

The Fate of Sulfur-Bound Hydrogen on Formation of Self-Assembled Thiol Monolayers on Gold: ^1H NMR Spectroscopic Evidence from Solutions of Gold Clusters

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The formation of self-assembled monolayers (SAMs) of thiols on gold surfaces has developed into a mature science with important interdisciplinary implications ranging from corrosion science to molecular recognition and nanotechnology.¹ Surprisingly, the nature of the thiol–gold bond is still subject to controversy, although numerous studies covering virtually all applicable characterization techniques have been reported.^{1b} The thiol–gold bond is most commonly described as a surface bound thiolate. The sulfur-bound hydrogen is generally assumed to be absent in these systems. In contrast, Nuzzo et al. reported that methanethiol under UHV conditions adsorbs to gold under hydrogen retention.² Recent ab initio calculations of methanethiol–gold surface and methanethiol–gold cluster systems by Andreoni and co-workers indicate that indeed a number of different scenarios are energetically possible.³ Besides chemisorbed thiolates on “bridge” sites these include also *intact* thiols on “atop” sites, and thiolates plus atomic hydrogen adsorbed to the metal surface. The presence of adsorbed disulfides as has been suggested from grazing angle X-ray studies⁴ seems energetically less favored.³ Most experimental studies of thiol–gold systems to date have been carried out on SAMs on macroscopic planar gold surfaces produced by immersion of the substrate in a solution of the thiol.^{1b–d,f} Since the development of monolayer protected clusters (MPCs) a broader range of techniques has become applicable and MPCs have been used successfully as model systems for SAMs on planar surfaces.⁵ It has been shown by Murray and co-workers, that such ligand place exchange reactions proceed via an associative mechanism.^{5g} This implies that the hydrogen of the incoming thiol can be removed easily during the replacement step by binding to the leaving thiolate ligand. This reaction is therefore different from the initial binding step of thiols to a “clean” gold surface where no obvious mechanism for hydrogen removal is available.

In this communication the first experimental evidence for *intact* thiols adsorbed to gold clusters is presented. It is shown that the loss of hydrogen can be prevented to some extent as long as there is no easy reaction path for hydrogen removal. The consequences of the presence of the hydrogen for the appearance of the ^1H NMR spectra of the clusters are demonstrated. The materials studied consist of gold clusters of 2–5 nm diameter stabilized by dodecyl sulfide. This quite weakly adsorbed thioether was found to be readily replaced by both thiols and disulfides, but unlike thiolates, it will not act readily as a proton acceptor during this process. The ligand replacement reactions and their products are shown in Figure 1. The corresponding spectroscopic evidence is given in Figure 2. Thioether-capped clusters were prepared following a recent report by Huskens and co-workers.⁶ These clusters dissolved readily in nonpolar organic solvents to give beautiful, intensely red-colored solutions, which could be evaporated on flat substrates to spontaneously form lustrous golden thin films. The clusters could be dried

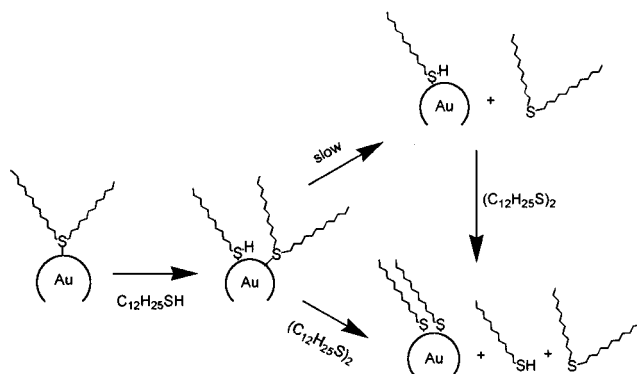


Figure 1. Reaction scheme of ligand addition and replacement reactions on the cluster surface. For clarity no more than two ligands are shown. The first step consists of the uptake of thiol (see Figure 2b) followed by either slow desorption of thioether and/or, after addition of excess disulfide, rapid replacement of ligand shell under release of free thiol and thioether (see Figure 2c). Stoichiometry of replacement reaction is not necessarily 1:1.

