Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules: Hydrogen-Bonding Interactions

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The first example of controlled hydrogen-bonding interactions between a self-assembled monolayer and vapor-phase probe molecules is reported. FTIR–external reflectance spectroscopic data and ellipsometric experiments confirm that 1-alkanoic acids containing 10 or more carbons specifically adsorb to a surface-confined monolayer of an acid-functionalized mercaptan, 3-mercaptopropionic acid, through hydrogen-bonding interactions.

Introduction

This is the third paper in a series intended to critically evaluate the chemical and physical interactions between vapor- and liquid-phase probe molecules and ordered, surface-confined monolayers.[1-3] Here, we report that surface-confined monolayers of acid-functionalized organomercaptans interact with vapor-phase acid molecules to yield hydrogen-bonded bilayers. These systems can serve as models for natural systems,[4] and they form a basis for molecular recognition-based chemical sensors.[5]

In the present paper, we take advantage of the affinity of functionalized organomercaptan derivatives for Au to create two-dimensional acid surfaces that interact with vapor-phase acid probe molecules.[6] Specifically, we discuss the interactions of 1-alkanoic acids ($CH_3(CH_2)_nCOOH$, $n = 0$–14) with Au surfaces modified by 3-mercaptopropionic acid ($Au/HS(CH_2)_2COOH$). For convenience, we have chosen to depict an idealized view of this chemical system in Scheme I. However, it is highly unlikely that this level of organization actually exists, since the degree of intermolecular interactions necessary to promote such structures is absent. Results obtained from FTIR–external reflectance spectroscopy (FTIR–ERS) and ellipsometric measurements suggest that face-to-face and lateral hydrogen bonding occur between the carboxyl groups located at the interface of the two acid layers as shown at the bottom of Scheme I. However, if the surface-confined monolayer is not acid functionalized, as shown on the right side of Scheme I, no hydrogen bonding occurs.

Experimental Section

3-Mercaptopropionic acid, $HS(CH_2)_2COOH$, 1-propanethiol, $HS(CH_2)_2CH_3$, and the 1-alkanoic acids were used as received from Aldrich Chemical Co. *trans*-Cinnamic acid (CNMA) was also used as received from Eastman Kodak Co. Au surfaces were prepared by e-beam deposition of 100 Å of Ti and 2000 Å of Au onto polished Si single crystalline wafers.

Scheme I

Face-to-Face H-Bonding   Lateral H-Bonding   No Adsorption

Prior to derivatization, the wafers were diced (2.5 × 1.2 cm), cleaned in a freshly prepared "piranha" solution (H_2SO_4/H_2O_2 (3:1); *caution*, this mixture reacts violently with organic materials, and it should not be stored in sealed containers), rinsed with deionized water (Milli-Q, Millipore), and then dried in flowing N_2. The Au substrate was immediately modified with $HS(CH_2)_2COOH$ or $HS(CH_2)_2CH_3$ by immersion in the saturated vapor for 20–30 min at 20–25 °C. Our previous results have shown that this treatment generally leads to multilayer condensation, so the surface was exposed to flowing N_2 to ensure that only one monolayer of $HS(CH_2)_2COOH$ or $HS(CH_2)_2CH_3$ remained on the surface.[2,7] The presence of a single monolayer after this treatment was confirmed by FTIR–ERS and ellipsometry. To confirm hydrogen-bonding-induced bilayer formation, the $Au/HS(CH_2)_2COOH$ or $Au/HS(CH_2)_2CH_3$ substrate was suspended about 2.5 cm above the solid- or liquid-phase 1-alkanoic acid in an apparatus resembling a sublimation chamber. The bottom of the chamber was heated to 60 °C in an oil bath for 20–30 min. Since this configuration probably results in sublimation of multilayers onto the modified Au surfaces, excess acid was desorbed in flowing N_2. The FTIR–ERS and ellipsometric measurements were performed immediately following these steps.

