Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 8. Reactions between Acid-Terminated Self-Assembled Monolayers and Vapor-Phase Bases

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We present the results of a study of the interactions between three different acid-terminated selfassembled monolayer (SAM) surfaces and three basic vapor-phase probe molecules. The SAMs are composed of 4-mercaptobenzoic acid (MBA), 3-mercaptopropionic acid (MPA), and 11-mercaptoundecanoic acid (MUA), and the vapor-phase probes are, in order of increasing solution-phase acidity, decylamine, pyridine, and pyrazine. Our results are based on data from surface infrared spectroscopy and thickness-shear mode mass sensors. We find that all three SAMs irreversibly bind approximately one monolayer of decylamine, although there are slight differences that correlate with the structural nuances of the SAMs. The MPA and MBA SAMs bind decylamine through an electrostatic interaction brought about by transfer of a proton from the acid to the base. Because the MUA SAM is more impenetrable than the others, complete proton transfer is hindered, and binding of decylamine arises through a combination of proton transfer and strong hydrogen bonding. In the presence of its vapor, pyridine adsorbs to MBA surfaces at near-monolayer coverage, but upon N₂ purging about two-thirds of it desorbs. Only one-half monolayer of pyrazine, which is less basic than pyridine, adsorbs to the MBA SAM, and upon N₂ purging, about two-thirds of it desorbs. The aliphatic acid SAMs follow a similar trend. The results of this study indicate that the extent of base binding correlates most strongly with the structural nuances of the acidic SAMs and the relative basicity of the vapor-phase bases. These results are relevant to SAM-based chemical sensors.

Introduction

In this paper we continue our investigation of chemistry at vapor-solid interfaces^{1–11} by studying interactions between acid-terminated, self-assembled monolayers (SAMs) and vapor-phase bases. The acidic SAMs are constructed from 4-mercaptobenzoic acid (MBA), 3-mercaptopropionic acid (MPA), and 11-mercaptoundecanoic acid (MUA). The vapor-phase probes are the bases decylamine, pyridine, and pyrazine. Depending on the chemical structures and relative acidities of the acids and

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We recently began a systematic study of molecular interactions between organized, surface-confined monolayers, and vapor-phase probe molecules.^{1–11} The longterm goal of this study is a complete understanding of the general rules that govern adsorption and reaction chemistry at vapor-solid interfaces near room temperature and atmospheric pressure. Vapor-surface interactions are of general technological interest for manipulating interfacial properties, which are critical to the fields of adhesion, lubrication, and corrosion, without the cost, disposal problems, and other complications associated with the use of solvents. However, there are also two key drawbacks to the implementation of solvent-free chemistry that place significant limitations on this approach. First, reactants and reaction byproducts must have an appreciable vapor pressure at the temperature employed for the reaction. Second, the use of catalysts for promoting specific chemical transformations is severely curtailed. At present, our interest is therefore primarily focused on weak molecular interactions, such as those arising from hydrogen bonding and acid-base (including protontransfer) interactions; however, we have also studied complexation interactions and covalent bonding. In this article we expand upon our previous reports of protontransfer and hydrogen-bonding interactions that occur at the interface between surface-confined SAMs and vaporphase probe molecules.⁴⁻⁸ Specifically, we have examined interactions between several different pairs of surfaceconfined acids and vapor-phase bases. We have also significantly improved the experimental design: most spectroscopic and all mass-balance data reported here were obtained in situ and in real time.⁷

There are at least three good reasons to study acid-

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base chemistry at vapor-solid interfaces. First, the acidity of molecules confined at the vapor-solid interface may be different from that of the same compounds in solution phases since surface- confined molecules are in close proximity to one another and restricted in their motional freedom.¹²⁻¹⁸ Second, because there is no solvent involved, a comparison of the results of vapor-solid interactions with those in solution phases can lead to a deeper understanding of solvation phenomena. Finally, a basic understanding of the principles of chemistry at the vapor-solid interface is essential for the rational design of chemically-sensitive interfaces for chemical sensors, which is one of our primary technological goals.⁵ For most applications only weak intermolecular interactions are useful in designing chemical sensors. For example, acid-base and hydrogen-bonding interactions are strong enough to reversibly bind vapor-phase analytes, but often not so strong as to irreversibly adsorb them.

We have used two complementary analytical techniques in this study: FTIR-external reflectance spectroscopy (FTIR-ERS) and nanogravimetry based on thickness-shear mode resonators (TSMRs). In-situ FTIR-ERS provides chemical and structural information as a function of time, but the technique is generally not quantitative. In contrast, mass-sensitive TSMRs provide quantitative information about surface coverage but little chemical information.

Here, we describe interactions between each of three acid-terminated SAMs and the three vapor-phase base molecules. Although the strength of the surface-confined acids is unknown at the present time,18 the liquid-phase acidity of the analogous alkanoic acids increases in the order: benzoic acid, $pK_a = 4.19$; propionic acid, $pK_a =$ 4.87; and octanoic acid, $pK_a = 4.89$. Previous studies have indicated that the apparent pK_a of acids often increases when they are confined to surfaces.¹²⁻¹⁸ For example, MUA SAMs cannot be completely deprotonated by vaporphase *n*-alkylamines.⁶ This interesting situation arises because of two distinct phenomena. First, acid-terminated SAMs may undergo strong intramonolayer lateral hydrogen bonding, which is revealed spectroscopically as a significant shift of the IR-active carbonyl stretching mode toward lower energy.¹¹ This results from steric confinement of the acid groups to particular geometries, which are conducive to hydrogen bonding, and the absence of competition from solvent for hydrogen-bonding sites. Second, complete deprotonation of an acid layer, and simultaneous protonation of the base layer, may be energetically unfavorable because of intralayer Coulomb repulsion.⁶ The phenomenon of reduced acidity is also observed for SAMs at the liquid-solid interface. For example, contact-angle titrations indicate a several-pHunit increase in the acidity of MUA when it is configured in a SAM.^{14,18} Other types of acid surfaces show similar increases in apparent pK_{a} .^{16–22}

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The liquid-phase pK_a values for the vapor-phase probe molecules decrease as follows: decylamine (10.64) >pyridine (5.25) > pyrazine (0.65). The results of our study of the interactions of these bases with the acid-terminated SAMs reveal that vapor-phase decylamine irreversibly binds to all three acid surfaces through primarily protontransfer interactions. In contrast, vapor-phase pyridine and pyrazine molecules interact with the acid surfaces primarily by hydrogen bonding interactions; the strength of the interaction depends on the particular acid-base pair.

