# **Self-Assembled Monolayers of Long-Chain Hydroxamic** Acids on the Native Oxides of Metals<sup>1</sup>

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Long-chain alkanehydroxamic acids adsorb on the native oxides of metals and formed oriented selfassembled monolayers (SAMs). This study examined SAMs of hydroxamic acids on the native oxides of copper, silver, titanium, aluminum, zirconium, and iron. These SAMs were characterized using wettability, X-ray photoelectron spectroscopy (XPS), and polarized infrared external reflectance spectroscopy (PIERS). Alkanehydroxamic acids give better monolayers than the corresponding alkanecarboxylic acids on certain basic metal oxides (especially copper(II) oxide). On the native oxide of copper (which has an isoelectric point greater than the  $pK_a$  of the hydroxamic acid), the ligand is bound to the surface predominantly as the hydroxamate. The strength of the interaction between copper oxide and the hydroxamate allows incorporation of polar tail groups into the monolayer. On acidic or neutral metal oxides (e.g.,  $TiO_2$ ), the predominant species bound to the surface is the hydroxamic acid. Alkanehydroxamic acids on titanium dioxide bind relatively weakly but, nonetheless, form SAMs that are more stable than those from carboxylic acids (although not as stable as those from alkanephosphonic acids).

### Introduction

We have examined the properties of self-assembled monolayers (SAMs) obtained by the adsorption of longchain alkanehydroxamic acids (general formula CH<sub>3</sub>- $(CH_2)_n CONHOH)$  onto the native oxides of freshly evaporated films of copper, silver, titanium, aluminum, zirconium, and iron and have compared these SAMs to others commonly used with these substrates. We have used wettability, X-ray photoelectron spectroscopy  $\left( XPS\right) ,$  and polarized infrared external reflectance spectroscopy (PIERS) in characterizing these monolayers. We conclude that monolayers of alkanehydroxamic acids (or their anions) are more stable than monolayers obtained by the adsorption of carboxylic acids on all of the surfaces (especially copper oxide and silver oxide), but they are less stable than monolayers obtained by the adsorption of alkanethiols to copper or silver.

Of the many systems available for the formation of selfassembled monolayers, monolayers obtained by the chemisorption of alkanethiols onto gold and silver, 2-4 monolayers obtained by the hydrolysis and polymerization of alkyl trichlorosilanes onto hydrated surfaces, 5,6 and monolayers obtained by the adsorption of carboxylic  $acids^{7-15}$  or phosphonic acids<sup>16</sup> onto metal oxides have been the most

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allows polar groups containing oxygen and nitrogen to be incorporated into the SAM.  $^{2,17,19}$ Alkanethiols do not adsorb, however, to the surfaces of many metal oxides.<sup>20</sup> Carboxylic acids and phosphonic acids adsorb, but the adsorption can be weak.<sup>7-16</sup> These

thoroughly studied.<sup>17</sup> SAMs of alkanethiolates on gold and silver are generally the most useful in scientific

applications,<sup>18</sup> because of their stability and because the

specificity of coordination of the sulfur atom to the metal

 (7) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. J. Colloid Sci. 1946,
 (7) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. J. Phys. Chem. 1965, 69,
 984–990. Golden, W. G.; Snyder, C. D.; Smith, B. J. Phys. Chem. 1982, 86 4675-4678

(8) Allara, D. L.; Nuzzo, R. G. Langmuir 1985, 1, 45-52. Allara, D. L.; Nuzzo, R. G. Langmuir 1985, 1, 52-66. Chen, S. H.; Frank, C. W. Langmuir 1989, 5, 978-987.

(9) Schlotter, N. E.; Porter, M. D.; Bright, T. B.; Allara, D. L. Chem. Phys. Lett. 1986, 132, 93-98.

(10) Chau, L.-K.; Porter, M. D. Chem. Phys. Lett. 1990, 167, 198-204.

(11) Allara, D. L.; Atre, S. V.; Ellinger, C. A.; Snyder, R. G. J. Am. Chem. Soc. 1991, 113, 1852–1854.
(12) Samant, M. G.; Brown, C. A.; Gordon, J. G., II Langmuir 1993,

9.1082-1085.

(13) Smith, E. L.; Porter, M. D. J. Phys. Chem. 1993, 97, 8032-8038. 14) King, D. E.; Czanderna, A. W.; Spaulding, D. J. Vac. Sci. Technol., A 1993, 11, 180-182.

(15) Tao, Y.-T. J. Am. Chem. Soc. 1993, 115, 4350-4358

(16) Lee, H.; Kepley, L. J.; Hong, H. G.; Akhter, S.; Mallouk, T. E.

J. Phys. Chem. 1988, 92, 2597-2601. Lee, H.; Hong, H. G.; Mallouk,

T. E.; Kepley, L. J. *J. Am. Chem. Soc.* **1988**, *11*, 618–620. Putviniski, T. M.; Schilling, M. L.; Katz, H. E.; Chidsey, C. E. D.; Mujsce, A. M.; M., Schning, M. L.; Ratz, H. L.; Onlasey, C. E. D.; Mujsče, A. M.; Emerson, B. Langmuir 1990, 6, 1567–1571. Katz, H. E.; Scheller, G.; Putviniski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. Science(Washington, D.C.) 1991, 254, 1485–1487. Frey, B. L.; Hanken, D. G.; Corn, R. M. Langmuir 1993, 9, 1815–1820. Schilling, M. L.; Katz, H. E.; Stein, S. M.; Shane, S. F.; Wilson, W. L.; Buratto, S.; Ungashe, S. B.; Taylor, G. N.; Putviniski, T. M.; Chidsey, C. E. D. Langmuir 1993, 9, 2156–2160. Langmuir 1993, 9, 2156-2160.

(17) For reviews, see: Bain, C. D.; Whitesides, G. M. Angew. Chem. Int. Ed. Engl. 1989, 28, 506-512. Whitesides, G. M.; Laibinis, P. E. Langmuir 1990, 6, 87-96. Ulman, A. An. Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly; Academic Press: San Diego, CA, 1991; Chapter 3.

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<sup>(2)</sup> Nuzzo, R. G.; Allara, D. L. J. Am. Chem. Soc. 1983, 105, 4481-4483. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. J. Am. Chem. Soc. **1987**, 109, 3559–3568. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. J. Am. Chem. Soc. 1989, 111, 321-335.

<sup>(3)</sup> Walczak, M. M.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. J. Am. Chem. Soc. **1991**, *113*, 2370–2378. (4) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh,

<sup>(5)</sup> Sagiv, J. J. Am. Chem. Soc. **1980**, 102, 92–98. Netzer L.; Sagiv, J. J. Am. Chem. Soc. **1983**, 105, 674–676. Moaz, R.; Sagiv, J. J. Colloid Interface Sci. 1984, 100, 465-496.

<sup>6</sup> Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. Langmuir 1989, 5, 1074-1087

systems also cannot be used to incorporate polar groups into a monolayer.<sup>11</sup> Phosphonic acids have large head groups and can be inconvenient to synthesize.

We have examined hydroxamic acids (1) as an alternative to carboxylic acids (3) for self-assembled monolayers on the surfaces of metal oxides because their complexation constants with metal ions in aqueous solution are several orders of magnitude larger than those of carboxylic acids<sup>21</sup> and because they have similar sizes. Synthesis of longchain hydroxamic acids is also straightforward.<sup>22,23</sup>



When complexed to a single metal ion in solution, the greater stability of complexes with hydroxamate relative to those with carboxylate reflects the larger bite size of the hydroxamate, which forms five-member chelate rings with metal ions (2). In contrast, carboxylate forms either strained, four-member chelate rings (4) or monodentate species.<sup>24,25</sup> We had hoped that this difference in binding constants in solution would also be reflected in the strength of binding of hydroxamic acids to the ions on the surface of a metal oxide. In fact, although hydroxamic acids do form more stable monolayers than carboxylic acids, they seem to use only one oxygen atom for coordination.

### Results

**Synthesis of Hydroxamic Acids.** The long-chain, methyl-terminated hydroxamic acids were synthesized by reacting the corresponding acid chloride and *O*benzylhydroxylamine, followed by removal of the benzyl group by catalytic hydrogenation over palladium on carbon (Scheme 1).<sup>22</sup> The hydroxyl-terminated hydroxamic acid

(19) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. J. Am. Chem. Soc. 1987, 109, 733-740.

(20) The exceptions being copper oxide, silver oxide, and possibly other soft metal oxides such as those on platinum, zinc, and lead. For studies on the removal the native oxides from copper and silver using alkanethiols, see ref 4 and Laibinis, P. E.; Whitesides, G. M. J. Am. Chem. Soc. **1992**, *114*, 9022–9028.

(21) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1977; Vol. 3. For comparison, the binding constants for acetohydroxamate with Fe<sup>3+</sup> and Al<sup>3+</sup> in aqueous solution are 2.6  $\times 10^{11}$  and 8.9  $\times 10^7$  M<sup>-1</sup>, respectively, and the binding constants for acetate with Fe<sup>3+</sup> and Al<sup>3+</sup> are 2.4  $\times 10^3$  and 3.2  $\times 10^1$  M<sup>-1</sup>, respectively.

(22) Hearns, M. T. W.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 22, 161–
173. Rowe, J. E.; Ward, A. D. Aust. J. Chem. 1969, 24, 4343–4350.
(23) Karunatne, V.; Hoveyda, H. R.; Orvig, C. Tetrahedron Lett. 1992, 33, 1827–1830.

(24) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th Ed.; Wiley-Interscience: New York, 1988.

(25) Entropy of formation (due to chelation) is the dominant factor in the strong binding between hydroxamic acids and discrete metal ions in aqueous solution. The enthalpies of formation for these complexes in water tend to be small and positive. For examples, see ref 21 and Monzyk, B.; Crumbliss, A. L. J. Am. Chem. Soc. **1979**, 101, 6203–6213.



was synthesized using 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) to couple the benzyl-protected hydroxylamine to 16-hydroxyhexadecanoic acid.<sup>23</sup> The same deprotection scheme was used for this compound.

