Interactions of Alcohols with Hydroxyl- and Methyl-Terminated Self-Assembled Monolayer Surfaces Studied by Temperature-Programmed Desorption

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Received: February 3, 1999; In Final Form: July 30, 1999

The interactions of low-molecular-weight *n*-alcohols (n-$C_xH_{2x+1}OH$ for $x = 1−6$) with 11-mercaptoundecanol ($HO(CH_2)_{11}SH$) or octadecyl mercaptan ($CH_3(CH_2)_{17}SH$) adsorbed onto a nickel(111) single-crystal surface were studied by temperature-programmed desorption (TPD). Angle-dependent X-ray photoelectron spectroscopy (ADXPS) was used to characterize the adsorption of $HO(CH_2)_{11}SH$ and $CH_3(CH_2)_{17}SH$ molecules to determine their arrangements on the nickel(111) surface. The TPD spectra for the desorption of alcohols from the hydroxyl-terminated and the methyl-terminated self-assembled monolayer surfaces at various alcohol fluences were analyzed by the threshold TPD method (TTPD) to determine their desorption energies as a function of the alcohol fluence. The TTPD-calculated alcohol desorption energies from the hydroxyl-terminated surface increased from 10 to 20 kJ mol^{-1} for the lowest fluences to 40−60 kJ mol^{-1} for the highest fluences; from the methyl-terminated surface the desorption energy increased from 10 to 25 kJ mol^{-1} for the lowest fluences to 45−55 kJ mol^{-1} for the highest fluences.

Introduction

Understanding the interactions of molecules with organic surfaces is important because of the extensive use of these surfaces for applications in a variety of fields such as biosensors for the healthcare industry,[1] coatings for the materials industry,[2] and fuel cells and solar devices for the transportation industry.[3] In addition to their own structure and physicochemical properties, how molecules interact with an organic surface also depends on the structure and physicochemical properties of the surface at any instant in time during the interaction.

The formation of an organic surface may be accomplished by the spontaneous adsorption of an organic molecule onto a metal or oxide surface. Organic surfaces formed in this way are called self-assembled monolayers (SAMs). The structure of SAMs is generally a highly organized and densely packed crystal-like monolayer film composed of organic molecules aligned in such a way as to lay open virtually any organic functional group to the outer exposed interface.[4] The spontaneous adsorption of *n*-alkanethiols of the form $HS(CH_2)_mR$ ($m \geq 9$, $R = CH_3$, OH, COOH, etc.) to gold surfaces is the most common and the most extensively characterized SAM-molecule−substrate pair.[4−6] At high coverages, the *n*-alkanethiol molecules bind to the gold surface via the sulfur atom with their alkyl chains fully extended away from the gold surface and the functional group R at the outer interface. Other molecule−substrate pairs shown to have been formed by self-assembly include *n*-alkanethiols on silver and platinum,[7] copper,[8] and nickel,[9,10] *n*-alkyl silanes on silicon dioxide,[11] and carboxylic acids on silver.[12] SAMs are appealing because surfaces of virtually any organic functional group can be formed for subsequent investigation.

In a previous study,[13] the interactions of straight-chain alcohols of various chain lengths with a carboxyl-terminated self-assembled monolayer surface were characterized by tem-

perature-programmed desorption (TPD) to determine their desorption energy and desorption order as a function of the alcohol surface coverage. The high-coverage experiments showed that the desorption energies were higher and relatively constant compared to the low-coverage experiments, possibly indicating the coverage-dependent formation of a hydrogen-bonding network in the alcohol monolayer and multilayer. In this paper, we present TPD data of the same series of straight-chain alcohols of various chain lengths desorbing, this time, from a hydroxyl-terminated surface and a methyl-terminated surface. From the TPD spectra, the desorption energies as a function of the alcohol surface coverage were extracted by the threshold TPD method to gain additional understanding of the hydrogen-bonding interactions that occur at organic surfaces.

Experimental Section

All experiments were completed in a custom-built multi-technique ultrahigh vacuum (UHV) chamber.[14] Although all of the following techniques were not employed for this study, the chamber can perform X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analysis, temperature-programmed desorption (TPD), scanning tunneling microscopy, and low-energy electron diffraction. In addition to the surface characterization capabilities of the chamber, it has an ion gun for sample cleaning and a collimated capillary array doser for controlled gas-phase molecular deposition. The chamber has a base pressure $<5.0 \times 10^{-11}$ Torr.

The procedures for cleaning the nickel crystal were previously described.[9] The nickel(111) single crystal was cleaned by a series of sputtering cycles and chemical treatments,[15] followed by high-temperature annealing cycles, and then finally characterized by AES and XPS to ensure its cleanliness (i.e., <0.1% surface contaminants) before thiol deposition. 11-Mercaptoundecanol ($HO(CH_2)_{11}SH$) and octadecyl mercaptan ($CH_3(CH_2)_{17}$-SH) are solids at room temperature, and they were vacuum distilled for purification prior to their exposure to the nickel

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ADXPS of 11-Mercaptoundecanol on Ni(111)
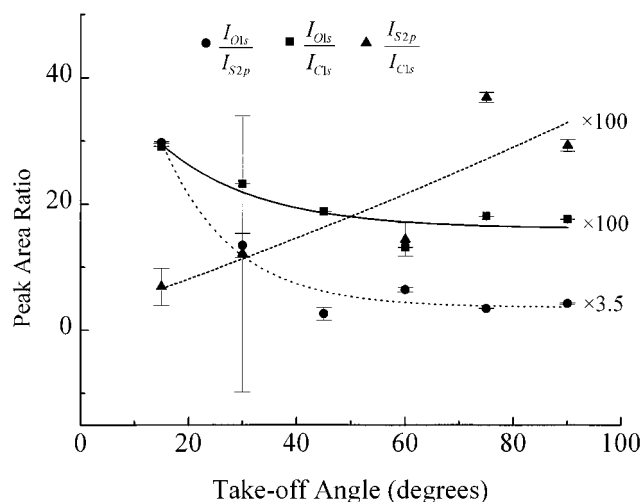
Figure 1. Plot of XPS peak area ratio versus takeoff angle. The high-resolution XPS peak area ratios for oxygen-to-carbon and oxygen-to-sulfur decrease with increasing takeoff angle indicating that the oxygen atoms in 11-mercaptoundecanol are closer to the UHV interface and that sulfur and carbon atoms are closer to the nickel surface. The error bars correspond to the errors associated with the determination of the areas under the XPS peaks.

crystal. The nickel crystal was exposed to the thiol of interest (warmed to slightly above room temperature to increase their vapor pressure to a few milliTorr) overnight in the sample introduction vacuum chamber. The sample introduction vacuum chamber is connected directly to the UHV analysis chamber and is isolated by a gate valve. Immediately after the deposition, the sample was transferred from the sample introduction chamber directly into the analysis chamber and was characterized by angle-dependent XPS (ADXPS).

