

Comparative Investigations of the Packing and Ambient Stability of Self-Assembled Monolayers of Alkanethiols on Gold and Silver by Friction Force Microscopy

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The frictional behavior of self-assembled monolayers (SAMs) formed by the adsorption of alkanethiols onto silver surfaces has been investigated by friction force microscopy (FFM) and compared with the behavior observed for SAMs on gold. Monolayers have been formed from adsorbates with different terminal group functionalities and alkyl chain lengths. Significant differences in frictional behavior are observed for monolayers on the two different substrates, and these may be interpreted in terms of variations in the packing density of the adsorbate molecules. The collapse of monolayer order following ambient oxidation may conveniently be studied using FFM, revealing that methyl terminated SAMs on silver exhibit substantially enhanced stability as a consequence of their increased packing density. Behavior is different for carboxylic acid terminated SAMs, indicating that the constraints on the packing of the two types of adsorbate are different.

Introduction

There is a growing body of literature on the characterization of organic monolayers, including self-assembled monolayers (SAMs), by friction force microscopy (FFM) and other techniques based on atomic force microscopy (AFM).^{1–8} It is clear that besides providing, under optimal conditions, high-resolution images that yield insights into molecular organization in such materials, FFM and related techniques can provide valuable insights into their interfacial behavior. Such insights are of fundamental importance in surface science, and have relevance to many applications, including our understanding of lubrication in both the classical context and in emerging technologies such as microelectromechanical systems. FFM studies of SAMs, including both alkylsilane monolayers^{9,10} and monolayers of alkanethiols on gold,^{1–8} have investigated the effect of a range of parameters, including adsorbate tail-group functionality,^{1–3,6,11} molecular organization,^{4,5,8,9,12–15} and interfacial interactions,¹⁰ on friction behavior. Recently, some workers have utilized a range of synthetic approaches to create adsorbate molecules with molecular structures designed to introduce differences in packing density and bonding in a controlled fashion, and these elegant studies have yielded important insights into the origins of friction at the molecular level.^{8,15,16} Many of the reported phenomena may be rationalized in terms of variations in the organization of molecules within SAMs. Harrison and co-workers have modeled the role of alkyl chain deformation in energy dissipation during sliding contact between molecular materials.^{17,18} Their simulations have revealed substantive differences in the extent of conformational change under comparable loading conditions in monolayers of hydrocarbon chains that exhibit differences in packing density.

While SAMs of alkanethiols have attracted widespread interest for many applications, the great majority of the published work relates to monolayers on gold. With the exception of the substantive investigations by Grunze and co-workers over several years,^{19–24} and some early investigations,^{25–27} there is comparatively little work in the literature relating to monolayers of alkanethiols on silver.^{28,29} However, there are good reasons for making comparative studies of SAMs on silver and gold. There are significant differences in the bonding and packing in monolayers formed on the two metals. For example, it is known that the packing density of methyl terminated thiols is somewhat greater on silver than on gold, leading to a smaller tilt angle (12° on Ag compared to ca. 30° on Au²⁶). The sulfur hybridization is also different on the two metals (sp on Ag compared to sp³ on Au),²⁴ possibly leading to a difference in the strength of the adsorbate–substrate interaction. These differences may have a profound influence on the behavior of the resulting materials. For example, Grunze and co-workers have demonstrated greater stability under electron bombardment for SAMs on silver,¹⁹ and Chenakin et al. have reported greater rates of sputter-induced damage in SAMs on Ag than in corresponding monolayers on Au.²⁹ It is possible that there may also be a difference in the stabilities of the SAMs to ambient oxidation, a critical factor in many applications. The ambient stabilities of SAMs on Ag and Au have not previously been compared systematically. Moreover, there are few studies by any techniques of monolayers of alkanethiols with polar terminal groups on silver substrates. It is not clear whether these adsorbates adopt closer packed structures on Ag than they do on Au, like their methyl terminated counterparts, and the relative stabilities of polar and methyl terminated SAMs on the two substrates are also of interest. In view of this, it is significant to note that there are, to our knowledge, no published studies of the friction behavior of SAMs on silver. In the present study, friction coefficients were measured for monolayers of carboxylic acid and methyl terminated thiols of two different alkyl chain lengths on gold and silver, to see how their friction properties were influenced

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by differences in molecular organization on the two substrates, to compare the organization of methyl and carboxylic acid terminated SAMs on Ag, and to examine the extent to which FFM data could be utilized to compare the relative stabilities of SAMs on silver and gold to ambient oxidation.