Experimental Section

Chemicals. The following chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received: 3-mercaptopropionic acid (MPA), HS(CH₂)₂COOH; 4-mercaptobenzene (MB), HS(C₆H₅); decylamine, NH₂(CH₂)₉CH₃; pyridine, NC₅H₅; pyrazine, NC₄H₄N. 4-Mercaptobenzoic acid (MBA), HS(C₆H₄)COOH, was purchased from Toronto Research Chemicals, Inc. (Downsview, Ontario, Canada), and used without further purification. 11-Mercaptoundecanoic acid (MUA), HS(CH₂)₁₀COOH, was synthesized according to a literature procedure.²³ Other chemicals were of reagent grade or better.

FTIR-ERS Measurements. Substrates for FTIR-ERS were diced (9 \times 34 mm) Si(100) wafers coated with a 15-nm-thick Cr adhesion layer and 200 nm of Au. Immediately prior to SAM derivatization, the substrates were rinsed with ethanol and then immersed in freshly prepared "piranha" solution (3H₂SO₄:1H₂O₂, Caution: this mixture reacts violently with organic materials, and it should not be stored in closed containers) for 30 s. The substrates were then rinsed thoroughly with deionized water (Milli-Q, Millipore, Bedford, MA) followed by ethanol and then dried under a N₂ stream. The substrates were immersed in 1 mM ethanolic solutions of the appropriate mercaptans for more than 48 h. Prior to analysis, the substrates were thoroughly rinsed with ethanol, soaked in water (pH = 6.0 ± 0.2) for 5 min (to ensure that the monolayers were fully protonated), and dried under a N₂ stream.

FTIR-ERS measurements were made using a Digilab FTS-40 FTIR spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid N2 cooled MCT detector. All spectra were obtained at 4 cm⁻¹ resolution using p-polarized light incident on the Au substrate at an angle of 84°. A custombuilt vapor-phase flow cell was employed for all FTIR-ERS measurements; it was described in detail previously.^{7,11} Briefly, the flow cell consists of a cover and a base, which are sealed together by mechanical compression of a silicone O-ring. Two NaCl windows on the ends of the flow cell permit external reflection spectra to be recorded in a manner that is similar to normal FTIR-ERS spectroscopy. Using this system, FTIR data acquisition and introduction of vapor-phase base probes can be performed simultaneously; however, the spectra of both the surface-confined probe and the vapor-phase probe present in the cell headspace are obtained simultaneously during probe dosing. This problem can be obviated by purging the headspace with N_2 prior to spectral acquisition, but this strategy may cause weakly bound analytes, which are in equilibrium with the vapor phase, to desorb.

The partial pressure of the vapor-phase reactant and the flow rate of the gas stream are set by two mass-flow controllers: one controls a N_2 stream (from a liquid-N₂ bleed-off) passing through a vial containing a solid or liquid reactant with a significant vapor pressure, and the other controls a pure N₂ stream, which is used to dilute the first. All experiments were performed at a constant flow rate of 0.5 L/min. The acid surfaces were dosed with a 50%-of-saturation decylamine vapor or a 20%-of-saturation pyridine or pyrazine vapor. Acid-base interactions at the vaporsolid interface were monitored continuously by recording FTIR spectra every 2 min. All spectra were obtained at 4 cm⁻¹

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resolution except Figure 1, which was obtained at 2 cm $^{-1}$ resolution. The number of co-added individual spectra is given in the figure captions. Spectra were obtained at 23.5 \pm 1 °C.

TSMR Device Measurements. The relationship between the frequency change (Δf) and mass-per-area (m_A) for deposition onto a TSMR is given by the Sauerbrey equation (eq 1).²⁴ Here,

$$\Delta f f_0 = -2 m_{\rm A} f_0 (\mu_0 \rho_0)^{-1/2} \tag{1}$$

 f_o is the resonant frequency of the TSMR and μ_q and ρ_q are, respectively, the shear modulus ($2.95 \times 10^{11} \text{ g/cm} \cdot \text{s}^2$) and density (2.65 g/cm^3) of quartz.²⁴ We deposit mass onto both electrodes of the TSMR device in our experiments.

AT-cut quartz devices, 9 MHz, purchased from Kyushu Dentsu Company Ltd. (Omura City, Japan), were used for all TSMR experiments. The TSMRs have crystal diameters of 8.0 mm and electrode diameters of 4.5 mm. Both the crystal and electrode surfaces were polished by the manufacturer. The electrodes consisted of 200 nm of Au deposited over a 15 nm Ni adhesion layer. The measurement system is comprised of two TSMRs (one is a control), a 5-V dc power supply (Newark 89F1268), a frequency counter (Hewlett-Packard 5384A), an oscillator circuit (Leybold Inficon 013–001), and a custom-built frequency filter.²⁵ The entire system is interfaced to an IBM-compatible computer (Scheme 1).

A flow cell, which is similar to that used in the FTIR-ERS experiments, houses the TSMRs so that all surface reactions can be followed in real time. The flow cell consists of a base and two cover plates; the TSMR holder is sandwiched between the two plates using Viton O-rings, which secure the oscillator perpendicular to the plates, and then the entire assembly is attached to the base using four screws. The TSMR devices were first rinsed with ethanol and then cleaned in an Ar plasma cleaner (Harrick Scientific Model PDC-32G, Ossining, NY) for 1 min, and finally rinsed with ethanol and dried under a N₂ stream prior to immersion in the mercaptan solutions. All other experimental conditions are identical to those used for FTIR-ERS: a constant flow rate of 0.5 L/min, dosing concentrations of 50%-of-saturation for decylamine and 20%-of-saturation for pyridine and pyrazine, and a temperature of 23.5 \pm 1 °C.