All XPS spectra were obtained using a Leybold−Heraeus EA10 energy analyzer and electronic components with an Al Kα X-ray source at a constant pass energy of 100 eV for survey scans and at 50 eV for higher resolution scans. As for the adsorption of 11-mercaptoundecanoic acid and octadecyl mercaptan on the Ni(111) surface,[9] ADXPS experiments showed that 11-mercaptoundecanol and octadecyl mercaptan indeed adsorbed onto the nickel surface, and that the hydroxyl terminal group (in the $HO(CH_2)_{11}SH$ molecules) and the methyl terminal group (in the $CH_3(CH_2)_{17}SH$ molecules) were disposed away from the nickel surface to the monolayer−UHV interface. In ADXPS, high-resolution XPS spectra were recorded at different takeoff angles. The takeoff angle is defined here as the angle between the sample plane and the center-line axis of the entrance slit of the energy analyzer. At low takeoff angles (e.g., 30°), there is a lower relative sampling of electrons from deeper in the sample, whereas at high takeoff angles (e.g., 90°), there is a higher relative sampling of electrons from deeper in the sample. By varying the takeoff angle, information about the arrangement of molecules on a surface can be obtained (see Figure 1 for $HO(CH_2)_{11}SH/Ni(111)$). A summary of the XPS peak area ratios of the elements in 11-mercaptoundecanol (i.e., O1s:C1s, O1s:S2p, and C1s:S2p) and in octadecyl mercaptan (i.e., C1s:S2p)[16] at their respective takeoff angles is shown in Table 1 and Figure 1.

TPD experiments were carried out in the UHV analysis chamber. The substrate was heated resistively via a button heater (SpectraMat) and its temperature was measured by a chromel−alumel thermocouple spot-welded to the side of the nickel crystal. In all cases a linear heating rate was employed through

feedback control. The desorption flux resulting from the thermal desorption process was detected by a computer-controlled, multiplexed quadrupole mass spectrometer that was fitted with a random-flux shroud that had a 5-mm entrance aperture located 5 mm from the front face of the Ni(111) crystal.[14] In each TPD experiment, the thiol-covered substrate was cooled by liquid nitrogen to $T \leq 115$ K before dosing the alcohol adsorbate of interest in UHV. TPD was carried out to only $T \leq 300$ K since the 11-mercaptoundecanol or octadecyl mercaptan monolayers begin to dissociate on and/or desorb from the Ni(111) surface at $T \approx 360$ K, about the same temperature that 11-mercaptoundecanoic acid began to dissociate/desorb on the Ni(111) surface (data not shown).[9]

Alcohols Are Hygroscopic. Methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, and *n*-hexanol ($>99.9\%$, Mallinckrodt) were freeze−pump−thawed three times and then purified by vacuum distillation over baked molecular sieves in a stainless steel, turbo-pumped gas handling system to remove residual oxygen and water, respectively. The purity of the alcohols and water was checked in vacuo by quadrupole mass spectrometry. Although these measures were taken to purify the alcohols, there was still water observed in desorption spectra for the high-molecular-weight alcohols (1-pentanol and 1-hexanol). The purity of the high-molecular-weight alcohols was checked by ^{1}H NMR and GC/MS; there was no detection of water in the alcohols by either technique. All adsorbates were dosed from a stainless steel gas handling system, connected directly to the UHV chamber, through a microcapillary array doser[17] to ensure uniform dosing across the substrate with a high local flux ($\approx 2.0 \times 10^{13}$ molecules s^{-1} cm^{-2}) and minimal background fluence.

Results and Discussion

Temperature-programmed desorption (TPD) is used to obtain information about the desorption process or processes occurring from a surface, the desorption energy, the preexponential factor, and the desorption order as a function of surface coverage. The technique is commonly used to study the interactions of gases with metal surfaces.[18−20] There are only a few examples in the literature where TPD was used to study the desorption processes of molecules from self-assembled monolayers.[9,13,21,22] This technique proves to be a promising tool to provide insight about the interactions that occur at organic surfaces, and could shed light on chemical sensor studies of similar adsorbate−substrate systems.[23,24]

The following discussion is divided into four subsections because the respective groups' desorption spectra are similar, suggesting that the desorption processes of the respective alcohol−substrate systems under investigation may be similar. They are (1) a discussion of the results from the desorption spectra for methanol, ethanol, 1-propanol, and 1-butanol desorption from the hydroxyl-terminated surface; (2) a discussion of the results from the desorption spectra for 1-pentanol and 1-hexanol desorption from the hydroxyl-terminated surface; (3) a discussion of the results from the desorption spectra for methanol, ethanol, 1-propanol, and 1-butanol desorption from the methyl-terminated surface; and (4) a discussion of the results of the quantitative analysis of the desorption spectra for the determination of desorption energy for the respective alcohol−substrate systems. Methanol, ethanol, 1-propanol, and 1-butanol will be referred to as the "low-molecular-weight alcohols" and 1-pentanol and 1-hexanol will be referred to as the "high-molecular-weight alcohols."

Methanol, Ethanol, 1-Propanol, and 1-Butanol Desorption. Due to the similarity in the desorption spectra for the low-

TABLE 1: XPS Peak Area Ratios for ADXPS of HO(CH₂)₁₁SH and CH₃(CH₂)₁₇SH on Ni(111)[a]

	XPS Peak Area Ratio				
takeoff angle (degrees)	hydroxyl-terminated surface (HO(CH₂)₁₁SH)			take-off angle (degrees)	methyl-terminated surface (CH₃(CH₂)₁₇SH)
	O1s:C1s	O1s:S2p	S2p:C1s		C1s:S2p
15	0.29 ± 0.01	8.50 ± 0.15	0.07 ± 0.03	10	1.05 ± 0.02
30	0.23 ± 0.01	3.84 ± 1.91	0.12 ± 0.22	30	0.57 ± 0.01
45	0.19 ± 0.02	0.74 ± 0.38	(b)	50	0.19 ± 0.01
60	0.13 ± 0.02	0.64 ± 0.04	0.14 ± 0.03	70	0.12 ± 0.01
75	0.18 ± 0.01	0.98 ± 0.07	0.37 ± 0.03	90	0.16 ± 0.01
90	0.17 ± 0.01	1.20 ± 0.13	0.29 ± 0.01		

[a] The errors for the peak area ratios are based on the errors associated with the integration of the peaks for peak area. [b] Very low signal.