**Preparation of Substrates and Monolayers.** Metal/ metal oxide substrates were prepared by electron-beam evaporation of 600-1000 Å of the pure metal onto silicon wafers that had been precoated with 50 Å of titanium as an adhesion promoter. The samples were exposed to air upon removal from the chamber, because we were interested in studying the adsorption of monolayers to the native oxides of the metals. In this paper, instead of writing "metal/metal oxide" for each reference to a substrate with a native oxide, we will refer to them simply as the metal oxide. The oxidation states of the metal in the native oxides are given in Table 1 and the Experimental Section.

Solutions of alkanehydroxamic acids and other adsorbates were prepared in either isooctane or ethanol and were not degassed. The nominal concentration in each of the solutions was 1 mM, although most of the hydroxamic acids were not soluble in isooctane to this extent. Substrates were left in solution for 1 to 2 days at room temperature. After removal from solution, the samples were rinsed with heptane and ethanol and then dried in a stream of nitrogen.

**Contact Angles on Monolayers of Hydroxamic Acids.** Table 1 summarizes advancing and receding contact angles of water and hexadecane on monolayers obtained by the adsorption of octadecanehydroxamic acid, stearic acid, octadecanephosphonic acid, and 16-hydroxyhexadecanehydroxamic acid on the six substrates surveyed in this study. We also present contact angles for monolayers of octadecanethiolate on copper, silver, and gold for comparison, and contact angles for surfaces obtained after attempting adsorptions of the hydroxamic acid onto gold. For consistency, all of the data in Table 1 were taken during this study, although several of these systems have been studied previously.<sup>2-17</sup>

The presence of a closest-packed, methyl-terminated monolayer is often indicated by an advancing contact angle of water (surface tension  $\gamma_{\rm LV} = 72$  mJ/m<sup>2</sup> at 25 °C)<sup>26–28</sup> above 110°, and an advancing contact angle of hexadecane ( $\gamma_{\rm LV} = 27$  mJ/m<sup>2</sup>)<sup>26–28</sup> above 45°.<sup>2 ·6.8.15</sup> Although contact angles do not provide any structural information about monolayers, they are useful as indicators of their quality. A low value of contact angle, relative to a structurally well-characterized system such as alkanethiolates on gold, indicates disorder (and/or lower coverage) in the mono-

<sup>(18)</sup> Applications of thiols on gold and silver: Chidsey, C. E. D. Science (Washington, D.C.) **1991**, 251, 919–922. Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. Science (Washington, D.C.) **1991**, 252, 688–691. Prime, K. L.; Whitesides, G. M. Science (Washington, D.C.) **1991**, 252, 1164–1167. Joyce, S. A.; Houston, J. E.; Michalske, T. A. Appl. Phys. Lett. **1992**, 60, 1175–1177. Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. J. Am. Chem. Soc. **1992**, 114, 9188–9189. Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. Science (Washington, D.C.) **1992**, 258, 1380–1382. Ross, C. B.; Sun, L.; Crooks, R. M. Langmuir **1993**, 9, 632–636. López, G. L.; Biebuyck, H. A.; Frisbie, C. D.; Whitesides, G. M. Science (Washington, D.C.) **1993**, 260, 647–649. López, G. L.; Albers, M. W.; Schreiber, S. L.; Carrol, R. W.; Peralta, E.; Whitesides, G. M. J. Am. Chem. Soc. **1993**, 115, 5877– 5878. Kumar, A.; Whitesides, G. M. Appl. Phys. Lett. **1993**, 63, 2002– 2004.

 <sup>(26)</sup> Jasper, J. J. J. Phys. Chem. Ref. Data 1972, 1, 841–1009.
 (27) Cognard, J. J. Chim. Phys. 1987, 84, 357–362, and references therein.

<sup>(28)</sup> These two probe liquids can provide different information about the surfaces, because the origins of their surface tensions are different. The surface tension of water is dominated by its polar component ( $\gamma_{LV,polar} \approx 50 \text{ mJ/m}^2$ ), and the surface tension of hexadecane originates entirely from dispersive interactions.<sup>27</sup>

## SAMs of Hydroxamic Acids

Table 1. Advancing and Receding Contact Angles of Water and Hexadecane (HD) on Monolayers of Octadecanehydroxamic Acid, Stearic Acid, Octadecanephosphonic Acid, 16-Hydroxyhexadecanehydroxamic Acid, and Octadecanethiol on Copper, Silver, Titanium, Zirconium, Iron, Aluminum, and Gold<sup>a</sup>

		contact angles on various SAMs (advancing,receding)/deg					
	adsorbate	isoocta	$ane^b$	ethanol <sup>b</sup>			
metal		H <sub>2</sub> O	HD	$H_2O$	HD		
Cu/Cu(II)	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	114, 104	47, 41	114, 101	49, 41		
	$CH_3(CH_2)_{16}COOH$	113, 107	49.44	111, 82	46, 38		
	$CH_3(CH_2)_{17}PO_3H_2$	115, 98	43, 35	112, 76	29, 0		
	$CH_3(CH_2)_{17}SH$	c		117.93	62, 28		
	HO(CH <sub>2</sub> ) <sub>15</sub> CONHOH	79, 40	0, 0	27, 12	22, 0		
$A\sigma/A\sigma(II)$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	113, 104	51, 46	113, 102	51, 44		
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	113, 107	52, 47	81, 61	21, 0		
	$CH_3(CH_2)_{17}PO_3H_2$	115, 103	46, 28	82,60	0, 0		
	$CH_3(CH_2)_{17}SH$	· –		113, 102	49, 43		
	HO(CH <sub>2</sub> ) <sub>15</sub> CONHOH	82.50	0, 0	68, 39	0, 0		
Ti/Ti(IV)	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	115, 105	46, 42	110, 85	45, 29		
	$CH_{2}(CH_{2})_{16}COOH$	107.71	45, 37	50, 15	0, 0		
	$CH_{2}(CH_{2})_{17}PO_{2}H_{2}$	115.100	42, 36	110, 95	41, 36		
	HO(CH <sub>2</sub> ) <sub>15</sub> CONHOH	83.60	0,0	77, 51	0, 0		
Al/Al(III)	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	113.104	47, 44	111, 93	46, 40		
	$CH_2(CH_2)_{16}COOH$	113.105	48.44	110, 82	43, 35		
	$CH_{2}(CH_{2})_{17}PO_{3}H_{2}$	115, 104	48.38	113, 83	37, 0		
	HO(CH <sub>2</sub> ) <sub>15</sub> CONHOH	49.29	0, 0	72, 36	0, 0		
Zr/Zr(IV)	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	123, 99	44.27	123, 95	43, 22		
	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	122, 100	47.29	116,75	23, 0		
	$CH_2(CH_2) = PO_2H_2$	123, 100	37, 20	119, 75	23, 0		
	HOUCHALLSCONHOH	_		50, 20	0.0		
Fe/Fe(III)	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	135, 95	23.15	131, 90	31, 16		
	CHa(CHa)taCOOH	136.84	22.0	121.65	23, 0		
	CH <sub>3</sub> (CH <sub>2</sub> ) -PO <sub>3</sub> H <sub>2</sub>	137,97	21.0	124.80	20, 0		
	HO(CH <sub>2</sub> ) <sub>15</sub> CONHOH	79.34	0.0	_			
Au	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CONHOH	106, 87	22, 0	84,63	0, 0		
114	$CH_3(CH_2)_{17}SH$	_	_	115, 103	49, 39		

<sup>a</sup> Metals were exposed to air and covered with native oxides before exposure to solutions containing the ligands. <sup>b</sup> Solutions from which monolayers were formed. <sup>c</sup> Denotes that monolayers were not made from these solutions.

layer; a value comparable to that of the ordered system does not necessarily indicate the same structure or a corresponding degree of order. Using contact angles, we can infer the quality of one type of SAM relative to others with analogous structures on the same metal, but not relative to SAMs on different metals, because the roughness of the surfaces of the various metals differ.<sup>29,30</sup> To reduce the variation in roughness of structures for a particular metal, all of the samples for each metal listed in Table 1 were taken from the same evaporation; the only exceptions were the monolayer of  $HO(CH_2)_{15}$ -CONHOH on silver oxide from ethanol and the two sets of monolayers on iron oxide. We infer from Table 1 that the quality of methyl-terminated SAMs obtained from each of the three acids formed from isooctane is greater than that of SAMs formed from ethanol, since they have higher advancing contact angles and lower values of hysteresis.<sup>30</sup>

Table 2 summarizes the decrease in contact angles on changing the solvent for adsorption from isooctane to ethanol. We use these values as qualitative indicators of the stability of the monolayers by assuming that ethanol competes for polar sites on the surface but that isooctane Table 2. Decrease in Advancing and Receding Contact Angles of Water  $(\Delta \theta^{\rm H_2O})$  and Hexadecane  $(\Delta \theta^{\rm HD})$  on Changing Solvent from Isooctane to Ethanol for Adsorptions of Octadecanehydroxamic Acid, Stearic Acid, and Octadecanephosphonic Acid  $(adv, rec)^a$ 

	$(CH_3(CH_2))$	6CONHOH	$(CH_3(CH_2)_{16}COOH$		$(CH_3(CH_2)_{17}PO_3H_2$	
metal <sup>h</sup>	$\Delta \theta^{\mathrm{H}_{2}\mathrm{O}}$	$\Delta \theta^{\rm HD}$	$\Delta \theta^{\rm H_2O}$	$\Delta \theta^{ m HD}$	$\Delta  heta^{ m H_2O}$	$\Delta \theta^{ m HD}$
Cu	< 2.3	<-2. < 2	<2,25	3, 6	3, 22	$14, \ge 35^d$
Ag	< 2, -2	< 2, < 2	32, 46	$31, \ge 47$	33, 43	≥46, ≥28
Ti	5, 20	< 2, 13	57, 56	$\geq 45, \geq 37$	5, 5	<2, <2
Al	< 2, 11	· 2.4	3, 23	5, 9	<2, 21	11, ≥38
Zr	$\leq 2.4$	$\le 2.5$	6.25	$24, \geq 29$	4, 25	<b>14</b> , ≥20