Experimental Section

Self-assembled monolayers were prepared by immersing freshly prepared substrates in 1 mmol dm⁻³ solutions of alkanethiols in degassed ethanol for 18 h. Cr was deposited onto glass microscope slides (no. 2 thickness, Chance Proper Ltd, UK) to a thickness of 2 nm prior to deposition of gold, while silver could be deposited directly onto the slides. Gold and silver were both deposited to a thickness of 25 nm, at a rate of 0.1 nm s⁻¹. Under these conditions, grain sizes were typically in excess of 50 nm, important in ensuring the preparation of high-quality monolayers.³⁰ Cantilevers for friction force microscopy were coated in the same way with gold and functionalized by immersion in a 1 mM solution of mercaptoundecanoic acid in ethanol for 18 h. All glassware was cleaned prior to use by immersion in Piranha solution (3 parts hydrogen peroxide to 7 parts concentrated sulfuric acid) for 30 min, followed by rinsing in copious quantities of deionized water and drying in an oven.

CAUTION: Piranha solution may detonate unexpectedly on contact with organic material.

Butanethiol (C₃CH₃ hereafter), dodecanethiol (C₁₁CH₃), and 3-mercaptopropanoic acid (C₃COOH) were obtained from Fluka and used as received. Mercaptoundecanoic acid (C₁₁COOH) was obtained from Aldrich and recrystallized twice from hexane prior to use. Advancing water contact angles were measured for representative SAMs and compared with literature values, to ensure monolayer purity was maintained.

Friction force microscopy was carried out using a Nanoscope IIIa Multimode Atomic Force Microscope (Digital Instruments, Cambridge, UK). The probes used were silicon nitride Nanoprobes (Digital Instruments, Cambridge, UK). The nominal force constants of these probes were 0.06 or 0.12 N m⁻¹. Force constants of individual cantilevers were measured using a routine contained within the microscope software and based upon the measurement of the thermal oscillations of the cantilever.³¹ No attempt was made to calibrate the torsional force constants of the cantilevers. Although a number of methods for accomplishing this have been published,^{32–34} it remains a challenging undertaking. Instead, we used an approach based upon internal normalization of friction coefficient data previously reported by a number of workers.^{11,16} A series of measurements of friction–load behavior was made using a single cantilever. Friction force measurements were made from friction loops, acquired in the scope mode, at 10 separate locations on the sample surface. The friction coefficients were then determined from the gradients of the detector response–load plots, determined using linear regression, and normalized by dividing each by the magnitude of the largest coefficient. Although this means that it is difficult to compare the absolute friction coefficients reported here with those acquired on other instruments, the relative magnitudes of the coefficients determined for the different SAMs are highly reliable. By utilizing this approach, it was possible to carry out multiple repeats of the friction coefficient determinations and average data recorded on different days using different cantilevers. The data presented here are the result of five repetitions, and the error bars shown are the standard error in the mean for each data point.

In the studies of SAM aging, samples were stored in covered plastic Petri dishes on a bench in the open laboratory. No attempt

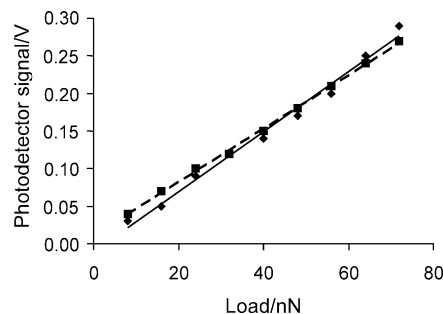


Figure 1. Variation in friction force with applied load for a C₁₀COOH functionalized tip in contact with monolayers of C₁₀COOH on gold (squares, dashed line) and silver (diamonds, solid line). The lines have been fitted by linear regression.