1-Butanol Desorption from HO(CH₂)₁₁SH/Ni(111)
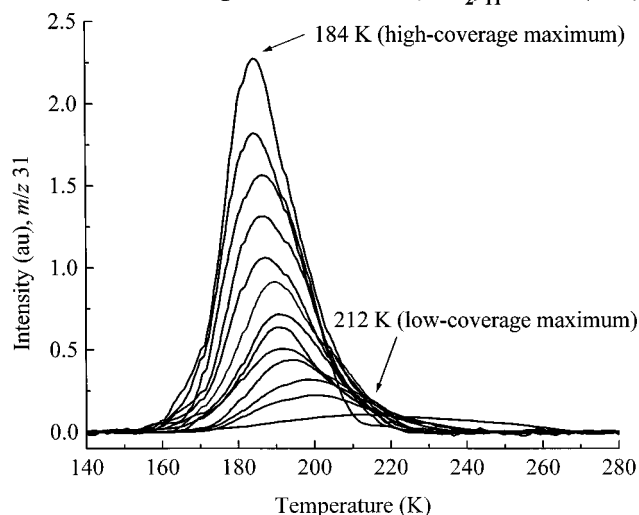
Figure 2. TPD spectra of 1-butanol desorption from HO(CH₂)₁₁SH adsorbed on nickel(111), with detection of m/z 31 (CH₃O⁺). The sample heating rate was 3 K s⁻¹; T_{ads} < 115 K.

molecular-weight alcohols from the hydroxyl-terminated self-assembled monolayer surface and to conserve journal space, only the desorption spectra for 1-butanol desorption for various fluences will be described. These are shown in Figure 2. Only one peak was observed in each desorption spectrum, indicating the presence of at least one desorption state or desorption process for each 1-butanol fluence. The temperature at the maximum rate of desorption shifted to lower temperatures as the fluence was increased, from 212 K for the lowest fluence to 184 K for the highest fluence. The shift to lower temperatures as the fluence was increased could be a consequence of increasing repulsive interactions of adsorbates on the hydroxyl-terminated surface. The desorption peak for the lowest fluence was relatively broad, and as the fluence was increased the peaks became narrower. The peak is symmetric about the desorption temperature at the maximum desorption rate for the lowest 1-butanol fluence, but for progressively higher fluences the peaks rise more rapidly with temperature than they fall, and have a long tail on their high-temperature side. The peak shape for 1-butanol (and the other low-molecular-weight alcohols) desorption from the hydroxyl-terminated surface thus exhibits a second-order-like desorption peak shape at the lowest fluence studied, although it would be difficult to imagine a physical scenario where this would be the case. Although there are several factors that influence the peak shape of a TPD spectrum, evidence for diffusion in the monolayer is illustrated by the long tails in the desorption spectra on the high-temperature side of the peaks.[25] The leading edges of the desorption spectra shifted to lower temperatures as the fluence was increased. There is

TABLE 2: TPD Peak Temperatures and TTPD Desorption Energies (from HO-terminated surface)[a]

| alcohol	$T_{des,l}$ (K)	$T_{des,h}$ (K)	$E_{d,l}$ (kJ mol⁻¹)	$E_{d,h}$ (kJ mol⁻¹)
methanol	180	152	~12	~60
ethanol	190	164	~20	~60
1-propanol	221	173	~8	~53
1-butanol	212	184	~18	~54
1-pentanol	209	197	~15	~40
1-hexanol	213	208	~17	~55

[a] $T_{des,l}$ (K) is the temperature at the peak maximum in the TPD spectrum for the lowest fluence. $T_{des,h}$ (K) is the temperature at the peak maximum in the TPD spectrum for the highest fluence. $E_{d,l}$ (kJ mol⁻¹) is the desorption energy at the lowest alcohol fluence calculated by the TTPD method. $E_{d,h}$ (kJ mol⁻¹) is the desorption energy at the highest alcohol fluence calculated by the TTPD method. The error for all $E_{d,h}$(TTPD) and $E_{d,l}$(TTPD) is ±2 kJ mol⁻¹. (Errors based on the standard error of the slopes from linear fit of respective Arrhenius plots; the scatter in the data is obviously significantly greater than the fit error.)

also undercutting of the tails on the high-temperature side of the spectra of the lower fluence experiments by the higher fluence experiments. This suggests that the process transformed from an apparent-second-order desorption process (probably a diffusion-dominated first-order process) at the lower fluences, to an apparent-zero-order desorption process at the higher fluences. Except for the abscissa values of the peak temperatures, the spectral features for 1-butanol desorption from 11-mercaptoundecanol are also observed for the other three low-molecular-weight alcohols, indicating that a similar desorption process might have occurred for these alcohols.

The peak maxima for the desorption of the lowest fluences of methanol, ethanol, and 1-propanol from the hydroxyl-terminated surface are 180, 190, and 221 K, respectively. This suggests that the length of the alkyl chain in the alcohols has an effect on the interactions of the alcohol with the hydroxyl-terminated surface. We will look at this further in a later section when we calculate and discuss the results in terms of desorption energies as a function of alcohol fluence. The peak maxima for the other low-molecular-weight alcohols (C₁–C₃) also shifted to lower temperatures as their fluences were increased, and they reached their lowest desorption temperatures for their highest fluences at 152 K for methanol, 164 K for ethanol, and 173 K for 1-propanol. These results are summarized in Table 2.