<sup>a</sup> Contact angles were taken from Table 1.  $\Delta\theta$  is the difference in contact angle between those monolayers prepared from isooctane and those prepared from ethanol ( $\Delta\theta = \theta$ (isooctane) –  $\theta$ (ethanol)). <sup>b</sup> Iron is not included because the substrates examined were not prepared in the same evaporation. <sup>c</sup> "<2" is used to indicate that changes in their contact angles of 2° or less are within the uncertainty of the measurements. <sup>d</sup> "≥" indicates that the contact angle of the monolayer formed with ethanol was zero, and the increase in surface free energy could be greater than that measured by the decrease in the contact angle.

does not. In general, differences in the contact angles were lowest for monolayers of the hydroxamic acid. These data thus suggest that monolayers from hydroxamic acids are more stable than monolayers of either carboxylic acids or phosphonic acids on all of the substrates examined except titanium oxide. The smallest changes in contact angles were observed for monolayers of hydroxamic acids on copper oxide and silver oxide, suggesting a high stability for the hydroxamic acid overlayer formed on these substrates. By this criterion, of the three acids, the carboxylic acid forms the least stable monolayers on all of the substrates. Although phosphonic acids are often used for the formation of self-assembled monolayers on zirconium oxide, the results in Tables 1 and 2 suggest

<sup>(29)</sup> The substrates of zirconium/zirconium oxide and iron/iron oxide, as we had prepared them, were much rougher than the other metals: advancing contact angles and values of hysteresis in the contact angles of water were consistently higher for monolayers on these substrates.<sup>30</sup> We have not investigated these substrates with the scanning probe microscope, and we are not able to quantitate their relative roughness.

<sup>(30)</sup> Hysteresis in contact angles, although poorly understood, is often attributed to the chemical heterogeneity or the roughness of an interface. Since we have attempted to control the relative roughnesses of our substrates for a given metal, we interpret the increase in hysteresis as an increase in the chemical heterogeneity of the surfaces. For examples of experimental and theoretical studies on hysteresis, see: Joanny, J. F.; de Gennes, P. G. J. Chem. Phys. **1984**, *81*, 552–562. de Gennes, P. G. Rev. Mod. Phys. **1985**, *57*, 827–863, and references therein. Schwartz, L. W.; Garoff, S. Langmuir, **1985**, *1*, 219–230. Chen, Y. L.; Helm, C. A.; Israelachvili, J. N. J. Phys. Chem. **1991**, *95*, 10736–10747.

that hydroxamic acids form monolayers of even higher stability on this substrate: this inference remains to be tested by direct competition. For titanium oxide, we infer that the phosphonic acid forms the most stable monolayers.

Hydroxamic acids do not form closest-packed monolayers on gold, although the measured contact angles indicate some partial layer is adsorbed from isooctane. The contact angles were only slightly lower than that expected for a methyl-terminated monolayer, but results from X-ray photoelectron spectroscopy (XPS) showed that the "monolayer" was approximately 11 Å thinner than a monolayer of octadecanethiolate on gold.<sup>31</sup> The adsorption of hydroxamic acids to gold presumably occurs by physisorption on the high-energy gold surface,<sup>32</sup> as gold does not form a stable oxide under ambient conditions; we have not determined the structure of this layer.

Adsorption of alkanethiols on copper modifies its surface more than does the adsorption of any of the acid adsorbates used in this study, as judged by the larger values of the contact angle hysteresis measured. Since the compositions of the interfaces present in the two monolaver classes are similar, we attribute the differences in hysteresis to variations in the microscopic roughness of the interface.<sup>30</sup> This roughening is presumably a direct consequence of the removal of the native oxide on copper that occurs during the adsorption of the alkanethiol, as has been shown by XPS.<sup>4,20</sup> The native oxide is not removed during the adsorption of the three acid adsorbates.<sup>33</sup> The adsorption of alkanethiols on the native oxide of silver does not roughen the surface in the same way, even though the thin native silver oxide layer is lost during the adsorption.4,34

The hydroxyl-terminated hydroxamic acid formed incomplete monolayers on most of the substrates studied here, with the single exception of the monolayer formed on copper oxide by adsorption from ethanol. We expected to measure an advancing contact angle of water below 30° for a complete monolayer of a hydroxy-terminated ligand;<sup>34,35</sup> the observed value is  $\theta_a \approx 27^\circ$  (Table 1). Most substrates gave advancing contact angles of water between  $50^{\circ}$  and  $80^{\circ}$ , suggesting the existence of nonpolar groups at the interface and possibly some "looping" of the hydroxyl group to the surface. Similar loop structures have been observed by Allara et al. with a long-chain  $\alpha, \omega$ -dicarboxylic acid adsorbate on several oxide surfaces.<sup>11</sup> X-ray photoelectron spectroscopy showed that the mass coverages of the hydroxyl-terminated hydroxamic acid monolayers were 6-10 Å less than those of monolayers of CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-CONHOH (see below).

When a monolayer of the hydroxyl-terminated hydroxamic acid was formed on copper oxide by adsorption from ethanol, the advancing contact angle of water indicated the formation of a well-defined hydrophilic structure. The advancing contact angle of hexadecane was nonzero; this value is consistent with the formation of a hydroxyl-terminated monolayer, on which a thin, adsorbed layer of water prevents the spreading of the contacting hydrocarbon liquid.<sup>36</sup> The measured thickness of this monolayer was intermediate between that of films formed by  $CH_3(CH_2)_{14}CONHOH$  and  $CH_3(CH_2)_{16}CONHOH$  (see Figure 3 and the accompanying text below), suggesting that the adsorption proceeds to high mass coverages in an isostructural manner. Solvent plays a very important role in this assembly, however. We found, for example, that the hydroxyl-terminated hydroxamic acid forms an incomplete monolayer on copper oxide when adsorbed from isooctane (the coverage was less than 70%).

Contact Angles on Monolayers of Hydroxamic Acids as a Function of Chain Length. Figure 1 presents contact angles of water and hexadecane on SAMs of hydroxamic acids with the general formula  $CH_3$ - $(CH_2)_nCONHOH$  on the native oxides of copper, silver, titanium, and aluminum as a function of n (the number of methylene groups). Monolayers on copper oxide and titanium oxide were formed by adsorption from both isooctane and ethanol: monolayers on silver oxide and aluminum oxide were formed only using isooctane as a solvent.

The contact angles measured on copper oxide were independent of n and of the solvent used for the adsorption. These results suggest that monolayers of hydroxamic acids on copper oxide have high stability. The trend in the data was similar for the monolayers on silver oxide prepared by adsorption from isooctane. On titanium oxide and aluminum oxide, little variation was observed in the chain length dependence of the contact angles for SAMs formed by adsorption from isooctane for  $n \ge 10$ ; below this chain length, the contact angles decreased and the hysteresis increased markedly. Binding of alkanehydroxamic acids to the surfaces of aluminum oxide and iron oxide thus appears to be weak, as judged by the ability of ethanol (or impurities such as water) to interfere with the formation of high coverage monolayers.

The contact angles for the monolayer with n = 15 on silver oxide were significantly lower than those of the two even-carbon chain lengths adjacent to it. The observed decrease is not due to an incompletely formed monolayer (as confirmed by XPS), but seems to be due to a change in the structure of the methyl groups at the interface (see below). This result is similar to the "odd-even" effects in contact angles which have been observed previously for monolayers of carboxylic acids<sup>15</sup> and alkanethiolates on silver.<sup>3</sup> We note, however, that the structural origins in the other examples may be very different from those which pertain here.

**Formation of Mixed Monolayrs on Copper Oxide.** We formed mixed monolayers by the competitive adsorption of  $HO(CH_2)_{15}CONHOH$  and  $CH_3(CH_2)_{14}CONHOH$  on copper oxide (Figure 2). These data demonstrate that these mixed monolayers can be used to tailor the wettability (and, by extrapolation, other properties) of these surfaces and illustrate the utility of hydroxamic acids in forming complex organic surfaces on copper oxide without significantly roughening the surface. These materials thus may have a significant advantage for the modification of the surfaces over the previously described alkanethiolate SAMs.

Relative Thicknesses of Monolayers of Hydroxamic Acids from X-ray Photoelectron Spectroscopy

<sup>(31)</sup> A "thinner" or "shorter" monolayer as determined by XPS implies incomplete formation of the monolayer. XPS is used to measure the attenuation of a signal from a substrate as a function of the amount of hydrocarbon on that substrate; the thickness of the monolayer is then determined after making several assumptions about this process (see eqs 1-3).

<sup>(32)</sup> Weak physisorption of amphiphilic molecules such as dodecanol from solution onto gold has been previously observed; see: Yeo, Y. H.; McGonigal, G. C.; Yackoboski, K.; Guo, C. X.; Thomson, D. J. J. Phys. Chem. **1992**, *96*, 6110–6111.

<sup>(33)</sup> The hydroxamic acids probably to dissolve some copper ions from the oxide: when SAMs of hydroxamic acids were formed on silver oxide from ethanolic solutions that had been used previously for copper oxide, copper was evident in the XPS, but samples on silver made from fresh solutions showed no copper (Folkers, J. P.; Whitesides, G. M. Unpublished results).

<sup>(34)</sup> Laibinis, P. E.; Whitesides, G. M. J. Am. Chem. Soc. **1992**, 114, 1990–1995.

 <sup>(35)</sup> Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110,
 6560–6561. Bain, C. D.; Evall, J.; Whitesides, G. M. J. Am. Chem. Soc.
 1989, 111, 7155–7164.