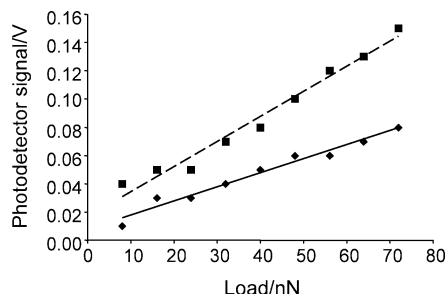


Figure 2. Variation in friction force with applied load for monolayers of C₁₁CH₃ on gold (squares, dashed line) and silver (diamonds, solid line).

was made to create an artificially controlled environment because the mechanism of SAM aging is not known. Sets of data were acquired over an extended period of time, so functionalized tips were not employed for these studies because of the risk of degradation of the monolayer deposited on the tip during the functionalization process. In all cases, measurements of friction data for aged SAMs were normalized to data acquired on the same day for a freshly prepared SAM of the same type. However, the same tip was used for all the experiments in a given set. Variation in the coefficients of friction of the unoxidized SAMs was within the expected limits of experimental error, indicating that there was no change in the performance of the tip due to contamination. By virtue of conducting the experiment in this way, all of the data for all of the samples were standardized such that the friction data acquired for different time points could be meaningfully compared.

For unoxidized SAMs, the FFM experiments were carried out under ethanol. Not only does this have the effect of eliminating capillary adhesion, and reducing sample contamination, but it also protects the thiols attached to the tip from oxidation. For the aged SAMs, the solubility of the sulfonates in ethanol (and many other suitable alternatives) meant that the data could not be acquired under liquid, and the experiments were thus all carried out under ambient conditions.

Results

The lateral component of the photodetector signal, proportional to the friction force, was measured for several SAMs and plotted as a function of the load (Figures 1 and 2). The photodetector response is used, rather than the friction force, because of the difficulties of calibrating the lateral deflection of the cantilever. For a particular cantilever geometry, the relationship between the normal and lateral force constants should be constant, so provided the normal load is properly

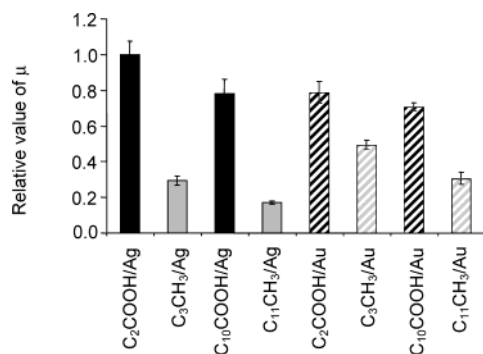


Figure 3. Histogram showing coefficients of friction of short- and long-chain methyl and carboxylic acid terminated SAMs on silver and gold substrates.

quantified, the variation in the lateral photodetector response with load directly reflects the friction-load behavior.

In previous studies of organic monolayers by friction force microscopy, Amonton's law

$$F = \mu L$$

(where F is the frictional force, μ is the coefficient of friction, and L is the load applied perpendicular to the surface) has usually been used to quantify friction-load relationships.^{1,2,5-8,11,12,16,33} In Figures 1 and 2 it is clear that the fit of the friction-load relationship to linear behavior is a good one and it is thus convenient to quantify the properties of specific SAM systems in terms of a coefficient of friction. It should be noted that in pull-off force measurements using AFM, paradoxically, Johnson-Kendall-Roberts (JKR) contact mechanics are generally found to apply.^{1,2,35} In the range of forces employed here, the discrepancy between the JKR model and the linear fit made using Amonton's law would be expected to be small, but the interpretation of the physical meaning of the friction-load relationship would be different. It is not within the scope of the present study to resolve this paradox. However, we have attempted to fit friction force data using the JKR model, and did not achieve a better fit to the data than was possible using Amonton's law. The use of friction coefficients to quantify the behavior of the systems under investigation offers the advantage that it enables ready comparison with previously published studies.