1-Pentanol and 1-Hexanol Desorption from Hydroxyl-Terminated Surface. The TPD spectra for 1-pentanol desorption and 1-hexanol desorption show different features compared to the desorption spectra for the low-molecular-weight alcohols. The TPD spectra for 1-pentanol desorption (monitored by m/z 31 (CH₃O⁺)) and 1-hexanol desorption (monitored by m/z 56 (C₃H₄O⁺)) for various fluences are shown in Figures 3 and 4, respectively. m/z 31 and m/z 56 were the major species in the

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1-Pentanol Desorption from 11-Mercaptoundecanol/Ni(111)
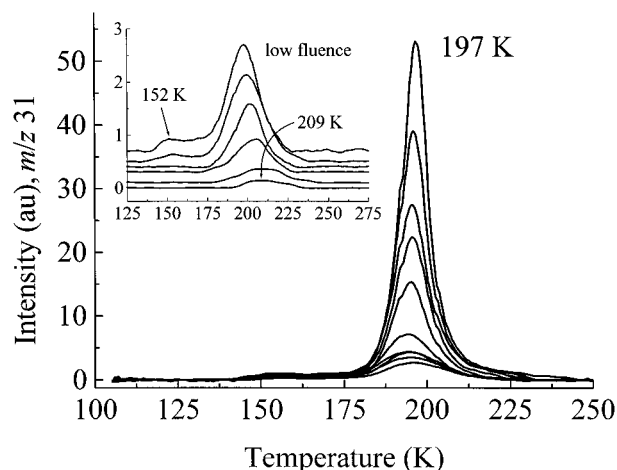
Figure 3. TPD spectra of 1-pentanol desorption from $HO(CH_2)_{11}SH$ adsorbed on nickel(111), with detection of m/z 31 (CH_3O^+). The inset shows the lowest fluences of 1-pentanol. The sample heating rate was 3 K s^{-1}; T_{ads} < 115 K.

1-Hexanol Desorption from $HO(CH_2)_{11}SH$/Ni(111)
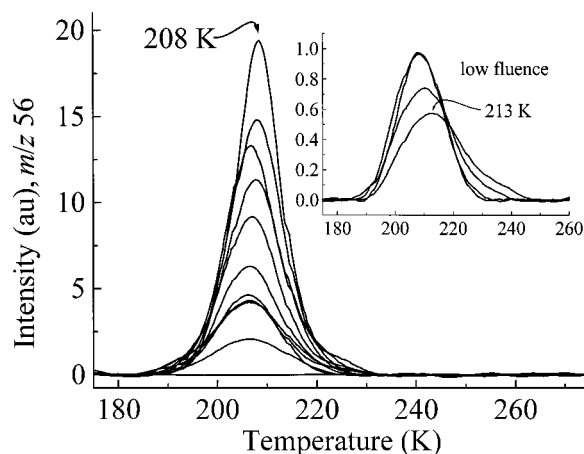
Figure 4. TPD spectra of 1-hexanol desorption from $HO(CH_2)_{11}SH$ adsorbed on nickel(111), with detection of m/z 56 ($C_3H_4O^+$). The inset shows the lowest fluences of 1-hexanol. The sample heating rate was 3 K s^{-1}; T_{ads} < 115 K.

cracking pattern for 1-pentanol and 1-hexanol, respectively, as measured by mass spectrometry, with a 70-eV electron ionization energy.

The TPD spectra for 1-pentanol and 1-hexanol desorption are narrower than for the low-molecular-weight alcohols' desorption spectra. Their peak shapes at the lowest fluences suggest a first-order desorption process.[26] As the 1-pentanol fluence was increased there was an increased presence of tailing on the high-temperature side of the desorption peaks, that, as we discussed above, might be due to diffusion in the monolayer. The spectra for 1-hexanol desorption, however, are more symmetric about the peak maximum as the fluence was increased, suggesting an apparent second-order desorption process.[26] The temperatures at the maximum desorption rates for the lowest and highest fluences for 1-pentanol and 1-hexanol are shown in Table 2. The desorption spectra initially shift to lower temperatures at the maximum desorption rates (see insets in Figures 3 and 4), and then appear to shift back to higher temperatures at an intermediate fluence.

At an intermediate fluence, a small shoulder was present in the pentanol desorption spectrum for m/z 31 at ~152 K, on the

1-Butanol Desorption from $CH_3(CH_2)_{17}SH$/Ni(111)
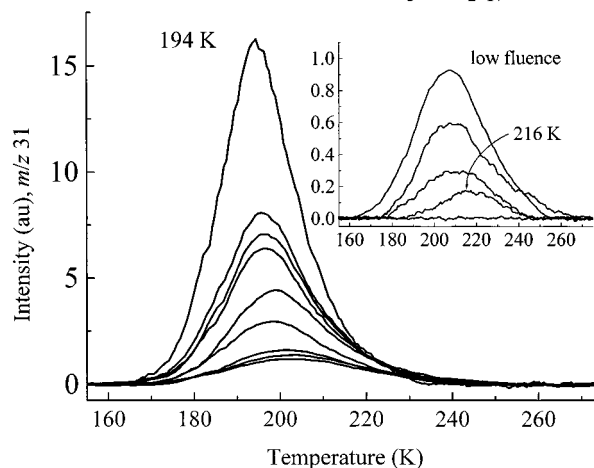
Figure 5. TPD spectra of 1-butanol desorption from $CH_3(CH_2)_{17}SH$ adsorbed on nickel(111), with detection of m/z 31 amu (CH_3O^+). The sample heating rate was 3 K s^{-1}; T_{ads} < 115 K.

low-temperature side of the major peak (~190 K). See inset in Figure 3. As the fluence was increased the area under the shoulder grew only marginally. In addition to m/z 31 (CH_3O^+), m/z 18 (H_2O^+) was also monitored by the mass spectrometer during 1-pentanol desorption. These spectra showed intensity at 152 K for m/z 18. The surface temperature during alcohol exposure to the hydroxyl-terminated surface was < 115 K, so it is conceivable that residual water could have adsorbed onto the surface prior to or during pentanol's adsorption. However, control TPD experiments were performed without the dosing of alcohol onto the cold hydroxyl-terminated surface (i.e., zero exposure of the alcohol) under the same vacuum conditions; there was no water desorption detected by the mass spectrometer in these control experiments. There was also no m/z 18 desorption intensity observed in any of the TPD spectra for the short-chain-alcohol desorption experiments. Thus, the procedures used here to purify the alcohols were not completely effective for the removal of water from 1-pentanol and 1-hexanol.[27]

Methanol, Ethanol, Propanol, and 1-Butanol Desorption from Octadecyl Mercaptan on Nickel(111). The similarity of the spectra for the alcohol desorption from the methyl-terminated surface indicates that the desorption processes for these alcohol−substrate systems were similar, and that they are not much different from the desorption spectra of alcohols from the hydroxyl-terminated surface (see Figure 2). Only the desorption spectra for various 1-butanol fluences from the methyl-terminated surface are shown in Figure 5 to conserve journal space. The inset in Figure 5 shows the desorption spectra for low-butanol-fluence experiments.