To determine the precision of the TSMR measurements, we performed several repetitive measurements on each of three different chemical systems and compared the results to a standard propagation-of-errors analysis. Both of these resulted in an absolute error of ± 7 ng/cm² or about $\pm 5\%$ of the mass corresponding to a single monolayer of decylamine. A detailed discussion of these results is provided in a forthcoming publication.²⁶



Figure 1. FTIR-ERS spectra of SAMs composed of (a) MUA, (b) MPA, and (c) MBA. Each spectrum is the sum of 256 individual spectra.

Results and Discussion

FTIR-ERS Characterization of Acid-Terminated Organomercaptan SAMs Confined to Au Surfaces. Figure 1 shows FTIR-ERS spectra of the acid-terminated organomercaptan SAMs used in this study. Figure 1a is the spectrum of Au/SH(CH₂)₁₀COOH (Au/MUA); the peak assignments are given in Table 1. The two prominent bands at 1740 and 1718 cm⁻¹ are C=O stretching modes corresponding to two surface-confined carboxylic acid conformations: non-hydrogen-bonded monomers and laterally hydrogen-bonded acid dimers or perhaps multimers, respectively.^{6,27} We have previously shown that this type of hydrogen bonding can increase the p K_a of surfaceconfined acid groups in solution,¹² and one of the main objectives of the present work is to better understand this phenomenon at the vapor–solid interface.

The spectrum of Au/SH(CH₂)₂COOH (Au/MPA) is shown in Figure 1b and the peak assignments are given in Table 1. The C–H stretching bands between 3000 and 2800 cm⁻¹ are much smaller in intensity than those of MUA, which is consistent with the smaller number of CH₂ groups, and they appear derivative-shaped as a result of imperfect background subtraction. The position of the C=O stretching mode, which is about the same intensity as in Figure 1a, indicates that the carboxyl terminal groups exist primarily in a laterally hydrogen-bonded configuration, which is probably a consequence of the poor structural order of these shorter SAMs.

Figure 1c is the spectrum of Au/SH(C₆H₄)COOH (Au/ MBA); the peak assignments for this monolayer are also provided in Table 1. The absorptions of the aromatic ring vibrations are strong in the low-frequency region, but the aromatic C–H stretch at 3050 cm^{-1} is weak. The intensity of the C=O stretch for the MBA monolayer is significantly stronger than the corresponding bands in the MUA and MPA spectra, which may result from an orientation effect,²⁸ an inherent enhancement in aromatic acids,²⁹ a somewhat different surface coverage brought about by a difference in molecular packing, or a combination of these three effects. In contrast to the spectra of Au/MUA and Au/MPA, the appearance of a single, sharp O–H stretching band at 3580 cm⁻¹ in the Au/MBA spectrum suggests a significant difference in the environment of most of the

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⁽²⁵⁾ The frequency filter consists of two capacitors (15 μ F) and an inductor (100 μ H). One of the capacitors is grounded and serves as a low-pass filter. The second coupling capacitor prevents the dc-input signal from going to the frequency counter. The inductor, which is directly connected to the dc input, blocks the ac signal generated by the oscillator from affecting the power supply.

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 Table 1. Peak Assignments for MUA, MPA, and MBA Monolayers Confined to Au Surfaces before (Figures 1) and after

 (Figures 2) Dosing with Decylamine^a

	MUA Au/HS(CH ₂) ₁₀ COOH		MPA Au/HS(CH ₂) ₁₀ COOH		MBA Au/HS(C ₆ H ₄)COOH	
acid layer	Figure 1a	Figure 2a	Figure 1b	Figure 2b	Figure 1c	Figure 2c
$\nu_{\rm OH}$					3580	-3580
$\nu_{\Phi,C-H}$					3050	
$\nu_{{ m NH_3^+}}$		3250 - 2600		3250 - 2600		3200 - 2600
$\nu_{\rm a,CH_3}$		2967		2967		2967
$\nu_{\rm a,CH_2}$	2920	2923		2925		2923
$\nu_{\rm s,CH_3}$		2880		2880		2880
$\nu_{\rm s,CH_2}$	2850	2854		2855		2853
$\nu_{C=0}$	1740, 1718	-1742^{b}	1720	-1727	1751	-1742
$\delta_{{ m a,NH}_3^+}$		1643 (sh)		1643 (sh)		1643 (w)
$\nu_{\Phi-\mathrm{ring}}^{c}$					1589	$-1591, 1582^{d}$
v_{a,COO^-}		1582		1584 (c)		1545
$\delta_{\alpha-\mathrm{CH}_2}$	1410 ^e		1420 ^e			
$\nu_{s,COO^{-}}$		1411 (c)		1402 (c)		1398
$\nu_{\mathrm{C-O}}{}^{f}$					1174, 1093	-1174, 1090

^{*a*} Key: sh, w, and c represent shoulder, weak, and centered, respectively. ^{*b*} "–" represents a negative peak in the spectrum. ^{*c*} $\nu_{\Phi\text{-ring}} =$ aromatic ring stretch. ^{*d*} The derivative shape results from a slight shift of the $\nu_{\Phi\text{-ring}}$ mode upon deprotonation. ^{*e*} The precise assignment of this band is in doubt; it has also been assigned to a combination of C–O stretch plus COH in-plane bend (see ref 27b) and a combination of the carboxylate stretch plus the α -CH₂ scissors mode (see ref 27c). ^{*l*} It is difficult to assign these bands with confidence, and they may arise from β_{C-H} modes (see ref 26).

surface-confined O–H groups. Taken together with the position of the carbonyl band, which shifts -50 cm^{-1} to lower energy for acid dimers in CCl₄,²⁹ we hypothesize there is very little intramonolayer hydrogen bonding in the MBA SAM. This view is also consistent with the surprisingly high absorbance of the O–H bond in the MBA spectrum: if MBA is oriented with its ring plane perpendicular to the substrate, then the surface infrared selection rule will favor absorption by the O–H dipole and, as a consequence hydrogen bonding, which results in attenuation of this band, is sterically hindered.²⁸ A detailed description of the structure and reactivity of all three mercaptobenzoic acid isomers will appear shortly.²⁶

Reactions between Acid-Terminated SAMs and Vapor-Phase Decylamine. We performed in-situ FTIR-ERS and TSMR analyses of the interactions between the three acid-terminated SAMs and vapor-phase decylamine. For the FTIR-ERS experiments, we exposed the SAMs to a pure N_2 stream for 15–20 min and then switched to a 50%-of-saturation decylamine vapor stream for 10 min. After dosing, we purged the substrate with pure N_2 for an additional 20 min at a constant flow rate of 0.5 L/min. Figure 2 shows the final FTIR-ERS spectra for the acidic SAMs after exposure to decylamine vapor and purging with pure N_2 . All the spectra presented in Figure 1 have been subtracted in each case to emphasize the reaction chemistry.