Figure 1 shows the variation in the photodetector signal with load for monolayers of mercaptoundecanoic acid (C₁₁COOH) on gold and silver. It may be seen from Figure 1 that the gradients of the friction-load plots are similar for both substrates for this adsorbate, but that the gradient is steepest (i.e., μ is largest) for the monolayer on silver.

Figure 2 shows friction-load plots for monolayers of dodecanethiol (C₁₁CH₃) on gold and silver. At any given load, the friction force (photodetector signal) measured for C₁₁CH₃ on a particular substrate is significantly less than that measured for C₁₁COOH on the same substrate. As was the case with the data in Figure 1, linear regression yielded a good fit to a straight line on both substrates. However, in contrast to the data in Figure 1, the friction forces measured for C₁₁CH₃ on Au are, at all loads, larger than those measured on Ag. The gradient of the friction-load plot (i.e., the value of μ) is clearly larger for C₁₁-CH₃ on Au than on Ag.

Figure 3 shows values of μ for a wider range of substrate/adsorbate combinations, determined from friction-load plots. The data for SAMs on gold are similar to those previously published. In brief, the carboxylic acid terminated SAMs exhibit

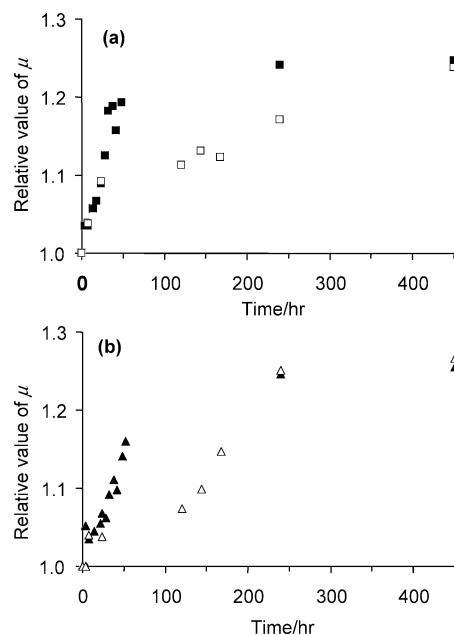


Figure 4. Variation in coefficients of friction of SAMs of C₃CH₃ (a) and C₁₁CH₃ (b) on Au (solid symbols) and Ag (open symbols), with storage time in air.

larger values of μ than the methyl terminated SAMs. The ratio of the values of μ for short (C₃) and long (C₁₁) methyl terminated SAMs is approximately 2:1, while the ratio of the values of μ for acid terminated SAMs of similar lengths is virtually unity. There are some significant differences in the behavior observed for the SAMs on Ag, however. The coefficients of friction of the methyl terminated monolayers (of either length) are approximately half those of monolayers of the same thiols on Au, and the ratio of the coefficients for the short- and long-chain monolayers is approximately 2 on both metals. In contrast, the coefficients of friction of the carboxylic acid terminated SAMs on Ag are slightly *greater* than those of monolayers of the same thiols adsorbed on Au, although the difference is small and, given the size of the error bars, is not statistically significant for C₁₀COOH. The difference in the value of μ for the short- and long-chain carboxylic acid terminated SAMs is not statistically significant on Au, and is also small on Ag, although there is a small difference for SAMs of short and long alkyl chain lengths on Ag.