Based on the appearance of the TPD spectra for 1-butanol (Figure 5) and the other alcohol desorption spectra from the methyl-terminated surface, there was one desorption state for each fluence, indicated by a single peak in their respective spectra. The peak maxima (i.e., "peak" temperatures) in the desorption spectra shifted to lower temperatures with increasing fluence, and there was an increased degree of tailing on the high-temperature side of the desorption spectra, increasing with fluence. As discussed before, tailing on the high-temperature side of a desorption spectrum indicates that there might have been diffusion of the alcohols into the monolayer after dosing and before TPD.[25] For low butanol fluence, the desorption spectra are more symmetric, suggesting an apparent-second-

TABLE 3: TPD Peak Temperatures and TTPD Desorption Energies (from CH$_3$-terminated surface)^a

adsorbate	$T_{des,l}$ (K)	$T_{des,h}$ (K)	$E_{d,l}$ (kJ mol^{-1})	$E_{d,h}$ (kJ mol^{-1})
methanol	197	164	~22	~48
ethanol	189	164	~12	~47
1-propanol	185	182	~21	~50
1-butanol	216	194	~23	~55

^{a} $T_{des,l}$ (K) is the temperature in Kelvin at the peak maximum in the TPD spectrum for the lowest fluence. $T_{des,h}$ (K) is the temperature in Kelvin at the peak maximum in the TPD spectrum for the highest fluence. $E_{d,l}$ (kJ mol^{-1}) is the desorption energy at the lowest alcohol fluence calculated by the TTPD method. $E_{d,h}$ (kJ mol^{-1}) is the desorption energy at the highest alcohol fluence calculated by the TTPD method. The error for all $E_{d,h}$(TTPD) and $E_{d,l}$(TTPD) is ±2 kJ mol^{-1}. (Errors based on the standard error of the slopes from linear fit of respective Arrhenius plots; the scatter in the data is obviously significantly greater than the fit error.)

order desorption process, and slightly more broad compared to the desorption spectra for high butanol fluence.

At face value, this fluence dependence of the maximum desorption rates (i.e., based on the shift of the peak temperatures to lower values) could indicate that alcohol−alcohol interactions on the methyl-terminated surface are repulsive with increasing alcohol fluence. Also, the strongest interactions of the various alcohols with the methyl-terminated surface occurred at the lowest alcohol fluences because the peak maxima in their desorption spectra were at their highest temperatures. The temperatures at the maximum desorption rates for the lowest alcohol fluence for the respective short-chain alcohols studied were similar; they were ~197 K for methanol, ~189 K for ethanol, ~185 K for propanol and ~216 K for butanol. The temperatures at the maximum desorption rates at low fluence for methanol, ethanol, 1-propanol, and 1-butanol were similar, suggesting that their interaction mode with the methyl-terminated surface was similar. If there are any subtle (aside from trends in the peak temperatures) differences between the desorption processes of different alcohols from the methyl-terminated surface, then these TPD experiments did not reveal them. Weak adsorbate−surface interactions are expected for alcohols that are capable of forming hydrogen bonds with a methyl-terminated surface that is not capable of forming hydrogen bonds. It is, therefore, reasonable to assume that these alcohol−substrate interactions are first- and zero-order desorption processes, depending on the adsorbate coverage. The peak maxima at the highest fluence for methanol, ethanol, 1-propanol, and 1-butanol desorption from the methyl-terminated surface increased with the number of carbons in the alcohol chain. The temperatures at the maximum desorption rates for methanol, ethanol, 1-propanol, and 1-butanol from the methyl-terminated surface are summarized in Table 3.

Analysis of TPD Spectra. In a TPD experiment the mass spectral intensity is measured as a function of the desorption temperature for a mass of interest, and the desorption rate is directly proportional to the mass spectral intensity for a fast-pumped UHV system.[28]

A very simple and common method to analyze TPD spectra for desorption energy is the Redhead analysis,[26] but since it assumes that the desorption energy is independent of coverage, the method is not appropriate to use to estimate the desorption energy for coverage-dependent desorption processes. The shift of the temperatures at the maximum desorption rates as a function of the coverage in the desorption spectra for the alcohols suggests that the desorption energies are a function of coverage. Thus, the TPD spectra are better analyzed for

TTPD-Calculated Desorption Energy of *n*-Alcohols from HO(CH$_2$)$_{11}$SH
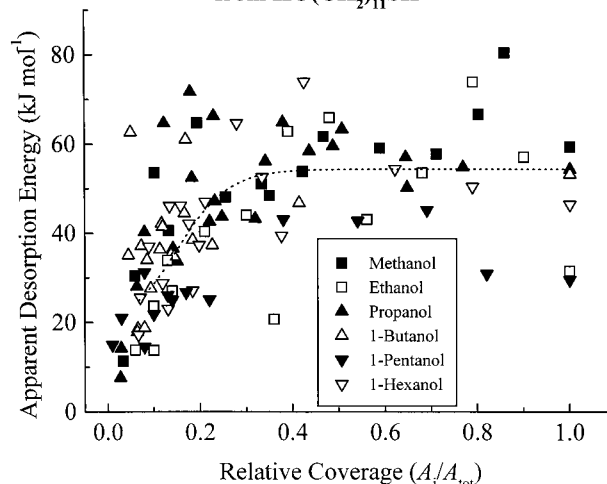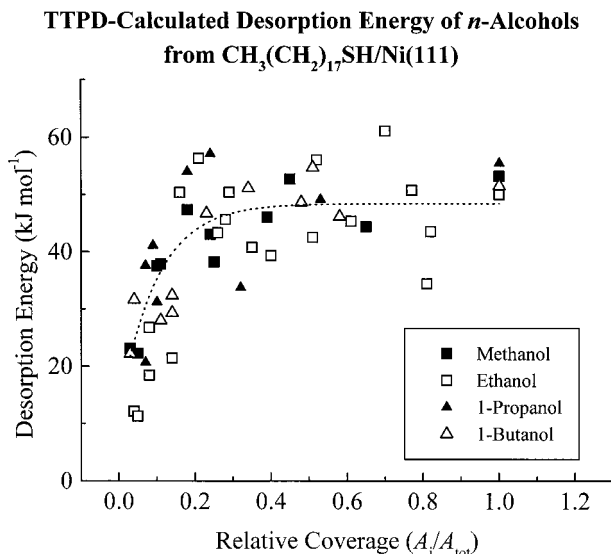
Figure 6. Threshold TPD desorption energy of methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol from HO(CH$_2$)$_{11}$SH adsorbed on nickel vs relative coverage. Relative coverage is defined as the initial peak area A_i divided by the peak area for the highest fluence experiment A_{tot}. We estimate that a relative coverage of approximately 0.2 on this abscissa corresponds to one monolayer.