The formation of an acid-base bilayer for each of the SAMs is supported by the following observations. First, four new, well-resolved, positive peaks that correspond to the C-H stretching modes of adsorbed decylamine are present in the high-frequency region of all three spectra. The assignments for these bands are given in Table 1. In all cases the positions of the methylene bands indicate that the adsorbed decylamine layer is in a configuration that is best characterized as liquid-like.³⁰ Well-packed, methyl-terminated SAMs are known to exist in a solidlike environment, which causes these bands to narrow and shift to significantly lower energies compared to their positions in Figure 2.³⁰ For example, the asymmetric and symmetric methylene C-H stretching bands in wellordered, methyl-terminated SAMs appear at 2918 \pm 1 and $2849 \pm 1 \text{ cm}^{-1}$, respectively, which compare to 2923



Figure 2. FTIR-ERS difference spectra for (a) MUA, (b) MPA, and (c) MBA SAMs obtained after dosing with decylamine vapor for 10 min and then purging with N_2 for 20 min. The spectra of the acid surfaces obtained prior to dosing (similar to those in Figure 1) have been subtracted. Each spectrum is the sum of 512 individual spectra.

 \pm 1 and 2854 \pm 1 cm⁻¹, respectively, for those shown in Figure 2. Importantly, the magnitudes of the C-H stretching bands for the three acid surfaces shown in Figure 2 indicate qualitatively that each acid-terminated SAM adsorbs approximately an equal surface concentration of base. Note, however, that there is a clear difference in the heights of the asymmetric methylene C-H stretching modes in the aliphatic versus the aromatic acids. The reduction in the magnitude of this mode for MBA, taken together with the enhancement of the symmetric C=O stretching mode discussed below, probably indicates that adsorbed decylamine is, on average, oriented with its long axis more perpendicular to the surface than when it adsorbs to the aliphatic acids. Finally, control experiments performed by dosing methyl-terminated SAMs with decylamine indicate no spectroscopic evidence for adsorption.⁷

The second piece of evidence supporting bilayer formation relates to the disappearance of the acid C=O stretching bands in the energy range 1755-1710 cm⁻¹ in

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all three spectra. In addition, the MBA surface indicates loss of the O-H stretching mode at 3580 cm⁻¹. Finally, there are new bands between 1590-1540 and 1415-1395 cm⁻¹ in all three spectra that result from the asymmetric and symmetric carboxylate stretching modes, respectively. These peaks indicate that proton transfer from the acids to the amines proceeds under these conditions and that a new, stable acid-base bilayer forms primarily by an ionic-bonding interaction. Additional evidence for this includes the broad bands between 3250 and 2600 cm⁻¹ which underlie the C-H stretching regions. We assign these bands to N-H stretching modes in NH₃⁺ that are often observed in zwitterion-like species of the form $RCOO^{-+}NH_3R'$.^{31,32} The two peaks at 1174 and 1093 cm⁻¹, which are apparent in Figure 1c, become negative after dosing with base (Figure 2c). These bands have been associated with the C-O stretch in monomeric carboxylic acids.³³ In contrast, we do not observe these bands in MPA or MUA SAMs, since they are initially present primarily in a hydrogen-bonded configuration.

In accordance with these observations, and those in our previously reported work,⁶ we propose a model for this bilayer structure like that shown in Scheme 2. Within our detection limit, vapor-phase decylamine binds to the MBA and MPA SAMs exclusively by an ionic protontransfer interaction. For energetic reasons, we believe this fully ionic configuration implies some degree of intercalation of the charged parts of the acids and bases.⁶ Proton transfer is also important in binding decylamine to MUA, but strong hydrogen bonding between acid groups and the structural rigidity of the aliphatic chains precludes intercalation of the ionic groups and leads to a combination of proton transfer and hydrogen bonding.⁶ We have previously discussed the nature of the interaction between decylamine and the aliphatic acids in detail.⁶ The three acid-base bilayer combinations discussed thus far are stable for many hours in a dry N₂ atmosphere, so at least on this time scale the reaction is irreversible. Moreover, we have attempted to remove the amine from all three surfaces using both ethanol and water vapors, but it is



Figure 3. Real-time TSMR data obtained by dosing (a) MUA, (b) MPA, and (c) MBA with decylamine. The numerical values are the percentage of the theoretical, single-monolayer coverage of the adsorbed decylamine after dosing.

sufficiently strongly bound that no displacement occurs. This resilience is at least in part due to the hydrophobic nature of the bilayer surface, which protects the ionic bond.

We used real-time nanogravimetry based on TSMR quartz oscillators to confirm and quantify the FTIR-ERS data for decylamine adsorption onto the acid surfaces. Figure 3 shows a plot of frequency shift versus time for TSMR devices coated with approximately one monolayer of MUA, MPA, and MBA during exposure to a N₂ stream containing decylamine. Between 0 and 18 min, we allowed the device frequency to stabilize under a pure N₂ purge stream. Between 18 and 30 min the N_2 stream was switched to a 50%-of-saturation decylamine-in-N₂ mixture; the frequency decrease corresponds to the adsorption of decylamine onto the SAM. Between 30 and 120 min, we purged the surface with pure N₂ to remove any decylamine condensed or otherwise weakly bound onto the acid surfaces. In agreement with the FTIR-ERS results, adsorption between the bases and the acidic SAMs is essentially irreversible on this 90-min time scale.