<sup>(36)</sup> Adamson, A. Physical Chemistry of Surfaces, 4th ed.; Wiley: New York, 1982; Chapter 3.



**Figure 1.** Advancing  $(\theta_a)$  and receding  $(\theta_r)$  contact angles of water and hexadecane (HD) on monolayers derived from the adsorption of hydroxamic acids of the general formula CH<sub>3</sub>-(CH<sub>2</sub>)<sub>n</sub>CONHOH, where n = 8, 10, 12, 14, 15, 16, onto the native oxides of copper, silver, titanium, and aluminum. Monolayers on copper and titanium were formed from isooctane and ethanol; monolayers on silver and aluminum were formed from isooctane. As a guide to the eye, the dashed lines in the plot for copper represent the average values of the contact angles for all values of n and both solvents: 118° for  $\theta_a^{H_2O}$ , 102° for  $\theta_r^{H_2O}$ , 48° for  $\theta_a^{HD}$ , and 35° for  $\theta_r^{HD}$ . For the monolayers on silver and sum the average contact angles for n = 15 were not used to calculate the average contact angles represented by the dashed lines; these values are 112° for  $\theta_a^{H_2O}$ , 104° for  $\theta_r^{H_2O}$ , 51° for  $\theta_a^{HD}$ , and 46° for  $\theta_r^{HD}$ .

(XPS). We have used the attenuation of an XPS signal due to various substrate core levels (specific details are given in the Experimental Section) to estimate relative thicknesses of the SAMs formed by the adsorption of hydroxamic acids with different chain lengths.<sup>4,34,37-39</sup> In this analysis, the intensity,  $I_{SAM}$ , of an XPS signal from



Figure 2. Contact angles of water on monolayers formed by the competitive adsorption of CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CONHOH and HO-(CH<sub>2</sub>)<sub>15</sub>CONHOH onto copper, plotted against the composition of the SAM presented as the mole fraction of the methylterminated component in the SAM (ZCH, SAM). The composition of the SAM was determined by XPS using the oxygen 1s signal for the terminal hydroxyl group on HO(CH<sub>2</sub>)<sub>15</sub>CONHOH. Monolayers were formed at room temperature from ethanolic solutions with a total concentration of hydroxamic acid of 1 mM for 5 days. Advancing contact angles are shown as filled circles; receding contact angles are shown as open circles. Lines through the data are provided as guides to the eye. The error bars represent the approximate accuracy of acquiring and fitting the XPS data. The error in the measurement of the contact angles is smaller than the size of the circles. Above the plot, XPS spectra are presented for the oxygen 1s region of monolayers of HO(CH<sub>2</sub>)<sub>15</sub>CONHOH (left) and CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CONHOH (right) on copper. The peak at lower binding energy  $(\sim 530 \text{ eV})$ is due to the oxide on the copper and the oxygens in the headgroup of the molecules. The peak at higher binding energy  $(\sim 532.5 \text{ eV})$  is due to the terminal OH.

a substrate covered with an alkyl-chain-terminated SAM is given by eq 1

$$I_{\rm SAM} = I_0 \beta \exp(-md/\lambda \sin \theta) \tag{1}$$

where  $I_w$  is the intensity of the signal without the monolayer,  $\beta$  scales the intensity for attenuation through the head group of the ligand, m is the number of carbon atoms in the alkyl chain (m = n + 1), d is the thickness for a methylene group,  $\lambda$  is the attenuation length (or escape depth) of the photoelectron through the hydrocarbon layer, and  $\theta$  is the angle between the plane of the surface and the detector (35°).<sup>37,40</sup> To obtain the value of d for a set of monolayers, we compare the intensity of the XPS signal from a SAM to that from the shortest chain length SAM<sup>39,41</sup>

<sup>(37)</sup> Bain, C. D.; Whitesides, G. M. J. Phys. Chem. **1989**, 93, 1670–1673.

<sup>(38)</sup> Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. J. Phys. Chem. 1991, 95, 7017-7021.

 <sup>(39)</sup> Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M.
 Langmuir 1991, 47, 3167–3173. Folkers, J. P.; Laibinis, P. E.;
 Whitesides, G. M. Langmuir 1992, 8, 1330–1341.

<sup>(40)</sup> Seah, M. P. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; John Wiley: Chichester, 1983; Chapter 5.

<sup>(41)</sup> Calculation of absolute thicknesses using this method requires determination of  $I_0$  and  $\beta$ . The primary reason we have not determined these quantities is that cleaning metal/metal oxide substrates by sputtering the surfaces with  $Ar^+$  ions in the XPS chamber often removes part of the oxide and changes the measured value of  $I_0$ .

$$(m - m_{\rm Sh})d = -\lambda \sin \theta \ln(I_{\rm m}/I_{\rm m_{\rm Sh}})$$
(2)

In eq 2,  $m_{\rm Sh}$  is the number of carbon atoms in the chain of the shortest molecule. We use an empirical equation to estimate the attenuation lengths (Å) of the photoejected electrons through the hydrocarbon layer (eq 3)

$$\lambda = 0.022E_{\rm k} + 9.0 \tag{3}$$

where  $E_k$  is the kinetic energy (eV) of the photoelectrons; the validity of this equation was established for SAMs of alkanethiolates on copper, silver, and gold.<sup>38</sup>

Results for monolayers of hydroxamic acids on the native oxides of copper, silver, and titanium are summarized in Figure 3. On copper oxide, a small decrease in thickness was observed for monolayers formed by adsorption from ethanol on to copper oxide relative to those formed using isooctane. Both sets of data yield the same value for the average increase in thickness per methylene group, 1.1 Å/CH<sub>2</sub>. The value expected for a trans-extended alkyl chain oriented perpendicular to the surface is 1.36 Å/CH<sub>2</sub>. From this value, we estimate that the average tilt of the chains in a monolayer of hydroxamic acids on copper oxide is approximately 20°, in agreement with results from infrared spectroscopy (see below).

On monolayers of hydroxamic acids on silver oxide formed by adsorption from isooctane, we calculate a value of d of 1.2 Å/CH<sub>2</sub> from the data. This value suggests a cant angle for the alkyl chain of about 18° from the surface normal; the uncertainty in this value is large ( $\pm$ 15° or  $\pm$ 0.1 Å/CH<sub>2</sub> for d), however, because of the limited number of points measured.

On titanium oxide, we observed differences in the thicknesses of monolayers formed by adsorption from isooctane or compared to those formed using ethanol as the solvent;<sup>32</sup> the data suggest lower coverages for the SAMs prepared using ethanol. These data are poorly fit by our analytical model and, thus, our ability to estimate a value of d is limited. For the isooctane samples, the data are linear (two separate sets of data for isooctane are included in Figure 3), but our analysis leads to an implausible estimated average increase in thickness per methylene group of 1.4 Å/CH2. Several experimental issues, especially the roughness of substrate, can lead to a large error in the calculated value of the attenuation length. Variations in the thickness of the native oxide among samples also are believed to contribute to this discrepancy. Similar systematic errors for SAMs on aluminum, iron, and zirconium oxides precluded measurement of values of d on these substrates.

Deprotonation of the Hydroxamic Acids on the Various Oxides from XPS. In the XPS data for monolayers of hydroxamic acids, the N1s core level spectra provided the most information on the nature of bonding that occurs between the hydroxamic acid and the various surfaces. Figure 4 presents N 1s spectra for octadecane hydroxamic acid as a solid and for monolayers adsorbed onto the native oxides of copper, silver, aluminum, and titanium. We calibrated the binding energies of these spectra by fixing the C 1s binding energy of the main Gaussian component (due to the  $CH_2$  groups) at 284.6 eV.42.43 The N 1s spectrum of the solid hydroxamic acid could be fit with a single peak centered at 400.7 eV. The spectra of the monolayers showed multiple components in the N 1s region: one centered at  $\sim 400.5$  eV (in agreement with the peak for the solid hydroxamic acid)



**Figure 3.** Relative thickness of monolayers formed from adsorption of hydroxamic acids of the general formula  $CH_3(CH_2)_nCONHOH$  and  $HO(CH_2)_{15}CONHOH$  onto the native oxides of copper, silver, and titanium. All thicknesses were determined relative to the monolayer of  $CH_3(CH_2)_8CONHOH$  from isooctane using the attentuation of the XPS signals from the substrates (see the text for details). Filled ( $\bullet$ ) and open ( $\odot$ ) circles represent methyl-terminated monolayers formed from isooctane dy the adsorption of  $HO(CH_2)_{15}CONHOH$  from isooctane ( $\bullet$ ) and from ethanol ( $\diamond$ ) are included at the position of 15 methylene units in the alkyl chain. Lines through the data were determined by least-squares fits to the data and were determined without the data for the hydroxyl-terminated monolayers.

and a second at  $\sim$ 398.9 eV.<sup>44</sup> The relative intensities of these peaks varied with the substrate used (as shown in Figure 4).<sup>44</sup> From these data, we conclude that on copper oxide and silver oxide the predominant species bound to the surface is the monodeprotonated hydroxamate, while on aluminum oxide and titanium oxide, the predominant species bound to the surface is the hydroxamic acid.

Data from the C 1s region also suggest varying extents of deprotonation in the different monolayers (Figure 5).<sup>45</sup> The peak due to the carbonyl occurs at 287.6 eV for the solid hydroxamic acid. In the monolayer, this peak is shifted to 287.0 and 286.5 eV on titanium oxide and copper

<sup>(42)</sup> Muilenberg, G. E., Ed., *Handbook of X-ray Photoelectron Spectroscopy*; Perkin Elmer Corp.: Eden Prairie, Mn, 1979. Wagner, C. D.; Gale, L. H.; Raymond, R. H. Anal. Chem. **1979**, *51*, 466-482.