desorption energy by a method that does not make this assumption, such as the threshold TPD (TTPD) method.[13,29]

In the TTPD method, a narrow temperature range in a TPD spectrum at the onset of desorption, corresponding to <2% of the total area under the desorption spectrum, is analyzed. This so-called threshold region is then used to make an Arrhenius plot (ln *rate* versus T^{-1}) where the slope is related to the desorption energy, and the *y*-intercept is related to the preexponential factor. This procedure can be repeated to extract a desorption energy from the desorption spectra at all coverages so that a plot of the apparent desorption energy as a function of coverage may be obtained with no a priori assumptions about the kinetics of the desorption process.

The desorption energies for methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol desorption from the hydroxyl-terminated surface and the desorption energies for methanol, ethanol, 1-propanol, and 1-butanol from the methyl-terminated surface were calculated using TTPD, and then plotted as a function of their relative coverage. See Figures 6 and 7. Additional details are given in an earlier reference. The estimated monolayer coverage for each adsorbate from both surfaces occurred at approximately 0.2 on this abscissa axis. Although the data are appreciably scattered, for the alcohol series C$_1$−C$_6$, the desorption energies calculated from TTPD increased from 10 to 25 kJ mol^{-1} for the lowest fluences from the hydroxyl- and methyl-terminated surfaces, to intermediate fluences where the desorption energies remained nearly constant at 40−60 kJ mol^{-1} for the highest fluences from these surfaces. The nearly constant desorption-energy region in Figures 6 and 7 for all alcohols probably indicates desorption from a condensed phase, which is commonly observed in multilayer systems.[30] At high fluence, the desorption energy E_d should approach the heat of sublimation ΔH_{sub} if there is desorption from a condensed phase. The TTPD-calculated desorption energies at the highest fluence generally increased with the number of carbons in the alcohol approaching their values for the heats of sublimation,[13] but within the scatter of these results the desorption energies at high fluences are similar.

The TTPD-calculated desorption energy of all alcohols that were studied from the hydroxyl- and methyl-terminated surfaces

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TTPD-Calculated Desorption Energy of *n*-Alcohols from CH₃(CH₂)₁₇SH/Ni(111)

Figure 7. Threshold TPD desorption energy of methanol, ethanol, 1-propanol, and 1-butanol from $CH_3(CH_2)_{17}SH$ adsorbed on nickel vs relative coverage. Relative coverage is defined as the initial peak area A_i divided by the peak area for the highest fluence experiment A_{tot}. We estimate that a relative coverage of approximately 0.2 on this abscissa corresponds to one monolayer. The dashed line is not a fit, but is meant merely to guide the eye.

increased as a function of alcohol coverage (see Figures 6 and 7), but the peak maxima in the their respective TPD spectra shifted to *lower* temperatures with alcohol fluence. The compensation effect is a coverage-dependent kinetic phenomenon occasionally thought to be observed in TPD spectra. This effect describes an accidentally coverage-independent desorption rate constant when the desorption energy and preexponential factor vary simultaneously with coverage. Niemantsverdriet and Wandelt studied the effects that the compensation effect has on TPD spectra.[31,32] Their studies indicated that if the compensation effect affected the desorption processes of an adsorbate–substrate system, then the trend observed in the desorption energy curves might result from an opposite trend in the shifts of desorption spectra. Said another way, if lateral interactions were involved, then a shift of the peak maxima to higher temperatures might not necessarily reflect attractive interactions of adsorbates on a surface, and vice versa.

The TPD spectra for the lowest fluence in each system reflects coverages significantly less than a monolayer and thus presumably represents the interaction between the adsorbate and the hydroxyl-terminated surface or the adsorbate and the methyl-terminated surface in the limit of low coverage and no island formation. The temperature at the maximum rate of desorption in each system was the highest for the lowest fluences (and hence, coverages) recorded, and increased linearly by ∼10 K per CH_2 group for the alcohols with up to four carbons for desorption from the hydroxyl-terminated surface. There was no further increase for the C_5 and C_6 alcohols. The peak temperatures in the desorption spectra for the lowest alcohol fluences from the methyl-terminated surface were more scattered. The temperatures at the maximum desorption rates for the lowest and highest fluences for each alcohol from the hydroxyl- and methyl-terminated surfaces are shown in Tables 2 and 3, respectively.

In the special case where the desorption energy is not dependent on coverage, the desorption energy is directly related to the temperature at the peak maximum in a TPD spectrum, i.e., $E_d \approx 25RT_{max}$, where T_{max} is the peak temperature.[25] Under these circumstances the trend of the desorption energies as a

function of coverage would, of course, follow the trend of the shift in temperatures at the peak maxima. At the lowest fluences for the alcohols studied ($E_d^{TTPD} \approx 10-20$ kJ mol^{-1}), it might be reasonable to assume that the interactions of the alcohols with the hydroxyl-terminated surface are hydrogen-bonding-like interactions ($E_{HB} = 10-40$ kJ mol^{-1}). The temperatures at the maximum desorption rates for these studies occurred at temperatures similar to those observed for the same alcohols desorbing from a carboxyl-terminated surface,[13] where hydrogen-bonding interactions were suggested to have been operating. The increase in the temperature at the peak maximum for the low-fluence desorption of the alcohol series C_1-C_4 from the hydroxyl-terminated surface (by ∼10 K per CH_2 group) suggests that there is an additional energy associated with each CH_2 group that corresponds to ∼2 kJ mol^{-1} per CH_2 group.

