chemisorption for **3** relative to that for **1**.

Conclusions

The adsorption profiles of **1**–**5** onto the surface of gold exhibit two kinetic regimes: a fast bulk adsorption followed by a slow crystallization process. Both the aromatic monothiol **2** and the aromatic disulfide **3** adsorb more slowly than the dithiol **1**. We propose that the observed differences in the rates of adsorption arise from the relative abilities of the adsorbates to chemisorb to the surface of gold. Other less obvious factors, however, might also give rise to the observed differences.

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