<sup>(43)</sup> Elements in monolayers on thick layers of oxide, such as that on aluminum, have higher binding energies than those on thin layers of oxide due to the inhomogeneous charging that occurs on the thicker oxide substrate. To correct for these differences, we have referenced the binding energies of elements in the monolayer relative to C 1s binding energy of the hydrocarbon at 284.6 eV.<sup>42</sup>

<sup>(44)</sup> The measured binding energies of the peaks in the N 1s region for the monolayer on silver are significantly lower than those for the other substrates (400.1 and 398.6 eV). These peaks are superimposed on the high-energy background following the Ag 3d peaks, which might complicate accurate determination of the binding energies. The noise in this spectrum limited our ability to determine an accurate ratio of acid to monoanion, although the monoanion is clearly favored.

<sup>(45)</sup> We used monolayers of  $\rm CH_3(\rm CH_2)_s\rm CONHOH$  to improve our sensitivity by decreasing the attenuation of the signal due to the carbonyl by the alkyl chain.



Figure 4. X-ray photoelectron spectra for the nitrogen 1s region of solid CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>CONHOH (bottom) and monolayers obtained by the adsorption of it onto the native oxides of copper, silver, aluminum, and titanium. Binding energies of the peaks are referenced to the carbon 1s peak for the alkyl chain at 284.6 eV. Relative intensities could not be compared directly as they were not referenced to a standard. "Ratio" refers to the relative intensities of the peaks ascribed to -CONHOH and -CONHO.

oxide, respectively. The observed line width is very broad for the titanium oxide supported monolayers and less so for the monolayers on copper oxide. We take this as evidence of a heterogeneous environment present at the headgroup on titanium oxide and, based on the clear distinctions observed in the N 1s region, attribute this line width to a heterogeneous state of protonation.

Orientation and Order in SAMs of Hydroxamic Acids from Polarized Infrared External Reflectance Spectroscopy (PIERS).<sup>46,47</sup> Inspection of the PIERS data (Figure 6, Table 3) reveals that the monolayers formed by hydroxamic acids on many of the substrates examined in this study (i.e. those on copper, silver, aluminum, and titanium) are characterized by highly organized structures. Quantitative evaluation, however, indicates that each differs in the orientation adopted by the chain. The mode assignments for the C-H stretching region follow from a similar analysis as that described for alkanethiolate SAMs on gold<sup>4</sup> and alkanecarboxylic acid SAMs on aluminum oxide.<sup>15</sup> In the discussion that follows, we analyze each system briefly in terms of an average structure defined by the model shown in Scheme 2. This model assumes that a best fit to the data involves a specific average orientation of an all-trans chain. Such a structure is described uniquely by the two angles,  $\alpha$  and  $\beta$ , shown in Scheme 2. The discussions that follow are qualitative



Figure 5. X-ray photoelectron spectra for the carbon 1s region of monolayers derived from the adsorption of  $CH_3(CH_2)_8$ -CONHOH onto copper oxide and titanium oxide, and of solid CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>CONHOH. Binding energies of the peaks are referenced to the carbon 1s peak for the alkyl chain at 284.6 eV. The dashed line through the spectra allows comparison of the binding energies of the peaks due to the carbonyl. Relative intensities could not be compared directly as they were not referenced to a standard.

in that we have not performed specific calculations for each of these SAMs but, rather, used the well-established structures and optical functions of the alkanethiolate monolayers on copper, silver, and gold as benchmarks for comparison. The C-H stretching region in the infrared spectra of hydroxamic acid SAMs on copper oxide demonstrates an intriguing similarity to those of alkanethiolates on gold. Both the relative and absolute intensities of the methyl and methylene modes suggest that the alkyl chains are canted from the surface normal direction. This structure involves a chain tilt,  $\alpha$ , of  $\sim 20^{\circ}$  (in agreement with the XPS results presented above) and a rotation of the plane of the trans-zigzag,  $\beta$ , of  $\sim 50-55^{\circ}$ . Significant differences in structure are also evident between the two systems. The frequency of the antisymmetric methylene stretch for the hydroxamic acid SAM on copper oxide is higher than that found for alkanethiolate SAMs on gold  $(2921 \text{ cm}^{-1} \text{ versus } 2919 \text{ cm}^{-1})$ . This observation suggests that the population of gauche conformations in the alkyl chains must be relatively high in this system. If so, the values of  $\alpha$  and  $\beta$  are at best approximate given that the model is based on an all-trans conformation of the chain. Still, the presence of a canted chain structure is strongly suggested by the data. The hydroxamic acid SAMs on copper oxide differ from the alkanthiolate SAMs on gold in another important respect. The data shown in Figure 6 show very little, if any, sensitivity to chain length as evidenced by alternations in the intensities of the methyl  $symmetric(r^{-})$  and in-plane antisymmetric  $(r_a^{-})$  stretching models. Alkanethiolate SAMs on gold show pronounced odd-even chain length progressions in the intensities of these modes, a feature consistent with a preferred absolute

<sup>(46)</sup> Greenler, R. G. J. Chem. Phys. **1966**, 44, 310–315.
(47) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. J. Phys. Chem. **1982**, 86. 5145-5150.



**Figure 6.** Polarized infrared external reflectance spectra for the C-H stretching region of monolayers of octadecane-, heptadecane-, and hexadecanehydroxamic acid on copper, silver, titanium, and aluminum. Scale bars are presented in the figures for comparison.

Table 3. Frequencies of Peaks in the Infrared Spectra for Monolayers of Octadecanehydroxamic Acid on Copper, Silver, Titanium, and Aluminum, and Octadecanethiolate (RS<sup>-</sup>) on Gold (all Frequencies in cm<sup>-1</sup>)

	-				
mode description <sup>a</sup>	Cu	Ag	Ti	Al	RS <sup>-</sup> /Au <sup>c</sup>
CH <sub>2</sub> , sym (d <sup>+</sup> )	2851	2851	2850	2851	2851
$CH_3$ , sym $(\nu^-)$	2880	2879	2882	2879	2878
$CH_2$ , asym $(d^-)$	2920	2917	2916	2922	2919
$CH_3$ , sym (FRC) <sup>b</sup>	$\sim \! 2938$	$\sim 2937$	$2953^{d}$	${\sim}2938$	$\sim 2936$
CH <sub>3</sub> , asym $(v_a^{-})^{e}$	2967	2965	2971	2967	2964

<sup>*a*</sup> Assignments of peaks from ref 4. <sup>*b*</sup> FRC = Fermi resonance splitting component.<sup>4 c</sup> For consistency, this spectrum was taken during the present study. <sup>*d*</sup> The assignment of this peak is uncertain; it may correspond to an out-of-plane antisymmetric methyl stretch. No peak is visible for the expected Fermi resonance peak at ~2935 cm<sup>-1</sup>. <sup>*c*</sup> The frequencies listed are for the in-plane antisymmetric stretch: the frequencies of the out-of-plane mode ( $\nu_b^-$ ) are uncertain (for most SAMs except as noted in *d*) given the weak appearance of this band as an unresolved shoulder on the  $r_a^-$  band at lower frequencies.

sign of the tilt angle,  $\alpha$ . The magnitude of the intensity progressions is "softened", however, by the presence of gauche conformers at the chain termina. In this respect, then, the hydroxamic acid SAMs on copper oxide appear to differ significantly from alkanethiolates on gold. One might assume, based on the model defined above, that the absolute sign of the chain cant angle,  $\alpha$ , must alternate in an odd-even series. There exists great uncertainty as to whether the head group bonding of the hydroxamate



at the surface is indeed fluxional, however. The density of gauche conformations, which we expect to segregate to the chain termina,  $^{1.47}$  is sufficiently high in this system to prevent us from reaching a definitive conclusion on this point. For example, relaxation of the chain ends via the gauche-trans isomerism might lead to similar surface structures (e.g. equivalent average orientations of the methyl groups) in an odd-even chain-length series which form a series of SAMs characterized by a single, absolute value of  $\alpha$ .

Structural arguments for hydroxamic acid SAMs on silver oxide are simpler. The mode assignments for these SAMs follow similarly from those described above. The low frequency of the d mode (2917 cm<sup>-1</sup>) suggests a structure with a few gauche conformations. The relative and absolute intensities of the  $d^-$  and  $d^-$  modes also suggest a unique structure for this SAM: the average values of the chain orientation parameters,  $\alpha$  and  $\beta$ , and unlike those found in any class of SAM studied to date. Using the models described above, we estimate that  $\alpha \approx$  $-14^{\circ}$  and  $\beta \approx 38^{\circ}$  in this system. The odd-even progression of intensities of the methyl  $\nu_{a}^{-}$  and  $\nu^{+}$  is pronounced, providing definitive evidence that the bonding geometry present at the headgroups is conserved. The single sign of  $\alpha$  and the absence of significant surface reconstructions due to the population of gauche conformations must result in a chain length dependence of the orientations of the methyl groups that terminate the chains. It is important to note that hydroxamic acid SAMS on both copper oxide and silver oxide are canted chain structures and that the gauche conformation densities must depend on more than just the presence of this structural feature. It seems likely that surface roughness (which we expect to be significantly higher for the copper oxide surface) must contribute significantly as well. It is particularly intriguing that the wetting data for the hydroxamic acid SAMs on silver oxide (Figure 1) also show odd-even progressions. This observation provides one of the best documented examples of this structural influence on wetting to date.