The measured mass changes resulting from decylamine adsorption onto the SAM surfaces after purging with N₂ for 30 min are 110, 130, and 160 ng/cm², or 0.69, 0.83, and 1.01 nmol/cm², for MUA, MPA, and MBA SAMs, respectively. If we assume that the mercaptans adsorb at 3-foldhollow sites of a defect-free Au(111) surface, we can calculate a theoretical, single-monolayer SAM coverage of 0.78 nmol/cm $^{2.34}$ If we further assume the theoretical, single-monolayer coverage of decylamine corresponds to a one-to-one reaction stoichiometry with the acidterminated mercaptan molecules and that the substrates have a surface roughness factor of 1.2 times that of the projected area,³⁵ then the measured adsorption stoichiometries are 75, 90, and 110% of maximum for MUA, MPA, and MBA, respectively. In a previous paper, we measured the mass of decylamine adsorbed onto a MUA surface and measured a coverage of 90% of the theoretical, single-monolayer coverage. These earlier data were obtained in a different laboratory using surface acoustic wave (SAW) devices rather than TSMRs; some other minor

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⁽³⁵⁾ We estimated the surface roughness factor of the active region of the TSMR devices by dosing it with a dilute vapor of CH₃(CH₂)₆SH. Several experiments indicate that the mass change due to CH₃(CH₂)₆-SH adsorption is $(120 \pm 10)\%$ of the theoretical, single-monolayer coverage (0.78 nmol/cm²) calculated assuming a flat Au(111) surface and a Au/CH3(CH2)6SH ratio of 3/1.

aspects of the experimental conditions were also somewhat different. We believe the difference between these measurements (75% vs 90%) reflects the maximum uncertainty in our mass measurements. The error associated with these measurements probably results primarily from an imprecise knowledge of the true active surface area of the quartz oscillators and slight differences in temperature during experiments. As discussed in the experimental section, our typical error is $\pm 7 \text{ ng/cm}^2$ for these vaporphase TSMR experiments, since virtually identical substrates and dosing conditions were used.²⁶ Also note that during the dosing period the decylamine surface coverage for all three acid surfaces is essentially identical, which provides additional support for our contention that precision associated with these measurements is higher than a simple comparison of the previous SAW results with the current TSMR results might suggest.

We propose that the order of decreasing decylamine coverage on the acid surfaces measured after N₂ purging correlates with the acidities of the carboxyl proton. That is, the likelihood of irreversible adsorption of decylamine depends primarily on the ability of the acid to transfer its proton. This in turn depends on the extent of intramonolayer hydrogen bonding and the ability of the bilayer to accommodate the electrostatic charge resulting from proton transfer, since the intrinsic solution-phase pK_a values are about the same for all three acids. We have previously shown that the structural rigidity of MUA renders it more strongly hydrogen bonded than MPA even though some of the MUA monolayer is present in the monomeric form.⁶ The presence of the O-H stretching mode for the MBA SAM at 3580 cm⁻¹ clearly indicates little or no hydrogen bonding. Therefore, the decrease in the strength of hydrogen bonding (MUA > MPA > MBA) tracks the acidity of the monolayers, at least as measured by this vapor-phase titration method. In addition to hydrogen bonding, the extent to which the bilayers can interpenetrate (Scheme 2) to accommodate the electrostatic interaction between the charged acids and bases will also play an important role in determining the energetics of the proton transfer. Clearly, the more rigid MUA monolayer will resist base intercalation, which is in accord with its reduced ability to promote bilayer formation compared to MPA and MBA. The key point is that the collective structural nuances of the SAMs control their acidity rather than intrinsic properties of the individual molecules.

Reactions between Acid-Terminated SAMs and Vapor-Phase Pyridine. To study the relative acidity of the surface-confined acids, we exposed them to pyridine, which is a significantly weaker liquid-phase base than decylamine. Because pyridine has a much higher vapor pressure than decylamine, we reduced its partial pressure during the dosing process to 20% of saturation. Otherwise, all the experimental conditions were identical to those used for the decylamine study. Figure 4 shows time-resolved FTIR spectra obtained by dosing of an Au/MBA surface with vapor-phase pyridine. The acid-terminated SAM spectrum obtained prior to dosing has been sub-tracted from the spectra in Figure 4.

Spectra 2 and 10 in Figure 4 were obtained during dosing, and spectra 11-21 were obtained while purging the base-dosed surfaces with pure N₂. During dosing, spectra 2 and 10 indicate absorptions due primarily to vapor-phase pyridine in the cell headspace:³⁶ most prominent are the aromatic C-H stretching modes between 3080 and 3010 cm⁻¹ and the C-C and C-N ring stretching bands between 1600 and 1430 cm⁻¹. The bands between 1330 and 960 cm⁻¹ are in-plane C-H bending modes mixed



Figure 4. Selected, time-resolved FTIR-ERS spectra of an MBA SAM during pyridine dosing (2 and 10) and after pyridine dosing and then purging with N_2 (11–21). The interval between the beginning of two consecutive spectra is 2 min. The spectrum of the acid surface obtained before dosing was subtracted from each of these spectra. Each spectrum is the sum of 64 individual spectra. Key bands discussed in the text are marked with asterisks. The absorbance scale for spectra 11–21 is three times more sensitive than the others.

with C-C modes. Combination bands and overtones arising from out-of-plane aromatic C-H bending modes (1000-700 cm⁻¹) are present between 2000 and 1800 cm^{-1.37} During purging, spectra 11–21 reveal small negative peaks at 3580 and 1745 cm⁻¹, which arise from at least partial elimination of the acid group O-H and C=O stretching modes, respectively. These bands can also be observed during dosing (spectra 2 and 10). These data suggest that adsorbed pyridine does not fully desorb from the MBA surface on the time scale of the experiment. Taken together with the absence of a carboxylate band, which we clearly observed for the Au/MBA/decylamine system, we conclude that pyridine interacts with the MBA SAM primarily through a relatively strong hydrogenbonding interaction. Additional evidence supporting this view comes from the two negative bands at 1177 and 1096 cm⁻¹, which arise from non-hydrogen-bonded carboxylic acid molecules; that is, the negative bands result from a change in conformation of the acid from monomeric to hydrogen-bonded with pyridine. These two negative bands are also apparent in the Au/MBA/decylamine spectrum (Figure 2c). We are unable to assign the positive band at 1290 cm⁻¹ with certainty since this is a complex region of the spectrum for acids, but it may arise from pyridine-induced dimerization of MBA.³⁸ It is also interesting to note that we do not observe any new positive bands attributable to the pyridine ring modes. This may be related to the orientation of the ring relative to the surface or simply the low, submonolayer coverage of pyridine (vide infra).