The effect of extended exposure of the SAMs to the laboratory ambient was explored using friction force microscopy. Attempts to carry out systematic studies of the aging of monolayers formed from polar adsorbates were frustrated by the tendency of the high surface energy films to attract contamination from the atmosphere. However, for methyl terminated SAMs, contamination of the surface by adsorption of adventitious material is not a significant concern. The coefficients of friction were measured as a function of exposure time in the laboratory ambient for samples of C₃CH₃ and C₁₁CH₃ SAMs on Ag and Au substrates at intervals from 0 to 450 h. The data are shown in Figure 4 and are normalized, for each SAM, to the value of μ determined for a fresh sample (i.e., exposure 0 h). For both adsorbates, the coefficient of friction rises on extended exposure to the laboratory ambient, and in both cases, the rate of change is substantially greater for monolayers on Au than on Ag.

Discussion

The length of the alkyl chain has a much greater influence on the coefficient of friction for methyl terminated SAMs

than for carboxylic acid terminated ones on both metals. In an earlier study, we reported that this was the case for monolayers of alkanethiols on Au.¹¹ The present study confirms that a similar relationship exists on Ag. For carboxylic acid terminated tips, as used here, strong hydrogen bonding is expected to occur between the tip and carboxylic acid terminated SAMs. This leads to extensive energy dissipation through shearing of the tip–SAM contact as the tip slides across the surface, and adhesive interactions appear to dominate the interaction. The interaction is much weaker when the SAM is methyl terminated, giving rise to a smaller coefficient of friction. The dissipation of energy is in this case dominated by the deformation of the adsorbate alkyl chains, which is strongly influenced by the length of the adsorbate alkyl chain, which determines the degree of monolayer ordering and the ease of inducing chain deformation. C₃H₇ SAMs are less closely packed than C₁₁H₂₃ SAMs, leading to greater ease of chain deformation and a higher rate of energy dissipation through, for example, the creation of gauche defects. However, although the tip–sample adhesive interaction is much stronger for carboxylic acid terminated SAMs, it is not so great that the contribution expected from chain deformation alone is negligible by comparison. Therefore, the absence of a difference between the coefficients of friction of short- and long-chain carboxylic acid terminated SAMs may not be interpreted as being due to the tip–sample interaction being so overwhelmed by adhesion that chain deformations are negligible. Rather, it suggests that the difference in structure between short- and long-chain adsorbates in carboxylic acid terminated SAMs is smaller than the corresponding difference between the structures of long- and short-chain methyl terminated monolayers. We have argued elsewhere that carboxylic acid terminated SAMs benefit from an additional stabilization energy due to hydrogen bonding between terminal groups.^{11,36} This may lead either to a more ordered structure or, more likely, given the confined environment of the SAM, to a less well ordered hydrogen-bonded structure, similar to a two-dimensional glass. Whichever of these models applies, it is clear that very similar considerations apply on SAMs of carboxylic acid and methyl terminated thiols on both Ag and Au.

The coefficients of friction of methyl terminated SAMs on Ag are approximately half of the values measured for the same adsorbates on Au. It has long been established that monolayers of methyl terminated thiols form more closely packed structures on Ag than on Au.^{37,38} The angle of cant of the alkyl chain is found to be ca. 11°, compared to nearer 30° on Au. While adsorbates are thought to pack in a ($\sqrt{3} \times \sqrt{3}$)-R30 structure in a SAM on Au, with the headgroups bonded to 3-fold hollow sites 0.499 nm apart (compared to an alkyl chain diameter of 0.45 nm), the structure is rather different on Ag. A number of models have been presented. In the most favored one, the adsorbates are described as adopting a ($\sqrt{7} \times \sqrt{7}$)-R10.9 structure in which the spacing between adsorption sites (ca. 0.44 nm) is very close to the diameter of an alkyl chain. This greater density in the packing of the adsorbate molecules causes stronger interchain interactions and leads to the formation of a denser, more ordered alkyl chain structure. A priori, therefore, one might expect that a smaller coefficient of friction would be measured for a tip in contact with a methyl terminated SAM on Ag than for a similar monolayer on Au. Because of the closer packing and greater order of the adsorbate molecules, energy dissipation through the creation of gauche defects and other chain deformations would be expected to be less facile. This is reflected in the experimental data. However, the extent

of the difference in the coefficient of friction is significantly greater (an increase of ca. 100%) than the difference in the packing density of the adsorbate molecules (estimated to be ca. 25% greater on Ag than on Au). This is not unexpected, given that the extent to which adsorbate alkyl chains may be deformed underneath the tip will not be expected to scale linearly with the adsorbate packing density. The large difference in the value of μ for Ag and Au underlines the exquisite sensitivity of friction force microscopy to molecular organization.