FTIR–ERS data were obtained using a N_2-purged Digilab FTS-40 FTIR spectrometer (Bio-Rad, Cambridge, MA) equipped with a Seagull variable-angle reflection accessory (Harrick Scientific, NY). The p-polarized light was focused on the Au surface at an 85° angle of incidence, and the reflected beam was detected by a liquid N_2-cooled MCT detector. After 256 scans at 2-cm^{-1} resolution, a triangular apodization was applied and the final absorption spectrum was baseline-corrected. Reference spectra were obtained from a freshly cleaned, naked Au surface. The ellipsometric measurements and data analysis have been described previously.[2,7]

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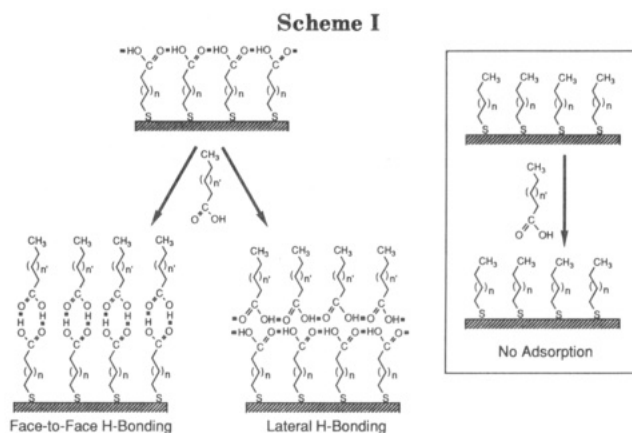
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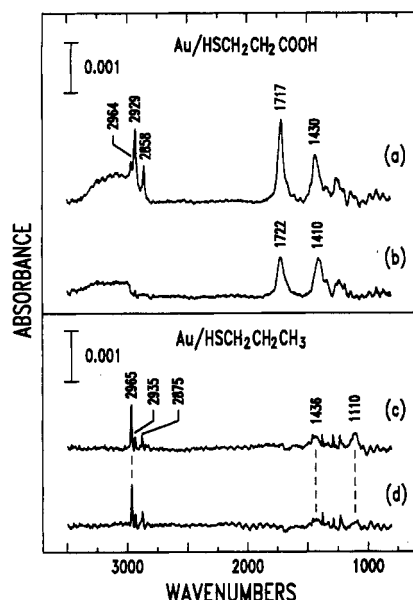
Figure 1. FTIR–ERS spectra of a Au/HS(CH₂)₂COOH surface before (b) and after (a) exposure to vapor-phase CH₃(CH₂)₁₂COOH and FTIR–ERS spectra of a Au/HS(CH₂)₂CH₃ surface before (d) and after (c) exposure to vapor-phase CH₃(CH₂)₁₂COOH. To ensure that the small frequency shifts of the peaks at 1717 and 1722 cm⁻¹ in (a) and (b), respectively, are statistically significant, we obtained spectra for 19 separate samples prepared identically to (a) and spectra for 9 separate samples prepared identically to (b). The standard deviation of the peak position is 1 cm⁻¹.

Results and Discussion

Figure 1 shows FTIR–ERS spectra for Au/HS(CH₂)₂COOH and Au/HS(CH₂)CH₃ surfaces before and after exposure to a saturated vapor of myristic acid, CH₃(CH₂)₁₂COOH. Prior to CH₃(CH₂)₁₂COOH modification, the HS-(CH₂)₂COOH spectrum, Figure 1b, shows absorptions at 1722 and 1410 cm⁻¹ that are consistent with literature reports.[8-11] After dosing, the presence of a second surface-confined CH₃(CH₂)₁₂COOH layer is confirmed by the appearance of the methyl C—H stretching vibration at 2964 cm⁻¹, the increased intensity of the methylene C—H stretching vibrations at 2929 and 2858 cm⁻¹, and the doubling of the intensity of the C=O stretching vibration at 1717 cm⁻¹, Figure 1a. The broad peaks centered at 3100 cm⁻¹ are due to O—H stretching, and the peaks near 1400 cm⁻¹ arise from C—H bending modes.

Control experiments were performed by exposing a methylated surface to vapor-phase 1-alkanoic acids, as illustrated on the right side of Scheme I. The FTIR–ERS spectrum of a surface-confined monolayer of HS (CH₂)₂CH₃ is shown in Figure 1d. The peak at 2967 cm⁻¹ is due to the asymmetric methyl C–H stretching vibration, and the asymmetric and symmetric methylene C–H stretching vibrations are at 2935 and 2875 cm⁻¹, respectively. Other peaks attributable to hydrocarbon backbone modes are present at lower energies.[12] The FTIR–ERS spectrum of the methyl surface after exposure to CH₃(CH₂)₁₂COOH, Figure 1c, is identical to the surface before acid dosing, Figure 1d. This result clearly shows that only the acid surface promotes bilayer formation.