⁽³⁶⁾ As presently configured, the vapor-flow cell requires that the IR beam interact with both vapor-phase base molecules in the cell headspace and molecules bound to the substrate (see ref 7). However, we have recently constructed a polarization-modulation FTIR apparatus that will permit vibrational analysis of only the surface-confined molecules in the presence of the dosing vapor. (See: Green, M. J.; Barner, B. J.; Saez, E. I.; Corn, R. M. Anal. Chem. **1991**, *63*, 55.)

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Figure 5. FTIR-ERS difference spectra: (a) MUA and (b) MPA SAMs during pyridine dosing; (e) MUA and (f) MPA SAMs after pyridine dosing and then purging with N_2 for 2 min; (c) MUA and (d) MPA SAMs during pyrazine dosing; (g) MUA and (h) MPA SAMs after pyrazine dosing and then purging with N_2 for 2 min. The spectrum of the acid surface before dosing was subtracted from each of these spectra. Each spectrum is the sum of 64 individual spectra. The circled regions of the spectra indicate where we would anticipate observing spectral changes resulting from perturbations to the acid groups during dosing. The absorbance scale for (e-h) is three times more sensitive than the others.

The FTIR-ERS data indicate that MUA and MPA SAMs exhibit lower reactivity toward pyridine than MBA. Spectra a and b of Figure 5 are difference spectra of the MUA and MPA SAMs obtained during pyridine dosing. The absence of negative peaks between 1745 and 1715 cm⁻¹ in these spectra indicate that surface-confined pyridine is insufficiently basic to extract a proton from MUA or MPA. If pyridine interacts weakly with the aliphatic acids through hydrogen bonding or van der Waals interactions, then its presence on the surface might be obscured by vapor-phase pyridine in the flow-cell head-space.³⁶

We obtained the difference spectra shown in parts e and f of Figure 5 after purging the flow cell with N_2 for 2 min to remove vapor-phase pyridine. The spectra suggest that N_2 purging removes all pyridine from the aliphatic acid surfaces. However, the absence of an IR signature for surface-confined pyridine does not absolutely confirm its absence on the surface, since the principal bands of flat-adsorbed pyridine, which does not chemically react with the acid, are surface-IR silent.²⁸ Alternatively, there may be a submonolayer coverage that is below our spectroscopic detection limit.

TSMR data for the acid-terminated SAM/pyridine systems are fully consistent with the FTIR-ERS experiments. Figure 6 shows plots of frequency shift versus time for TSMR devices modified with acid-terminated SAMs during exposure to pyridine vapor. Between 0 and 15 min the SAM-coated devices were equilibrated with a pure N_2 purge. Between 15 and 35 min the surface was exposed to pyridine vapor, and during the final 15 min a N_2 purge was introduced to remove any weakly-bound pyridine from the SAM. The mass changes resulting from pyridine adsorption during dosing of the MUA, MPA, and



Figure 6. Real-time TSMR data obtained by dosing (a) MUA, (b) MPA, and (c) MBA with pyridine. The numerical values are the percentage of the theoretical, single-monolayer coverage of the adsorbed pyridine during and after dosing.

MBA SAMs are 65, 70, and 75 ng/cm², respectively. Using the same set of assumptions discussed earlier for calculating the surface concentration of a full monolayer, these coverages amount to 90, 95, and 100% of the theoretical, single-monolayer coverages for MUA, MPA, and MBA SAMs, respectively, during dosing. In contrast to the results obtained using decylamine, about half to two-thirds of the pyridine is sufficiently weakly bound to the acid surfaces that it desorbs immediately during N₂ purging. On the time scale of these experiments, which in some cases lasted up to 3 h, 45, 35, and 35% of the theoretical, single-monolayer coverage of pyridine remains on the MUA, MPA, and MBA surfaces, respectively. Recall that the FTIR-ERS results indicated complete loss of pyridine from the MPA and MUA surfaces. This apparent inconsistency can be reconciled, but that discussion is deferred until after we present the FTIR-ERS and TSMR data obtained from pyrazine dosing of the acid-terminated SAMs.

Reactions between Acid-Terminated SAMs and Vapor-Phase Pyrazine. We also studied the interaction between the three acid-terminated SAMs and pyrazine, which is a very weak base. The experimental conditions were identical to those used for the pyridine system. Figure 7 shows time-resolved difference spectra for an MBA SAM during dosing (spectra 2 and 10) and during purging with pure N_2 (spectra 11-21). Spectra 2 and 10 reveal absorptions primarily due to vapor-phase pyrazine; these include aromatic C-H stretching modes between 3100 and 3000 cm⁻¹, the C–C and C–N ring stretching bands between 1450 and 1370 cm⁻¹, and the C–H in-plane bending modes mixed with C–C vibrations between 1200 and 980 cm^{-1.39} We estimate that the partial pressure of pyrazine is roughly half that of pyridine by comparing the intensity of these bands in, for example, spectra 2 in Figures 4 and 7 and assuming the two bases have the same extinction coefficient.

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Figure 7. Selected, time-resolved FTIR-ERS spectra of an MBA SAM during pyrazine dosing (2 and 10) and after pyrazine dosing and then purging with N_2 (11–21). The interval between the beginning of two consecutive spectra is 2 min. The spectrum of the acid surface obtained before dosing was subtracted from each of these spectra. Each spectrum is the sum of 64 individual spectra. Key bands discussed in the text are marked with asterisks. The absorbance scale for spectra 11–21 is three times more sensitive than the others.