The hydroxamic acid SAMs on aluminum oxide exhibit structural features that appear to be intermediate between those of SAMs on silver oxide and on copper oxide. The density of gauche populations is likely to be large (d<sup>-</sup> at  $\sim$ 2922 cm<sup>-1</sup>). Although the average chain tilt is small, we estimate an approximate structure with  $|\alpha| \approx 8^{\circ}$  and  $\beta \approx 47^{\circ}$ . This description of the chain structure is, at best, approximate because of the complex chain confor-



**Figure 7.** Competitive adsorptions of  $HO(CH_2)_{15}CONHOH$ against  $CH_3(CH_2)_{15}SH$  (open circles), against  $CH_3(CH_2)_{14}COOH$ (open squares), and against  $CH_3(CH_2)_{14}CONHOH$  (filled circles) onto copper from ethanol. All mixed monolayers were formed from ethanolic solutions containing a total concentration of adsorbate of 1 mM at room temperature for 1 day. Surface composition was determined by relating the measured advancing contact angle of water to the surface compositions determined in Figure 2 (see text). Lines through the data are present as guides to the eve.

mations noted above. It initially seems contradictory that the chains are relatively uncanted yet still contain a large gauche population. Whether surface roughness or some other defect structure is responsible for this combination of features is unclear at present. Nevertheless, the data compel a model of a highly oriented chain, albeit one with a complex conformational architecture.

We cannot estimate the orientation of the alkyl chains in the monolayers of hydroxamic acids on titanium oxide, because the modes seen in the C-H stretching region are exceedingly complex and are superimposed on a nonlinear substrate background (by necessity, a gold mirror was used as a reference). The organization of the alkyl chains in these SAMs is unclear to us. One might assume that the alkyl chains are predominantly in a trans zigzag arrangement, given that the stretching frequency of the  $d^-$  band occurs at 2916 cm<sup>-1</sup>. The broadness and complexity of the lineshapes, however, strongly suggest that these structures are disordered.

Examination of the spectra of the various SAMs in the low-frequency region below 2000 cm<sup>-1</sup> was relatively uninformative with one significant exception. Modes corresponding to the stretching vibrations of the carbonyl groups were not observed in any of the spectra. This result implies that either the transition moment of the carbonyl group, and therefore the C=O bond, is oriented parallel to the surface or that the bond between the carbon and the oxygen has substantial single-bond character and as a result is shifted to a much lower frequency. For the monolayers on silver oxide, a peak is observed at about 1395 cm<sup>-1</sup>. By comparison with studies on the infrared spectra of metal hydroxamates, we assign this band as being due predominantly to the C-N stretching motion.48 The presence of this band, in conjunction with the absence of intensity in the carbonyl region, suggests that the C=O bond is oriented largely parallel to the surface and that both oxygens are not bound to the surface in the form of a chelate.

Competitive Adsorption of Hydroxamic Acids and Other Adsorbates on Copper Oxide. Figure 7 qualitatively examines the relative affinities of different head groups for copper oxide. We used wettability to follow the competitive adsorptions of  $HO(CH_2)_{15}CONHOH$  against

## Scheme 3. Qualitative Ranking of Strengths of Adsorption

Ranking of substrates for affinities to hydroxamic acids:  ${\rm CuO}_X~\sim~{\rm AgO}_X~>~{\rm AlO}_X~\sim~{\rm ZrO}_X~\sim~{\rm FeO}_X~>~{\rm TiO}_X>>~{\rm Au}$ 

Ranking of affinities of ligands for copper and silver oxides:

RSH -> FCONHOH > RCOOH ~ RPO3H2

Ranking of affinities of ligands for aluminum, zirconium, and iron oxides:

FORMER > RELARD > ROOOH

Ranking of affinities of ligands for the moidic metal oxide surface of titanisms

FPC:Ho > RCONHOH >> RCOOH

 $CH_3(CH_2)_{14}$ "HG", where the head group ("HG") was either COOH or  $CH_2SH$ ; we include "HG" = CONHOH for comparison. We approximated the composition of the SAMs by relating the advancing contact angles of water on the monolayers to the surface composition measured by XPS (Figure 2). Although the advancing contact angles are not linear in the composition of the SAM, we assume that the wettabilities of the mixed SAMs depend only on the amount of each tail group in the SAM and not on the head group of the methyl-terminated molecule.<sup>49</sup> We have not established whether these results reflect kinetic or thermodynamic affinities.

These results show that the hydroxamic acid is favored on the surface over the carboxylic acid, by a factor of approximately 4:1 (this value was determined from the compositions of the solution needed to form monolayers with normalized advancing contact angles of 0.5). It also shows that the thiol has a higher affinity for the surface of the copper oxide than does the hydroxamic acid; the last data point, for example, is for a solution composition of 30:1 which gives a monolayer that is approximately 25% in hydroxamic acid.

## Discussion

Long-chain alkanehydroxamic acids form stable, oriented monolayers on all of the substrates with native metal oxides surveyed in this study. Scheme 3 summarizes rankings of the interactions we have investigated in this study. These conclusions were reached from the various experiments described in this paper. We discuss each of these rankings in turn.

Basic metal oxides are better substrates for hydroxamic acids than acidic metal oxides. Hydroxamic acids form monolayers of higher stability on metal oxides with isoelectric points (IEPs) greater than the  $pK_a$  of the acid ( $pK_a$  of acetohydroxamic acid = 9.3)<sup>21</sup> than on metal oxides with IEPs lower than the  $pK_a$  (Table 4).<sup>50-53</sup> Most of the values in Table 4 were not measured on native oxides, but they are nontheless useful for

<sup>(48)</sup> Brown, D. A.; McKeith, D.; Glass, W. K. *Inorg. Chim. Acta* **1979**, 35, 57–60. Brown, D. A.; Roche, A. L. *Inorg. Chem.* **1983**, 22, 2199–2202.

<sup>(49)</sup> We are assuming that the distribution of molecules in the SAM is independent of the head group, and, therefore, the structure of the alkyl chains. This assumption becomes invalid when the structures and the packing of the alkyl chains of the single-component SAMs are significantly different.

<sup>(50)</sup> Parks, G. A. Chem. Rev. 1965, 65, 177-198.

<sup>(51)</sup> Kallay, N.; Torbíc, Z.; Golíc, M.; Matijevíc, E. J. Phys. Chem. **1991**, *95*, 7028-7032.

<sup>(52)</sup> Kallay, N.; Torbíc, Z.; Barouch, E.; Jednacak-Bišan, J. J. Colloid Interface Sci. **1987**, 118, 431–435.

<sup>(53)</sup> Chau, L.-K.; Porter, M. D. J. Colloid Interface Sci. **1991**, 145, 283–286.

Table 4. Published Values of Isoelectric Points (IEPs) ofMetal Oxides and Degree of Deprotonation ofSurface-Bound Hydroxamic Acida

[RCONHO <sup>-</sup> ] <sub>surf</sub> / [RCONHOH] <sub>surf</sub>		

Values taken from Figure 4. <sup>*b*</sup> Values taken from refs 51 and 52. Values taken from ref 50. <sup>*d*</sup> Value taken from ref 53. <sup>*e*</sup> This value is for the naturally occurring mineral. Other values listed in ref 50 were measured on synthetic  $ZrO_2$  made under strongly acid or strongly basic conditions; the conditions of preparation appeared to influence the measured value of the IEP. <sup>*l*</sup> Nitrogen 1s spectra were not taken for these samples.

rationalizing the trends we have observed.<sup>54</sup> According to the data in Table 4, the most stable monolayers should form on silver oxide and copper oxide. We note that there is only a very loose correlation between values of IEP and the ratios of deprotonated hydroxamic acid to protonated hydroxamic acid inferred from the N 1s spectra (Figure 4).

Although thiolates are more stable on copper and silver, hydroxamic acids present a versatile alternative for these metals. Our results indicate that thiolates form the most stable system of monolayers on copper and silver.<sup>55</sup> Hydroxamic acids form more stable overlayers than carboxylic acids or phosphonic acids on these substrates (Scheme 3) and provide an important system for the formation of thin organic films on the native oxides of copper and silver. There are two advantages to the use of hydroxamic acids rather than thiols on copper and silver. First, in the case of copper oxide, the hydroxamic acid forms a strong bond to the surface but does not etch the surface during formation as much as the thiol does. Second, hydroxamic acids are not as prone to oxidation as thiols and may be more stable to long-term exposure to ambient conditions.<sup>20,56</sup> Monolayers of thiolates photooxidize on the surface, forming labile metalsulfonate linkages with the surface.<sup>20,56</sup> The oxidative stability of the hydroxamic acids suggests their use as an alternative to thiols as protective coatings. Potential uses of these monolayers will likely be found in lithography, corrosion resistance, and tribology.<sup>19,20</sup>

Hydroxamic acids present an alternative and improvement to other organic acids for the formation of self-assembled monolayers on most acidic metal oxides. Hydroxamic acids form stable monolayers on "acidic" metals oxides (i.e., those with isoelectric points lower than the  $pK_a$  of the hydroxamic acid),<sup>54</sup> although they are bound predominantly as the parent acid. On the native oxides of aluminum, zirconium, and iron, hydroxamic acids appear to form more stable monolayers than either carboxylic acids or phosphonic acids (Scheme 3). The smaller size of the hydroxamic acid compared to the phosphonic acid may allow the formation of more coherent and perhaps more ordered monolayers (n zirconium oxide and therefore also be useful in some technical applications on zirconium oxide for which phosphonic acids have been used.<sup>16</sup>

Self-assembled monolayers have not been previously studied on the surface of titanium oxide. Our results suggest that on titanium oxide, phosphonic acids form more stable monolayers than either hydroxamic or carboxylic acids (Scheme 3). From the PIERS data, it seems unlikely that well-ordered monolayers of alkane hydroxamic acids are obtained on titanium dioxide. The contact angles show that their stability is not as great as that of phosphonic acid SAMs. Carboxylic acids do not form complete monolayers on titanium oxide from ethanol.