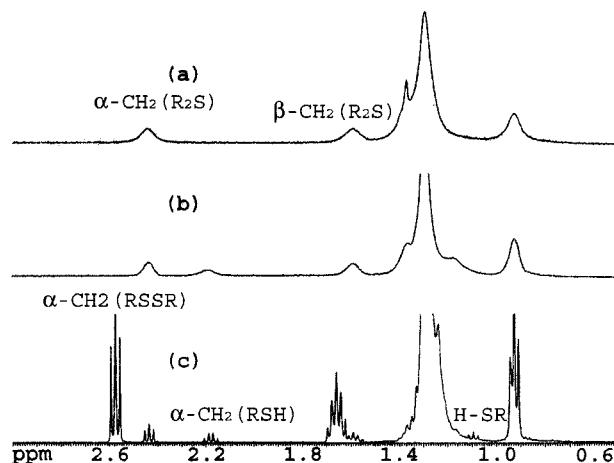


Figure 2. ^1H NMR spectra of (a) dodecyl sulfide-capped gold clusters in perdeuterated benzene (4 mg clusters in 0.5 mL solvent), (b) clusters after addition and uptake of 2 molar equiv of dodecanethiol with respect to thioether in the ligand shell, and (c) after ligand shell replacement and release of free dodecanethiol (α -methylene quartet centered at 2.18 and S–H triplet at 1.10 ppm) and dodecyl sulfide (α -methylene triplet at 2.44 ppm) following addition of excess dodecyl disulfide (α -methylene triplet at 2.58 ppm).

and redissolved, but tended to aggregate irreversibly when stored as a dry product. Elemental analysis of our preparations gave C 5.8%, H 0.9%, and Au 92.6%. An average empirical formula of $\text{Au}_{24}(\text{C}_{12}\text{H}_{25})_2\text{S}$ would require C 5.65%, H 0.99%, and Au 92.73%. The stoichiometry of the ligand addition and exchange experiments is based on this formula. Experiments were carried out by adding aliquots of dodecanethiol and dodecyl disulfide to samples containing 4 mg of thioether-capped clusters dissolved in 0.5 mL of per-

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deuterated benzene. No precautions were taken to exclude oxygen. The attachment of thiol to the clusters followed by the exchange of the ligand shell by addition of a 5-fold excess of disulfide was monitored by ^1H NMR spectroscopy (Bruker Avance 400 MHz) (Figure 2). Cluster-bound and solution-free species can easily be distinguished using this technique by the sharpness of the multiplets and their chemical shifts (referenced to benzene). The peaks corresponding to the α -methylene protons of the cluster-bound species are significantly broadened and their multiplicity can no longer be determined. In the case of thiolate ligands the α -methylene peaks disappear completely. The reasons for the peak broadening, which impedes an exact quantitative analysis, are still subject to discussion.⁵ⁱ