Alkanethiols with carboxylic acid terminal groups do not pack more closely on silver than on gold. The mean coefficients of friction of carboxylic acid terminated SAMs on Ag are slightly larger than values determined for monolayers of the same adsorbates on Au (although for C₁₀COOH the difference is not statistically significant). In contrast, the coefficients of friction of methyl terminated SAMs are much less on Ag than on Au. The most reasonable explanation for this is that the bulk of the carboxylic acid tail group prevents the acid terminated adsorbates from adopting on Ag the highly close-packed structure adopted by methyl terminated thioliates. The spacing between adsorption sites on Ag(111) is thought to be approximately equal to the diameter of an alkyl chain, while the spacing between the 3-fold hollow sites on Au is slightly larger.^{38,39} On Au the carboxylic acid group may be accommodated without disrupting the favored ($\sqrt{3} \times \sqrt{3}$)-R30 arrangement of the thiolate headgroups. However, on Ag, we conclude that adoption of the favored S bonding structure would lead to a conflict between the packing requirements of the headgroup and the dimensions of the carboxylic acid tail group. The result is a modification of the surface structure to resolve this conflict, and a much looser structure is adopted by the polar thioliates on Ag than by the methyl terminated ones. There are few other published data with which to compare this finding, although one previous report⁴⁰ describes a similar observation in the case of thiols that incorporate biphenyl groups close to the sulfur headgroup, where a modification of the packing arrangement was also postulated. The paucity of data on ω -functionalized alkanethiols on Ag provides no direct precedent. However, it is hard to conceive of an alternative solution that fits the data better. The present data illustrate not only the power of FFM as a means of investigating molecular organization at interfaces, but also the subtle balance of parameters that control organization in SAMs and the importance of the terminal group in determining monolayer structure.

Methyl-terminated SAMs on Ag are substantially more stable than monolayers of the same adsorbates on Au. Long-term exposure of SAMs to the laboratory atmosphere is likely to lead to the oxidation of adsorbate headgroups to sulfonates.^{41,42} While the photochemical oxidation of SAMs has been studied extensively,^{43–48} their ambient oxidation has been examined rather more sparsely.^{49–51} The most relevant study to date was published by Schoenfish and Pemberton, who studied monolayers on both Ag and Au and suggested that ozone was the most likely oxidant in the laboratory atmosphere.⁵¹ They also suggested that, contrary to the accepted view, SAMs on Ag were more stable than those on Au. The likely effect of oxidation of SAMs by the action of ozone may be predicted from the work of Poirier et al.,⁵² who used scanning tunneling microscopy (STM) to characterize the reaction at the molecular level. They reported that oxidation of SAMs proceeds through a variety of intermediate phases, which incorporate both ordered and disordered regions, to a final phase in which a fluid-phase oxidized thiol layer forms with a density 3/5 that of the original densely packed thiolate layer. It is expected, therefore, that these

changes in adsorbate chemistry will also be accompanied by changes in their frictional behavior, as previously reported by Kiely and Houston in their study of hexadecanethiol on Au:⁵³ the fluid-phase layer is expected to exhibit a larger coefficient of friction (because of the greater number of pathways for energy dissipation) than the unoxidized, densely packed phase.