#### **Experimental Section**

General Information. Decanoyl chloride (98%), dodecanoyl chloride (98%), tetradecanoyl chloride (97%), hexadecanoyl chloride (98%), heptadecanoyl chloride (98%), and octadecanoyl chloride (99%) were purchased from Aldrich and used as received; 16-hydroxyhexadecanoic acid (99+%), 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide, and O-benzylhydroxylamine hydrochloride were obtained from Sigma and used without further purification. Stearic acid and palmitic acid were available in the laboratory and were not purified prior to use. Octadecanephosphonic acid was synthesized using the Michaelis-Arbuzov reaction.57 Isooctane (99+%, Aldrich) and hexadecane (anhydrous. Aldrich) were precolated twice through neutral alumina (Fisher); ethanol (Pharmco) was used as received. Copper (Aldrich), silver (Johnson Matthey Electronics), titanium (Aesar), aluminum (Alfa), iron (Alfa), and zirconium (Aldrich) used for evaporations were of 99.99% or higher purity. Single-crystal silicon wafers oriented in the [100] direction were obtained from Silicon Sense (Nashua, NH). For infrared spectroscopy, wafers were 2 in. in diameter and 0.01 in. thick; for all other uses, wafers were 100 mm in diameter and  ${\sim}500~\mu\text{m}$  thick.

General Synthesis of O-Benzylhydroxamates. A solution of the acid chloride (20 mmol), O-benzylhydroxylamine (21 mmol), and pyridine (21 mmol) was stirred in dry THF for 1 h at room temperature and subsequently refluxed for 1 h. The solution was concentrated and the residue was redissolved in 200 mL of ethyl acetate. This solution was extracted twice with 100-mL portions of 0.25 M KHSO<sub>4</sub>, once with 100 mL of saturated NaHCO<sub>3</sub> and once with 100 mL brine. The organic layer was subsequently dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1). Ammonia was bubbled through to precipitate traces of the free acid as the ammonium salt. The solution was filtered. After evaporation of the solvent, the corresponding O-benzylhydroxamate was obtained (92–98% crude yield).

**N-(Benzyloxy)decanamide.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (br s, 1 H), 7.35 (br s, 5 H), 4.88 (br s, 2 H), 2.01 (br, 1.6 H), 1.57 (m, 2 H), 1.23 (br m, 12 H), 0.85 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for  $C_{17}H_{28}NO_2$  (M + H<sup>-</sup>) 278.2120, found 278.2100.

**N-(Benzyloxy)dodecanamide.** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (br s, 1 H), 7.38 (br s, 5 H), 4.90 (br s, 2 H), 2.35 (br, 0.4 H), 2.03 (t, 2 H, J = 7 Hz), 1.59 (m, 2 H), 1.25 (br m, 14 H), 0.88 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>19</sub>H<sub>32</sub>NO<sub>2</sub> (M + H<sup>+</sup>) 306.2433, found 306.2428. Anal. Calcd for C<sub>19</sub>H<sub>31</sub>NO<sub>2</sub>: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.77; H, 10.64; N, 4.51.

**N-(Benzyloxy)tetradecanamide.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\partial$  7.95 (br s, 1 H), 7.36 (br s, 5 H), 4.90 (br s, 2 H), 2.01 (br, 2 H), 1.58 (m, 2 H), 1.23 (br m, 20 H), 0.86 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>21</sub>H<sub>36</sub>NO<sub>2</sub> (M + Na<sup>+</sup>) 356.2565, found 356.2550. Anal. Calcd for C<sub>21</sub>H<sub>35</sub>NO<sub>2</sub>: C, 75.63; H, 10.58; N, 4.2. Found: C, 75.51; H, 10.97; N, 4.21.

**N-(Benzyloxy)hexadecanamide.** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\partial$  8.02 (br s, 1 H), 7.36 (br s, 5 H), 4.88 (br s, 2 H), 2.35 (br s, 0.4 H), 2.01 (s, 2 H), 1.60 (m, 2 H), 1.23 (br m, 24 H), 0.86 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>23</sub>H<sub>40</sub>NO<sub>2</sub> (M + H<sup>+</sup>)

<sup>(54)</sup> The most relevant set of IEPs were determined using metal beads by measuring the uptake of charged latex particles, although zirconium, iron, and silver were not studied.<sup>51,52</sup> The IEP of the native oxide of silver was measured by measuring contact angles as a function of the pH of the drop.<sup>53</sup>

<sup>(55)</sup> A 1:1 solution of octadecanethiolate and octadecane hydroxamic acid in ethanol yielded a monolayer on silver oxide that was 9:1 in favor of thiolate by XPS: Folkers, J. P.; Whitesides, G. M. Unpublished results.

<sup>(56)</sup> Monolayers of thiolate are prone to oxidation even on gold. For examples on gold, see: Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, 7, 1398–1405. Huang, J.; Hemminger, J. C. J. Am. Chem. Soc. **1993**, 115, 3342–3343.

<sup>(57)</sup> Kosolapoff, G. M. J. Am. Chem. Soc. **1945**, 67, 1180–1182. Bhattacharya, A. K.; Thyagarajan, G. Chem. Rev. **1981**, 81, 415–430. (58) Microanalyses were performed by Oneida Research Services in Whitesboro, NY.

362.3059, found 362.3036. Anal. Calcd for  $C_{23}H_{39}NO_2$ : C, 76.4; H, 10.87; N, 3.87. Found: C, 76.25; H, 11.29; N, 3.54.

**N-(Benzyloxy)heptadecanamide.** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  8.12 (br s, 1 H), 7.36 (br s, 5 H), 4.88 (br s, 2 H), 2.35 (br s, 0.4 H), 2.01 (br, 2 H), 1.58 (m, 2 H), 1.23 (br m, 26 H), 0.86 (t, 3 H, J = 6 Hz); HRMS (EI) calcd for C<sub>24</sub>H<sub>42</sub>NO<sub>2</sub>(M<sup>+</sup>) 375.3138, found 375.3126. Anal. Calcd for C<sub>24</sub>H<sub>41</sub>NO<sub>2</sub>: C, 76.75; H, 11.0; N, 3.73. Found: C, 76.74; H, 11.14; N, 3.65.

**N-(Benzyloxy)octadecanamide.** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (br s, 1 H), 7.38 (br s, 5 H), 4.90 (br s, 2 H), 2.03 (br, 2 H), 1.60 (m, 2 H), 1.25 (br m, 28 H), 0.88 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>25</sub>H<sub>44</sub>NO<sub>2</sub> (M + H<sup>+</sup>) 390.3372, found 390.3358. Anal. Calcd for C<sub>25</sub>H<sub>43</sub>NO<sub>2</sub>: C, 77.07; H, 11.12; N, 3.59. Found: C, 77.17; H, 11.09; N, 3.49.

Synthesis of 16-Hydroxy-N-(benzyloxy)hexadecanamide. 16-Hydroxy-N-(benzyloxy)hexadecanamide was prepared by a slight variation of a method for synthesizing trihydroxamic acids that can tolerate hydroxyl groups.<sup>23</sup> The pH of a solution of 1 g (3.67 mmol) of 16-hydroxyhexadecanoic acid and 0.604 g (3.85 mmol) of O-benzylhydroxylamine hydrochloride in THF/  $H_2O\ (2:1)$  was adjusted to 4.8 by adding 1 N NaOH. A 1.41-g (7.34 mmol) portion of 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide was added in small amounts to the stirred solution and the pH was held approximately constant by adding 1 N HCl. After being stirred for an additional 6 h, the reaction mixture was extracted twice with 200-mL portions of ethyl acetate. The combined organic phases were extracted, washed with 150 mL of saturated NaHCO<sub>3</sub>, 150 mL of 0.5 M citric acid, 150 mL of water, and 150 mL of brine, and dried over  $Na_2SO_4$ . The solution was concentrated and the residue was purified by column chromatography (silica: hexane ethyl acetate methanol 7.6.2) Yield: 0.8 g. 60%. HNMR 250 MHz, CDCl, (0.7.95) br s. 1 H . 7.38 (br s, 5 H), 4.90 (br s, 2 H), 3.63 (t, 2 H, J = 7 Hz, 2.35 (br. 0.4 H), 2.02 (br, 1.6 H), 1.59 (m, 4 H), 1.25 (br m, 22 H); HRMS (FAB) calcd for  $C_{23}H_{40}NO_3$  (M + H<sup>-1</sup> 378.3008, found 378.2983. Anal. Calcd for C<sub>23</sub>H<sub>39</sub>NO<sub>3</sub>: C, 73.17; H. 10.41; N, 3.71. Found: C, 73.01; H, 10.29; N, 3.57.

General Synthesis of Hydroxamic Acids. The O-benzylhydroxamates (20 mmol) were dissolved in 200 mL of ethanol and hydrogenated for 6-12 h at a H<sub>2</sub> pressure of 1 atm using 50 mg of Pd on carbon as catalyst. The solutions were filtered over Celite and concentrated, yielding 95–100% of the free acid. Upon recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) 70–80% of the hydroxamic acid were recovered.

**N-Hydroxydecanamide.**<sup>59</sup> <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.32 (s, 0.9 H), 9.67 (s, 0.1 H), 8.97 (s, 0.1 H), 8.65 (s, 0.9 H), 2.25 (t, 0.2 H, J = 7 Hz), 1.92 (t, 1.8 H, J = 7 Hz), 1.47 (q, 2 H, J = 7 Hz), 1.3–1.1 (br m, 12 H), 0.86 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>10</sub>H<sub>22</sub>NO<sub>2</sub> (M + H<sup>-</sup>) 188.1650, found 188.1626. Anal. Calcd for C<sub>10</sub>H<sub>21</sub>NO<sub>2</sub>: C, 64.13; H, 11.3; N, 7.48. Found: C, 63.91; H, 11.38; N, 7.4.

**N-Hydroxydodecanamide.** <sup>1</sup>H NMR (250 MHz, DMSO- $d_6$ )  $\delta$  10.32 (s, 0.9 H), 9.71 (s, 0.1 H), 8.97 (s, 0.1 H), 8.65 (br s, 0.9 H), 2.24 (br, 0.2 H), 1.92 (t, 1.8 H, J = 7 Hz), 1.55–1.4 (m, 2 H), 1.3–1.1 (br m, 16 H), 0.86 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>12</sub>H<sub>26</sub>NO<sub>2</sub> (M + H<sup>+</sup>) 216.1963, found 216.1948. Anal. Calcd for C<sub>12</sub>H<sub>25</sub>NO<sub>2</sub>: C, 66.93; H, 11.7; N, 6.5. Found: C, 67.00; H, 11.37; N, 6.4.