The desorption of alcohols from the methyl-terminated surface is not likely to involve hydrogen-bonding interactions because the methyl terminal group is not capable of forming hydrogen bonds. Although the temperatures at maximum desorption rates at the lowest alcohol fluences are more scattered on the methyl-terminated surface, the difference between, say, methanol and 1-butanol in their desorption energies at low alcohol fluences might be related to the length of the alkyl chain of the alcohol. The similarity of the desorption spectra and the values and trends in desorption energy curves for the methyl-terminated surface and the hydroxyl-terminated surface is surprising given that one system is capable of hydrogen bonding (OH surface) with the alcohols and the other is not (CH_3 surface).

If it were assumed that only hydrogen bonding was reflected in the TPD spectra for alcohol desorption from the hydroxyl-terminated surface, then one should expect that the desorption temperatures for each adsorbate–substrate system would be similar. Instead, the range of desorption temperatures observed for the adsorbate–substrate systems studied indicates that more than just hydrogen bonding occurred. It is likely that at less-than-monolayer coverages, molecules are oriented with their hydrocarbon backbone parallel to the surface. This suggestion about the orientation of linear-chain alcohols on this organic surface is similar to the interpretation of other studies of linear-chain alcohol interactions with metal surfaces.[30] If this is true in the low-coverage limit, then the sum of adsorbate–surface interactions is composed of a component due to hydrogen bonding and a component due to hydroxyl–CH_2 van der Waals interactions (increasing for the alcohol series C_1-C_4).

The TTPD-derived desorption energies from the hydroxyl-terminated surface and the methyl-terminated surface increased with alcohol coverage, as shown in Figures 6 and 7, implying increasing attractive interactions between adsorbates. In the low-coverage limit, where isolated adsorbates cannot form a hydrogen-bonding network (with the hydroxyl-terminated surface), the desorption energy is lower than for monolayer coverages, where there can be a monolayer network of hydrogen bonding, both from adsorbate to substrate and between adsorbates.

Preexponential Factors for Alcohol Desorption from Organic Surfaces. The trend in the preexponential factor curves (i.e., preexponential factor versus relative coverage) was similar to the trend in the desorption energy curves for alcohol desorption from organic surfaces. This similarity between the preexponential factor and desorption energy curves suggest that there is correlation between the desorption energy and preexponential factor for alcohol desorption from organic surfaces. The preexponential factor and desorption energy curves for 1-propanol desorption from the hydroxyl-terminated surface are

Desorption Energy and Pre-Exponential Factor Curves for 1-Propanol Desorption from HO Surface
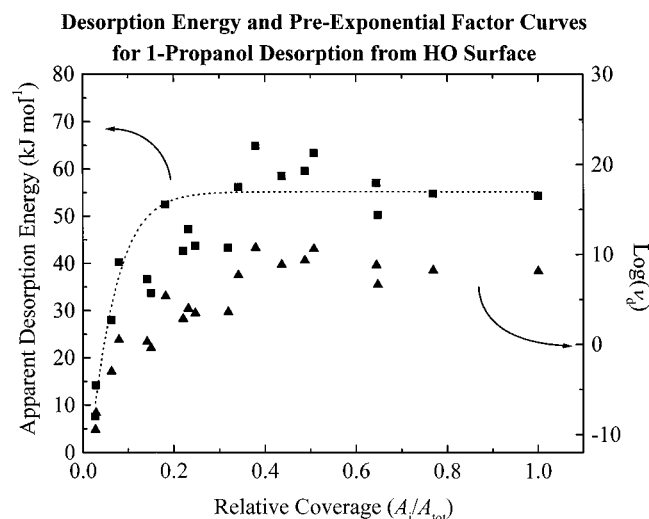
Figure 8. Desorption energy and preexponential factor for 1-propanol desorption from HO(CH$_2$)$_{11}$SH adsorbed on nickel versus relative coverage. The apparent desorption energies and preexponential factors were determined from the TTPD method. Relative coverage is defined as the initial peak area A_i divided by the peak area for the highest fluence experiment A_{tot}. The dashed line is not a fit, but is meant merely to guide the eye.

TPD Peak FWQM versus Relative Coverage for 1-Propanol Desorption from HO Surface

Figure 9. TPD peak width at one-quarter height 1-propanol desorption from HO(CH$_2$)$_{11}$SH adsorbed on nickel vs relative coverage. Relative coverage is defined as the initial peak area A_i divided by the peak area for the highest fluence experiment A_{tot}. The dashed horizontal line is the theoretical peak width for an ideal first-order process. See text for discussion.

shown in Figure 8. The preexponential factors calculated (TTPD) for alcohol desorption from the organic surfaces generally increased from extremely small values at low coverage to ~10^{10} s^{-1} at ~0.2-relative coverage (approximately one monolayer) and remained constant for all higher coverages. The correlation observed between the preexponential factor and the desorption energy for these adsorbate−substrate systems might not explain the much-lower-than-expected preexponential factors calculated. A possible explanation for the lower-than-expected preexponential factors might be the diffusion of alcohol molecules into the monolayer before a TPD experiment and then back out during a TPD experiment.

A "typical" preexponential factor for a first-order desorption is thought to be about 10^{13} s^{-1} based on transition state theory. Low preexponential factors indicate that desorption occurred through a so-called "tighter" (greater attraction with the surface) transition state.[32] It is possible that diffusion might result in unnaturally low preexponential factors because molecules may be physically trapped between the alkyl chains of the SAM after entering the monolayer via defect sites. If diffusion occurred for alcohol desorption at low coverages from organic surfaces, the nearly constant preexponential factor at approximately one monolayer and above was probably because there were fewer defect sites available where diffusion could occur. If this is true, then the interactions expected for the alcohol desorption from organic surfaces at high coverage should be closer to the expected values for a first-order desorption (10$^{13\pm3}$ s^{-1} based on transition state theory). The preexponential factor curves at higher relative coverage for alcohol desorption from organic surfaces (see Figure 9) indicate that the preexponential factors are close to the values expected for first-order desorption based on transition-state theory.