Ellipsometric data confirm the affinity of CH₃(CH₂)₁₂COOH for the Au/HS(CH₂)₂COOH surface, but not for the Au/HS(CH₂)₂CH₃ surface. For example, the measured thicknesses of the mono- and bilayer structures used to obtain the FTIR–ERS data shown in parts b and a of Figure 1, respectively, were 1 and 6 Å. The low thickness value for the HS(CH₂)₂COOH monolayer results from a slight contamination of the reference Au substrate used for the ellipsometric measurement and the inherent difficulty of obtaining highly accurate data from such thin organic layers. The theoretical increase in thickness for ordered, close-packed bilayer structures, such as those shown in Scheme I, would be 3–4 times larger than our measured value. This indicates that surface-confined CH₃(CH₂)₁₂COOH is present as a disordered, loosely packed submonolayer. Within the accuracy of our ellipsometric measurements, the thickness of the Au/HS(CH₂)₂CH₃ control surface did not change after exposure to CH₃(CH₂)₁₂COOH. The key point, therefore, is that less than one monolayer of CH₃(CH₂)₁₂COOH adsorbs to the acid surface, and none adsorbs to the methyl surface.

Closer examination of the FTIR–ERS data presented in Figure 1 provides additional evidence for hydrogen bonding between the Au/HS(CH₂)₂COOH and CH₃(CH₂)₁₂COOH layers. The band at 1722 cm⁻¹ in Figure 1b has been assigned to the C=O stretching vibration for a laterally hydrogen-bonded carboxylic acid terminal group, as shown in Scheme I.[8a,11] After CH₃(CH₂)₁₂COOH exposure, the band shifts to 1717 cm⁻¹, Figure 1a. It has been shown previously that a 16-cm⁻¹ shift in the C=O stretching frequency of 1-alkanoic acids from about 1726 to 1710 cm⁻¹ corresponds to a structural change from a lateral hydrogen-bonded configuration to a face-to-face dimer configuration.[8a,10,13] On the basis of the observed frequency shift of 5 cm⁻¹, we propose a model in which adsorbed CH₃(CH₂)₁₂COOH is hydrogen-bonded to surface-confined HS(CH₂)₂COOH in both face-to-face and lateral configurations. This situation should result in two peaks: one for each configuration. However, we observe only a broad, about 60-cm⁻¹ fwhm, unresolved feature characterized by a peak position that is sensitive to the overall binding configuration.

The positions of the methylene stretching peaks of the Au/HS(CH₂)₂COOH/HOOC(CH₂)₁₂CH₃ bilayer at 2929 and 2858 cm⁻¹, Figure 1a, provide additional support for our model of a loosely packed, bilayer structure. These frequencies are nearly identical to the corresponding frequencies found for disordered bulk- or liquid-phase polymethylene vibrations, 2928 and 2856 cm⁻¹,[14] and they can be contrasted with the frequencies observed when about a monolayer of CH₃(CH₂)₁₂COOH is intentionally condensed onto the non-hydrogen-bonding Au/HS(CH₂)₂CH₃ surface, Figure 2. In this case, we oberved narrower methylene stretching peaks having frequencies of 2918 and 2848 cm⁻¹. These data indicate that simple condensation results in a solidlike phase of face-to-face hydrogen-bonded dimers, whereas interacting bilayer-type structures are more liquidlike.[14]

We obtained additional evidence for hydrogen bonding of vapor-phase probe molecules to surface-confined, acid-functionalized mercaptans by using *trans*-cinnamic acid, CNMA, as the probe molecule, Figure 3. The C=O

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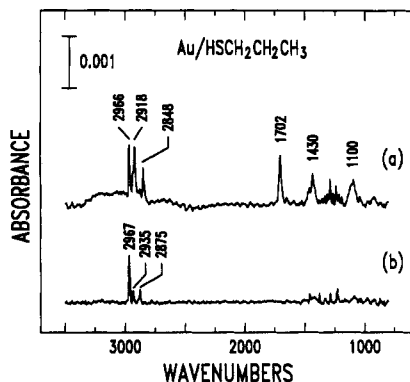
Figure 2. FTIR–ERS spectra of an HS(CH₂)₂CH₃-modified Au surface before (b) and after (a) condensation of a layer of solid-phase CH₃(CH₂)₁₂COOH. The amount of condensed CH₃(CH₂)₁₂- COOH was controlled by the dosing time and temperature so that the magnitude of the condensed-phase acid peaks at 1702 cm⁻¹ would be comparable to the peak intensities expected for a hydrogen-bonded bilayer of Au/HS(CH₂)₂COOH/HOOC-(CH₂)₁₂CH₃, Figure 1a.