**N-Hydroxytetradecanamide.** <sup>1</sup>H NMR (250 MHz, DMSOd<sub>6</sub>)  $\delta$  10.3 (s, 0.9 H), 9.74 (s, 0.1 H), 8.97 (s, 0.1 H), 8.64 (s, 0.9 H), 2.23 (br, 0.2 H), 1.91 (t, 1.8 H, J = 7 Hz), 1.55–1.4 (m, 2 H), 1.35–1.15 (br m, 20 H), 0.84 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>14</sub>H<sub>30</sub>NO<sub>2</sub> (M + H<sup>-</sup>) 244.2276, found 224.2261. Anal. Calcd for C<sub>14</sub>H<sub>29</sub>NO<sub>2</sub>: C, 69.09; H, 12.01; N, 5.75. Found: C, 68.95; H, 11.88; N, 5.60.

**N-Hydroxyhexadecanamide.** <sup>1</sup>H NMR (250 MHz, DMSOd<sub>6</sub>)  $\delta$  10.3 (s, 0.9 H), 9.71 (s, 0.1 H), 8.96 (s, 0.1 H), 8.64 (s, 0.9 H), 2.22 (br, 0.2 H), 1.90 (t, 1.8 H, J = 7 Hz), 1.55–1.4 (m, 2 H), 1.35–1.15 (br m, 24 H), 0.84 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for  $C_{16}H_{34}NO_2$  (M + H<sup>+</sup>) 272.2589, found 272.2573. Anal. Calcd for  $C_{16}H_{33}NO_2$ : C, 70.8; H, 12.25; N, 5.16. Found: C, 70.74; H. 12.48; N, 5.10.

**N-Hydroxyheptadecanamide.** <sup>1</sup>H NMR (250 MHz, DMSOd<sub>6</sub>)  $\partial$  10.3 (s, 0.9 H), 9.71 (s, 0.1 H), 8.97 (s, 0.1 H), 8.64 (s, 1 H), 2.23 (br, 0.2 H), 1.91 (t, 2 H, J = 7 Hz), 1.55–1.4 (m, 2 H), 1.35– 1.15 (br m, 26 H), 0.84 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>17</sub>H<sub>35</sub>NO<sub>2</sub>Na (M + Na<sup>+</sup>) 308.2565, found 308.2575. Anal. Calcd for C<sub>17</sub>H<sub>35</sub>NO<sub>2</sub>: C, 71.53; H, 12.36; N, 4.91. Found: C, 71.12; H, 12.35; N, 4.80.

**N-Hydroxyoctadecanamide.** <sup>1</sup>H NMR (250 MHz, DMSOd<sub>6</sub>)  $\delta$  10.31 (s. 0.9 H), 9.71 (s. 0.1 H), 8.97 (s. 0.1 H), 8.64 (s. 1 H), 2.22 (br, 0.2 H), 1.91 (t. 1.8 H, J = 7 Hz), 1.6–1.1 (br m, 30 H), 0.84 (t, 3 H, J = 7 Hz); HRMS (FAB) calcd for C<sub>18</sub>H<sub>38</sub>NO<sub>2</sub> (M + H<sup>+</sup>) 300.2902, found 300.2895. Anal. Calcd for C<sub>18</sub>H<sub>37</sub>NO<sub>2</sub>: C, 72.19; H, 12.45; N, 4.68. Found: C, 72.23; H, 12.68; N, 4.6.

**16,N-Dihydroxyhexadecanamide.** <sup>1</sup>H NMR (300 MHz, MeOH- $d_4$ )  $\delta$  3.43 (t, 2 H, J = 7 Hz), 1.97 (t, 2 H, J = 7 Hz), 1.55–1.35 (m, 4 H), 1.3–1.1 (br m, 22 H); HRMS (FAB) calcd for C<sub>16</sub>H<sub>34</sub>NO<sub>3</sub> (M + H<sup>+</sup>) 288.2539, found 288.2541. Anal. Calcd for C<sub>16</sub>H<sub>33</sub>NO<sub>3</sub>: C, 66.86; H, 11.57; N, 4.87. Found: C, 66.95; H, 11.58; N, 4.75.

**Preparation of Substrates.** The copper, silver, zirconium, iron, and aluminum films (1000 Å; thinner films, generally 600–800 Å, were used for aluminum, because of the high power needed to evaporate the metal) were prepared by evaporation of the metals onto silicon wafers primed with 50 Å of titanium as an adhesion layer: titanium (1000 Å) was evaporated directly onto the silicon wafers. All metals were evaporated at a rate of 3 Å/s. The evaporations were performed in a cryogenically pumped electron-beam evaporator base pressure  $\leq 1 \times 10^{-7}$  Torr). After evaporation the chamber was backfilled with nitrogen. The samples were transferred through air to the solutions of the hydroxamic acids within 5–10 min.

**Preparation of Monolayers.** Monolayers were formed from solutions in either isooctane or ethanol with concentrations of 1 mM in adsorbate. The hydroxamic acids, however, were not soluble in isooctane at 1 mM, but enough dissolved to form monolayers. Monolayers for infrared spectroscopy were formed in glass Petri dishes, which had been cleaned with "piranha solution" (7:3 concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub>) at ~90 °C for 30 min, rinsed with deionized water, and dried in an oven at 125 °C prior to use.

WARNING: Piranha solution should be handled with caution; it has detonated unexpectedly.<sup>60</sup> For all other uses, monolayers were formed in single-use glass scintillation vials (20 mL). The slides were removed from solutions after 1-2 days, rinsed with ethanol and heptane, blown dry with N<sub>2</sub>, and characterized. The method for forming solutions for mixed monolayers has been described previously.<sup>34,35,39</sup>

Measurement of Contact Angles. Contact angles were measured on a Ramé-Hart Model 100 goniometer at room temperature and ambient humidity. Water for contact angles was deionized and distilled in a glass and Teflon apparatus. Advancing and receding contact angles were measured on both sides of at least three drops of each liquid per slide; data in the figures represent the average of these measurements. The following method was used for measuring contact angles: A drop approximately  $1-2 \ \mu L$  in volume was grown on the end of the pipette tip (Micro-Electrapette syringe; Matrix Technologies: Lowell, MA). The tip was then lowered to the surface until the drop came in contact with the surface. The drop was advanced by slowly increasing the volume of the drop (rate  $\sim 1 \ \mu L/s$ ). Advancing contact angles of water were measured immediately after the front of the drop had smoothly moved a short distance across the surface. Receding angles were taken after the drop had smoothly retreated across the surface by decreasing the volume of the drop.

**X-ray Photoelectron Spectroscopy (XPS).** X-ray photoelectron spectra were collected on a Surface Science SSX-100 spectrometer using a monochromatized Al K $\alpha$  source ( $h\nu = 1486.6$ eV). The spectra were recorded using a spot size of 600  $\mu$ m and a pass energy on the detector of 50 eV (acquisition time for one

<sup>(59)</sup> Two sets of peaks in the <sup>1</sup>H NMR are observed for the hydrogens on the oxygen and nitrogen in the hydroxamic acid and the hydrogens in the methylene group  $\alpha$  to the hydroxamic acid. These two sets correspond to *E* and *Z* conformations of the hydroxamic acid. For more detail. see: Brown, D. A.; Glass, W. K.; Mageswaran, R.; Girmay, B. *Magn. Reson. Chem.* **1988**, *26*, 970–973. Brown, D. A.; Glass, W. K.; Mageswaran, R.; Mohammed, S. A. *Magn. Reson. Chem.* **1991**, *29*, 40– 45.

<sup>(60)</sup> Several warnings have appeared concerning "piranha solution": Dobbs, D. A.; Bergman, R. G.; Theopold, K. H. Chem. Eng. News **1990**, 68 (17), 2. Wnuk, T. Chem. Eng. News **1990**, 68 (26), 2. Matlow, S. L. Chem. Eng. News **1990**, 68 (30), 2.

scan was approximately 1.5 min). For the monolayers, spectra were collected for carbon, nitrogen, and oxygen using the 1s peaks at 285. 400. and 530 eV, respectively; the binding energies for elements in the monolayer were referenced to the peak due to hydrocarbon in the C 1s region, for which we fixed the binding energy at 284.6 eV.<sup>42</sup> Spectra for the solid hydroxamic acid were collected using an electron flood gun of 4.5 eV to dissipate charge in the sample. The following signals were used for the substrates: Cu 2p<sub>3/2</sub> at 932 eV for Cu(0), and at ~934 eV for Cu(II); Ag 3d<sub>5/2</sub>, 3d<sub>3/2</sub> at 368 and 374 eV for all oxidation states of silver; Ti 2p<sub>3/2</sub>, 2p<sub>1/2</sub> at 454 and 460 eV for Ti(0), and at 459 and 464.5 eV for Ti(1V); Al 2p at 73 eV for Al(0), and at 75 eV for Al(III); Zr 3d<sub>5/2</sub>, 3d<sub>3/2</sub> at 179 and 181 eV for Zr(0), and at 183 and 185.5

eV for Zr(IV); Fe  $2p_{1/2}$ ,  $2p_{3/2}$  at 706.5 eV and 719.5 eV for Fe(0), and at 710 and 723.5 eV for Fe(III).<sup>42</sup> The binding energies for the substrates were not standardized to a reference sample. All spectra were fitted using an 80% Gaussian/20% Lorentzian peak shape and a Shirley background subtraction.<sup>61</sup>

**Infrared Spectroscopy.** The experimental apparatus for taking infrared spectra has been described previously.<sup>4,8</sup> The angle between the incident beam and the surface normal was approximately 85°.

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<sup>(61)</sup> Shirley, D. A. Phys. Rev. B 1972, 5, 4709-4714.