The width and position of a TPD spectrum at its peak maximum are dependent on the preexponential factor. Several TPD spectra were simulated (not shown to conserve journal space) using the Polanyi−Wigner equation varying the preexponential factor, for a fixed desorption energy E_d of 40.3 kJ mol^{-1}, a heating rate β of 3 K s^{-1} and an initial coverage θ of 0.5 monolayer. As expected, the preexponential factor plays a
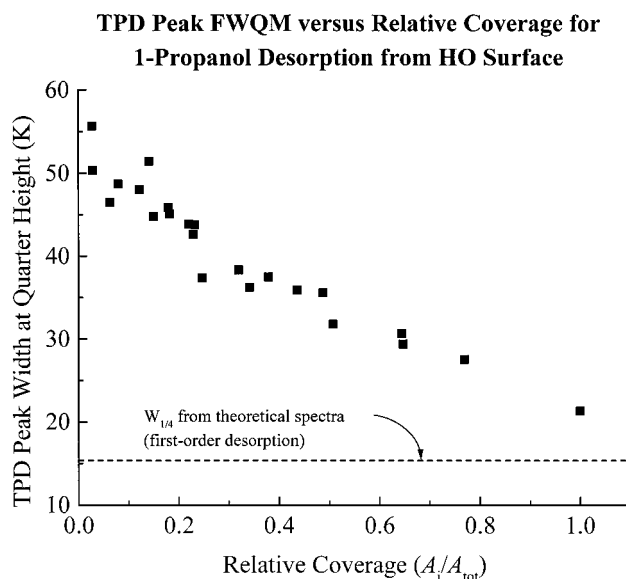
significant role in the peak position and the peak width, even for a fixed desorption energy, E_d.

The tailing seen on the high-temperature side of most TPD spectra here, especially starting from low coverages, suggests that there is a significant amount of diffusion, and that this effect is most prominent at low initial coverages. In Figure 9 it can be seen that peak width, measured at one-quarter height (FWQH), is greatest at the lowest coverages, and decreases with coverage to a value that approaches the FWQH of an ideal first-order process (no diffusion out of the monolayer) at higher coverages. At low coverages when these sites are likely to be the only desorption states populated, TPD peak widths are at their greatest due to the diffusion-induced tailing on the high-temperature side of the peak. At high coverages when the defect sites in the self-assembled monolayer are already populated with adsorbates at the beginning of the TPD experiment, diffusion out of these "channels" prior to desorption occurs during the early stages of the experiment and does not play a broadening role in the peak shape on the high-temperature side of the peak. Although the TTPD analysis does not rely on peak shape in the last stages of the experiment, the observations nevertheless suggest the presence of a significant physical effect (diffusion out of the monolayer). We interpret this as evidence that unusually low preexponential factors ν_d are due to diffusion out from between of the chains of the self-assembled monolayer. Desorption energies and preexponential factors were also calculated using the so-called "complete analysis," but using this method introduced a whole different set of problems that we might choose to explore in a forthcoming publication.

Conclusion

The desorption spectra of methanol, ethanol, 1-propanol, and 1-butanol from 11-mercaptoundecanol on Ni(111) showed a transition from an apparent second-order desorption process to an apparent zero-order desorption process. The desorption spectra of 1-pentanol and 1-hexanol from 11-mercaptoundecanol showed a transition from an apparent first-order desorption process to an apparent second-order desorption process with

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coverage. It is likely that diffusion affected TPD line shapes in such a manner as to cause what was actually a first-order desorption process to exhibit second-order line shapes.

At the lowest alcohol fluences for the low-molecular-weight alcohols from the hydroxyl-terminated surface, the desorption temperature at the peak maxima in the TPD spectra increased linearly by ~10 K (~2 kJ mol^{-1}) per CH_2 or CH_3 group. This suggests that methanol, ethanol, 1-propanol, and 1-butanol may have oriented with their carbon chains parallel to the hydroxyl-terminated surface, at least at low coverages. For alcohol chain lengths greater than 4, the desorption temperatures at the peak maxima for the lowest fluences were the same within experimental error. The desorption experiments from the methyl-terminated surface for methanol, ethanol, 1-propanol, and 1-butanol indicated that the desorption processes for these adsorbate–substrate systems might be similar on the basis of the similarity of their desorption spectra. It was surprising to find that the desorption spectra corresponding to the octadecyl mercaptan SAM surface were similar to the desorption spectra corresponding to the 11-mercaptoundecanol surface.

Although the interactions of short-chain alcohols with the hydroxyl- and methyl-terminated surface should, in principle, be a first-order desorption process, it was difficult to discern this on the basis of the TPD line shapes because of tailing on the high-temperature side of the desorption spectra for all short-chain alcohols.

TTPD was used to analyze the desorption spectra of alcohols (n-$C_xH_{2x+1}OH$ for $x = 1-6$) from 11-mercaptoundecanol and octadecyl mercaptan to determine their desorption energies as a function of alcohol coverage. The desorption energies for all alcohols studied increased from ~10–20 kJ mol^{-1} for their lowest coverages to ~40–60 kJ mol^{-1} for their highest coverages from the hydroxyl-terminated surface, and increased from ~10–25 kJ mol^{-1} for their lowest coverages to ~45–55 kJ mol^{-1} for their highest coverages from the methyl-terminated surface. At high alcohol coverages, the alcohol molecules are closer to each other on the surface and might form a network of hydrogen bonds (leading to a higher desorption energy) in addition to its hydrogen bonding interactions with the hydroxyl-terminated surface. The increasing trend in the desorption energy curve from the methyl-terminated surface (see Figure 7) might also be due to the coverage-dependent development of a hydrogen-bonding network within the adsorbate monolayer.

The similarity of the desorption energies of alcohols from the methyl- and hydroxyl-terminated surfaces might be due to desorption from a similar intermediate surface whose composition and morphology is not shown. Since the TPD spectra suggest that the adsorbate is *absorbed* by the SAM, perhaps by way of a defect site, the intermediate surface could be a mixture of alcohols (adsorbates) that were trapped near the terminus of the monolayer and HO- or CH_3-terminal groups, depending on the SAM deposited upon it. Therefore, any subsequent adsorbate–substrate interactions would be a reflection of interactions with this so-called intermediate surface, resulting in similar desorption energies. Also, surface morphology is a critical component of analysis models of TPD spectra, for which the surface is generally assumed to be homogeneous. Not much is known about the surface homogeneity for alkanethiols on nickel, aside from what these experiments show us.

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$$RO^- + H_2O \xleftarrow{\ HO^\bullet\ } R{-}OH \xrightarrow{\ H_3O^+\ } R{-}OH_2^+ + H_2O$$

It is also known that reactions of alcohols with nickel surfaces do not produce water. Adsorbed CO and H are produced at low temperatures and CO (g) and H$_2$ (g) at high temperatures ($T > 400$ K). (See Russell, et al. *Surf. Sci.* **1987**, *183*, 316.) Thus, it is not likely that pinhole or other defects in the SAM film, exposing the nickel substrate, are likely to be the cause of the observed water.
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