FTIR-ERS indicates that the amount of pyrazine that adsorbs to the MBA surface during dosing is almost equal to that observed for the MBA/pyridine system (compare spectra 2 in Figures 4 and 7). As for the pyridine/MBA system, we believe the interaction between pyrazine and the MBA SAM is best characterized as arising from hydrogen bonding. Evidence for this view is similar to that discussed for the pyridine/MBA interaction. For example, there are negative bands at 3580 and 1745 cm⁻¹ that correspond to loss of the monomeric acid O-H and C=O stretching modes. Negative C-O bands, which are present at around 1177 and 1096 cm⁻¹ for pyridine dosing of MBA, may be obscured in spectra 2 and 10 by the vaporphase pyrazine band at 1145 cm⁻¹. As with pyridine dosing of MBA, we do not observe the presence of carboxylate bands, which rules out a proton-transfer interaction between pyrazine and MBA. Interestingly, we do observe a new, positive band at 1710 cm⁻¹. This band, which is part of the derivative-shaped feature centered around 1727 cm⁻¹, might indicate that adsorbed pyrazine induces laterally hydrogen-bonded dimers of MBA to form; at least this interpretation is consistent with a 35 cm^{-1} shift in the MBA C=O band. In contrast to the pyridine/MBA system, we are unable to detect any bands corresponding to the presence of surface-confined pyrazine after purging the SAM surface with pure N₂ for just 2 min. This suggests that pyrazine, which is a much weaker liquid-phase base than pyridine, interacts with MBA only weakly.

In analogy to results obtained using pyridine, we observe no spectroscopic evidence for interactions between pyrazine and the MUA and MPA SAMs. Parts c and d of Figure 5 are FTIR-ERS spectra for MUA and MPA SAMs, respectively, obtained during exposure to pyrazine vapor. All spectra indicate absorptions due primarily to vaporphase pyrazine. Parts g and h of Figure 5 are spectra of MUA and MPA SAMs, respectively, after purging with N₂ for 2 min to remove pyrazine in the cell headspace. There is no evidence for the presence of pyrazine irreversibly bound to the aliphatic SAM surfaces.

In contrast to FTIR-ERS, the TSMR data reveal irreversible adsorption of a small amount of pyrazine to all three acid surfaces. Figure 8 shows TSMR data before, during, and after pyrazine dosing. During dosing, the



Figure 8. Real-time TSMR data obtained by dosing (a) MUA, (b) MPA, and (c) MBA with pyrazine. The numerical values are the percentage of the theoretical, single-monolayer coverage of the adsorbed pyrazine during or after dosing.



surface coverages due to pyrazine are 50, 40, and 45 ng/ $\rm cm^2$ or 65, 50, and 60% of the theoretical, single-monolayer coverage for MUA, MPA, and MBA SAMs, respectively. For the MPA and MBA SAMs, this is roughly half the surface coverage we observed during pyridine dosing, and for MUA it is about one-third lower. After purging with N₂, the surface coverages are reduced to 35, 30, and 20% of the theoretical, single-monolayer coverage for MUA, MPA, and MBA SAMs, respectively.

A Model for Pyridine and Pyrazine Adsorption on Acid-Terminated SAMs. For both pyridine and pyrazine dosing of the MUA and MPA surfaces, we observe no spectroscopic indication of probe adsorption. However, TSMR data indicate a relatively high surface coverage during dosing and a significant surface coverage of the bases after N₂ purging. For the MBA/pyridine system we observe both spectroscopic and TSMR evidence for a high surface concentration of the base during dosing, and only partial desorption of pyridine after N₂ purging. The MBA/ pyrazine system is somewhat different in that we observe spectroscopic and TSMR evidence for base adsorption during dosing, but only a small TSMR indication for adsorption after N₂-purging. Control experiments performed by dosing a nonreceptive methyl-terminated SAM confined to a TSMR with pyridine and pyrazine reveal no adsorption before or after N_2 purging. How do we reconcile the apparently conflicting TSMR and FTIR-ERS data for these systems?

We propose the models shown in Scheme 3 for pyridine and pyrazine dosing of the MBA surfaces. The top part of Scheme 3 shows that during dosing approximately one full monolayer of pyridine adsorbs to the MBA surface through a hydrogen-bonding interaction. This coverage is consistent with the TSMR data (bottom of Figure 6). Hydrogen bonding between pyridine and MBA is supported by the FTIR-ERS data shown in Figure 4. The bands associated with non-hydrogen-bonded MBA become negative during dosing, but no new bands that might signal proton transfer from MBA to pyridine are evident.

After the pyridine/MBA surface is purged with N_2 for a few minutes, the TSMR data indicate that about onethird of the pyridine remains on the MBA surface. This result is in general accord with the change in magnitude of the negative bands associated with non-hydrogenbonded MBA indicated by asterisks in Figure 4. We believe that after purging, pyridine is adsorbed on the surface with its ring oriented more-or-less parallel to the Au substrate. By virtue of the IR surface selection rule, this orientation will render pyridine IR-silent.²⁸

The only significant inconsistency between this model and our data relates to the absence of a new MBA C=O band corresponding to the hydrogen-bonded MBA/pyridine moiety. To account for this observation, we propose that there are many distinct configurations of the hydrogen bond between pyridine and MBA other than the simple dimer configuration that is operative when acid-terminated SAMs are dosed with alkanoic acids (top of Scheme 2).⁴ A wide variety of configurations will tend to broaden the carbonyl peak and render it undetectable in the infrared. Although this hypothesis is highly speculative, it is consistent with the observation that, upon N₂ purging, about one-third of the pyridine monolayer remains on the surface while two-thirds desorbs.

Arguments similar to those invoked for pyridine hold for the pyrazine/MBA system with a few exceptions. First, the FTIR-ERS data indicate reversible adsorption of pyrazine to the MBA surface (Figure 7). This is in contrast to pyridine, which the spectroscopic data indicate is partially irreversibly bound to MBA (Figure 4). Within the context of our model, the weaker pyrazine interaction is ascribed to its lesser basicity. The other major difference between the spectra of the aromatic bases and MBA is a new positive peak at 1710 cm^{-1} evident during pyrazine dosing (spectrum 2, Figure 7). This band may originate from a shift in the MBA C=O band to lower energy and indicate that pyrazine induces dimerization of surfaceconfined MBA (middle of Scheme 3). The TSMR data indicate that during dosing only approximately one-half of a monolayer of pyrazine adsorbs onto the MBA surface (that is, the pyrazine-to-MBA ratio is 1:2). This suggests that the aromatic nitrogens play an important role in surface adsorption since pyridine, which contains only a single nitrogen, adsorbs to form a complete monolayer. As observed for pyridine, roughly two-thirds of the pyrazine desorbs from the MBA surface upon N_2 purging. This suggests that pyrazine also adsorbs in multiple configurations, some of which are more stable than others.