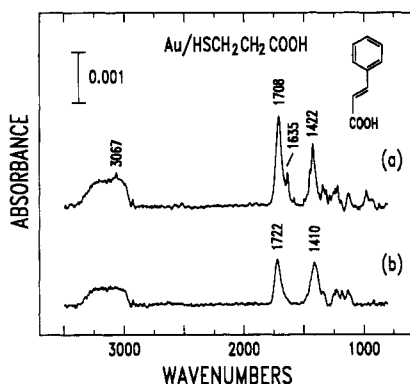**Figure 3.** FTIR–ERS spectra of an Au/HS(CH₂)₂COOH surface before (b) and after (a) exposure to vapor-phase CNMA. The structure of CNMA is shown in the upper right corner of the figure.

stretching vibration for the CNMA face-to-face dimer occurs at 1684 cm⁻¹.[15] Therefore, hydrogen-bonding interactions between an adsorbed CNMA layer and Au/HS(CH₂)₂COOH should result in a significant shift of the C=O stretching absorption to lower energy than was observed for the Au/HS(CH₂)₂COOH/HOOC(CH₂)₁₂CH₃ bilayer. The observed C=O streching vibration for hydrogen-bonded CNMA on the Au/HS(CH₂)₂COOH surface is 1708 cm⁻¹. This value is higher than the C=O stretching frequency estimated for the mixed face-to-face HS(CH₂)₂COOH/CNMA dimer, 1696 cm⁻¹,[16] but lower than the frequency observed for the Au/HS(CH₂)₂COOH/HOOC(CH₂)₁₂CH₃ bilayer. This result supports our earlier contention that the two layers are interacting through hydrogen bonds.

We estimated the interlayer adsorption energy, E_{ads}, by systematically changing the length of the vapor-phase

probe molecule. For COOH(CH₂)ₙCH₃, n = 0–14, no adsorbed 1-alkanoic acid can be detected on the Au/HS-(CH₂)₂COOH surface when $n \leq 8$, but submonolayer coverage of the probe molecule is found for $n \geq 10$. In other words, acids with $n \leq 8$ have a mean adsorbate lifetime, τ, that is shorter than the time scale (about 500 s) of an ex situ FTIR–ERS experiment at room temperature. If one assumes first-order desorption kinetics for the hydrogen-bonded acid,[7,8b] then τ equals the reciprocal of the desorption rate constant, k, which can be expressed as $k = \nu \exp(-E_a/RT)$, where ν is a preexponential frequency factor, and E_a is the activation energy for desorption.[17] Assuming that ν is 1×10^{13} s⁻¹ and that $E_{ads} = E_a$,[17] one obtains an E_{ads} value of 21.4 kcal/mol at 25 °C for τ = 500 s.

There are two contributions to the total adsorption energy: (1) the energy of the hydrogen bond; (2) the van der Waals energy between adjacent chains. For close-packed alkanes, the latter contribution is about 0.8 (kcal/ mol)/CH₂.[8a] Since decanoic acid is the lightest acid that binds to the Au/HS(CH₂)₂COOH surface, we can estimate the strength of the hydrogen-bonding part of E_{ads} to be 21.4 – (8 × 0.8) = 15 kcal/mol. For an O—H⋯O=C-type hydrogen-bonding interaction, the total bonding energy is about 7.5 kcal/mol.[18] Therefore, our estimate of 15 kcal/ mol is reasonable if we assume that each acid dimer results from two hydrogen bonds. Of course this is a very rough estimate, and the excellent agreement between this calculation and our experimental results, while gratifying, is probably somewhat fortuitous.

Conclusions

To summarize, we have shown that vapor-phase 1-alkanoic acid probe molecules are receptive to selective hydrogen-bonding interactions with acid-terminated monolayer surfaces. We propose a model in which the surface-confined HS(CH₂)₂COOH layer promotes both intermolecular face-to-face bonding between HS(CH₂)₂COOH and the second adsorbed acid layer *and* intralayer lateral hydrogen bonding.

Hydrogen bonding is the third type of molecular interaction between surface-confined monolayers and solution- or vapor-phase probe molecules that we have reported; the first two involved electrostatic interactions[1] and covalent bonding.[2] Future publications will focus on detailed mechanistic studies of these interactions, other types of intermolecular interactions, and the application of chemically sensitive monolayers to molecular recognition-based chemical sensors.[3]

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