These predictions are borne out by the data. Figure 4 shows that, for all of the SAMs studied here, the coefficient of friction increases as time progresses and the monolayers become progressively oxidized. Comparison of the data for Ag and Au substrates in Figure 4 also reveals a marked difference in the rates of change of the coefficients of friction for monolayers on the two metals. In particular, the rates of oxidation of both C_3CH_3 and $C_{11}CH_3$ are faster on Au than on Ag. For $C_{11}CH_3$, a simple analysis of the kinetics of oxidation based upon the assumption of first-order kinetics (as described in our earlier work⁴⁵) leads to a rate constant of 0.0006 h^{-1} on Ag and 0.0021 h^{-1} on Au. The increase in μ for C_3CH_3 on Ag is more rapid than is the case for $C_{11}CH_3$, but is still substantially less rapid (with a rate constant of 0.0007 h^{-1}) than the increase in the value of μ for $C_{11}CH_3$ on Au. It has been widely reported that increasing the adsorbate alkyl chain length leads to increasing SAM stability, and we have previously demonstrated that the rates of photooxidation of SAMs are similarly correlated with their alkyl chain lengths.^{45,46} That a short-chain SAM on Ag is so much more stable than a much longer adsorbate on Au emphasizes the extent of the stabilization that is enjoyed on Ag. These data provide clear support for the earlier conclusion drawn by Schoenfish and Pemberton.⁵¹

In our earlier studies of the photooxidation of SAMs, we postulated that the rate-determining step was penetration of active oxygen species to the S-metal interface, and that differences in the rates of reaction for monolayers of different chain lengths could be explained by differences in the packing density. For disordered short-chain monolayers, penetration of active species to the S-metal bond is rapid, while it is slower for long-chain adsorbates that pack in ordered structures. The data in Figure 4 show that the same holds true of the ambient oxidation of SAMs: for both metals, the shorter adsorbate (C_3CH_3) oxidizes faster than the longer one ($C_{11}CH_3$). In a similar way, it seems likely that the greater packing density of methyl terminated SAMs on Ag compared to analogous monolayers on Au would contribute to a reduced rate of oxidation by ambient species.

We also reported differences in the photochemistry of SAMs on Au and Ag,^{46,47} and it is possible that the differences in bonding between SAMs on Ag and Au may also contribute to the differences in stability reported here. A full resolution of this question requires a spectroscopic investigation, therefore. If the differences in stability reported here are wholly attributable to packing density differences, then we predict that the stabilities of carboxylic acid terminated SAMs on Ag should be slightly less than those of similar SAMs on Au, in accordance with the conclusions about packing density deduced above. However, if the nature of the S-metal bond plays an important role, then carboxylic acid terminated SAMs should also exhibit reduced rates of degradation. FFM data for the polar SAMs are unreliable because of the high rates of contamination that they exhibit. Whatever the balance of molecular packing and S-metal bonding that is responsible, however, the stabilization of methyl terminated SAMs on Ag is very great indeed.

Conclusions

Friction force microscopy has provided some novel insights into the structures of SAMs on silver. Not only do the data

suggest that the packing of methyl terminated thiols on Ag is much greater than on Au, but they also suggest that the structures adopted by carboxylic acid terminated thiolates are different, being constrained by the comparative bulk of the terminal group, which prevents the adoption of the very close-packed structure adopted by methyl terminated adsorbates. The coefficients of friction of carboxylic acid terminated SAMs are thus slightly larger on Au than on Ag. For both metals, the structure of the carboxylic acid terminated SAM seems to be much less strongly influenced by the alkyl chain packing, with the result that there are only small differences in the coefficients of friction for short- and long-chain adsorbates, while the difference is large for methyl terminated SAMs. The rates of degradation of methyl terminated SAMs on Ag following extended exposure to the atmosphere are much smaller than those observed for corresponding SAMs on Au, indicating a substantially enhanced stability. The enhancement is such that butanethiol SAMs on Ag are significantly more stable than monolayers of dodecanethiol on Au, even though the ratio of the alkyl chain lengths is ca. 3:1. FFM is found to be a very powerful tool for exploring SAM structure and for studying the evolution of monolayer structure during surface reactions.

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