To learn more about the interaction between aromatic acids and bases, we dosed the MBA SAM with benzene, which cannot participate in hydrogen bonding, and followed the results by FTIR-ERS (Figure 9) and TSMR microbalance (Figure 10a). We were surprised to find that during dosing the data were remarkably similar to those we obtained for the MBA/pyrazine system: adsorption of about 65% of the theoretical, single-monolayer coverage and adsorbate-induced hydrogen bonding (note the negative peak at 1750 cm⁻¹ and the positive peak at 1710 cm⁻¹ in Figure 9). Even more surprising, we found that upon N₂ purging benzene did not desorb, which is in contrast to our observation of partial pyrazine desorption, despite its high vapor pressure. On the basis of these



Figure 9. Selected, time-resolved FTIR-ERS spectra of an MBA SAM during benzene dosing (2 and 10) and after benzene dosing and then purging with N_2 (11–21). The interval between the beginning of two consecutive spectra is 2 min. The spectrum of the acid surface obtained before dosing was subtracted from each of these spectra. Each spectrum is the sum of 64 individual spectra. Key bands discussed in the text are marked with asterisks. The absorbance scale for spectra 11–21 is three times more sensitive than the others.



Figure 10. Real-time TSMR data obtained by dosing (a) MBA, (b) MB, and (c) MUA SAMs with benzene. The numerical values are the percentage of the theoretical, single-monolayer coverage of the adsorbed pyrazine during or after dosing.

observations, we suggest that benzene intercalates into the MBA adlattice (bottom of Scheme 3) and induces MBA hydrogen bonding. Apparently the interaction between the pyridine and pyrazine nitrogens and the MBA acid group prevents penetration and results in an overall weaker interaction than the π -stacking interaction that we believe is responsible for benzene retention.

To better understand this benzene-dosing experiment, we prepared a monolayer from mercaptobenzene (MB) and dosed it with benzene vapor. The TSMR (Figure 10b) and the FTIR-ERS (not shown) data indicate *no* adsorption during or after dosing. This result unambiguously implicates the MBA acid group as assisting intercalation and irreversible binding of benzene, possibly through distortion of the monolayer packing.

As mentioned above, there is no direct spectroscopic evidence for pyridine or pyrazine binding on the alkanoic acids before or after N_2 purging. That is, we do not observe the appearance or disappearance of any peaks attributable to the surface-confined bases during or after N_2 purging

 Table 2.
 Summary of TSMR Data Obtained before and after N2 Purging of the Acid-Base Adducts^a

	decylamine		pyridine		pyrazine		benzene	
	before	after	before	after	before	after	before	after
MUA	110	75	90	45	65	35	<5	<5
MPA	110	90	95	35	50	30		
MBA	130	110	100	35	60	20	65	60

^{*a*} Numerical values correspond to the percentage of the theoretical, single-monolayer coverage of the bases on the acid-terminated SAMs after correction for Au surface roughness.

(Figure 5). The presence of such peaks could be masked by the vapor-phase bases in the cell headspace during dosing. However, the TSMR data indicate that nearly a full monolayer of pyridine adsorbs to the acid surfaces prior to N₂ purging and that approximately half of this amount binds irreversibly (Figure 6). The same situation exists for pyrazine, except only one-half of a monolayer initially adsorbs and half of that desorbs after N2 purging (Figure 8). That is, more of the stronger base, pyridine, adsorbs to the acid surfaces than does pyrazine both during and after exposure to the bases. We reconcile the FTIR-ERS data, which indicate a much lower level of base adsorption than the TSMR data, by noting that low coverages and unfavorable orientations of the bases may reduce the magnitude of their IR absorption below our detection limit. Moreover, the MBA bands that change upon pyridine or pyrazine dosing are all associated with the unique non-hydrogen-bonded configuration of MBA. The aliphatic acids, which are largely hydrogen bonded prior to dosing, undergo less dramatic structural changes, and thus their spectra are less information-rich during and after dosing. There is no significant level of interaction between Au/MUA and benzene (Figure 10c), which is consistent with the lower monolayer free volume in the alkanoic SAMs and the model shown in Scheme 3.

Conclusion

We have described the results of an in situ FTIR-ERS/ TSMR analysis of nine acid-base reactions at the vaporsolid interface. As shown in Table 2, the magnitude and reversibility of base binding to a particular acid surface correlates well to the liquid-phase pK_a of the base: stronger bases bind more extensively and more persistently. For a particular base, the situation is somewhat more complex. The extent and tenacity of binding of decylamine, which undergoes a proton-transfer reaction with all the acidic SAMs, depends primarily on cooperative effects within the SAM; that is, structural nuances, rather than the intrinsic properties of the component molecules, are key. However, the aromatic bases, which bind to the acids primarily through hydrogen bonding interactions, do not show such a correlation. Instead, the acidic SAMs that undergo extensive intramonolayer hydrogen bonding (MUA and MPA) are generally slightly more conducive to hydrogen bonding with the aromatic bases compared to MBA.

Another important result of this study is that FTIR-ERS, by virtue of its low sensitivity and dependence on molecular orientation, may not by itself be a reliable gauge of surface interactions and chemistry. TSMR devices and other nanobalances also suffer from interferences, such as changes in film conductivity and viscoelasticity, but we have no evidence of these effects being operative in the present study.⁴⁰ Clearly, a full understanding of surface chemistry requires a combination of analytical tools.

Finally, we emphasize that vapor-surface interactions such as those described in this paper are highly complex and very difficult to fully quantify. Moreover, the techniques we have used only probe average reactant and product configurations on the surface, but it is apparent that these averages represent a summation of many different types of individual configurations. Thus, the models presented in this paper should be viewed with skepticism until better analytical tools are available to more fully disclose the nature of acid-base chemistry at the vapor-solid interface. Nonetheless, we view this work as an important step for the present purpose, which is to develop a better understanding of probe-surface interactions to facilitate the design of better chemically sensitive interfaces for chemical sensors.

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