The first observation immediately after addition of the thiol (2 molar equiv with respect to the thioether present in the ligand shell) is the appearance of two additional broad peaks in the NMR spectrum at 2.19 and 1.17 ppm (Figure 2b), which are proposed, on the basis of chemical shift comparisons, to correspond to the α -methylene proton of the *intact* adsorbed thiol and to the still present thiol proton, respectively. We interpret this to indicate the quantitative uptake of the thiol into the ligand shell, which is surprisingly not accompanied by simultaneous release of thioether. No attempts were made to isolate these ligand-enriched clusters. Free thioether finally begins to appear in solution after approximately 30 min as indicated by a sharp triplet at 2.44 ppm (see Supporting Information). The release of thioether could be related to the movement of some of the adsorbed thiols from "atop" to "bridge" sites and might be accompanied by loss of hydrogen. This is at present purely speculative and further investigations of the detailed ligand shell dynamics are needed. To show clearly that adsorbed *intact* thiols are indeed present, the ligand shell was then substituted by the addition of 5 molar equiv of disulfide. This led to the formation of the well-known thiolate-capped clusters under immediate release of free *intact* thiol and thioether (Figure 2c).⁷ A slightly decreased amount of thiol is released even if the disulfide is added 18 h after the addition of the thiol, indicating that the loss of hydrogen is very slow in these systems. The elemental composition of the final ligand-exchanged product was not detectably different from that of the starting material, which shows that the surface coverage by thioether is comparable to that by thiolates, although with approximately only half the number of sulfur–Au interactions. The sulfur content has not been determined in this work. The broad features at 2.19 and 1.17 ppm in Figure 2b are converted after ligand replacement to the characteristic sharp α -methylene quartet centered at 2.18 ppm and the S–H triplet at 1.10 ppm of the free thiol in solution, indicating that the hydrogen must have been present even in the adsorbed species. It is noteworthy that the adsorbed species of both *intact* thiols and thioethers give rise to such broad peaks corresponding to the respective α -methylene protons, while these features are absent in the final thiolate-capped product.

It is at present not possible to discriminate between hydrogen still bound to the sulfur or adsorbed on the gold surface. A combination of both seems the most likely scenario.³ The desorption of molecular hydrogen via adsorbed atomic hydrogen is, in fact, a feasible mechanism of hydrogen loss in these systems as well as in SAMs on macroscopic surfaces. This is supported by experiments in which less than 2 molar equiv of thiol were added. One equivalent (see Supporting Information) gives qualitatively the same result as two, i.e., initial quantitative attachment followed by desorption of thioether and finally recovery of some free thiol after ligand exchange with disulfide. Half an equivalent of thiol or less leads, however, to complete uptake of thiol under loss of hydrogen. No broad peaks at 2.19 or 1.17 ppm can be detected, and no free thiol appears in solution after ligand exchange with excess disulfide. This suggests

that at lower thiol coverage hydrogen is rapidly removed from the system within the time scale of the NMR experiment, probably due to a comparatively high mobility of adsorbed atomic hydrogen on the cluster surface, which is less crowded with ligands than in the case of higher thiol loading. This suggestion is consistent with the theoretical prediction that hydrogen cleavage is energetically favored when a path for formation of molecular hydrogen is provided.³

In conclusion it has been shown experimentally that thiol–gold systems in which *intact* thiols are still present can be prepared under certain conditions and are easily characterized by ^1H NMR spectroscopy. The route for hydrogen removal might thus be an important parameter that could influence formation kinetics, structure, and stability of SAMs of thiols on gold. Thioether-capped clusters seem to provide an interesting new model system for macroscopic gold surfaces.

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Supporting Information Available: ^1H NMR spectra in perdeuterated benzene of (a) dodecyl sulfide (20 mM), (b) dodecanethiol (30 mM), (c) dodecyl disulfide (20 mM), (d) dodecyl sulfide-capped clusters after addition of 1 equiv of dodecanethiol (spectrum taken 45 min after addition), and (e) the same clusters after addition of excess dodecyl disulfide and release of free dodecanethiol [the solutions of the clusters contained 4 mg of clusters in 0.5 mL solvent] (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481. (b) For an exhaustive review up to 1995 see: Finklea, H. O. In Bard, A. J.; Rubinstein, I., Eds. *Electroanal. Chem.* **1996**, *19*, 109. (c) Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117. (d) Rohwerder, M.; Stratmann, M. *MRS. Bull.* **1999**, *24*, 43. (e) Boal, A. K.; Rotello, V. M. *J. Am. Chem. Soc.* **2000**, *122*, 734. (f) Holmlin, R. E.; Haag, R.; Chabinyo, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **2001**, *123*, 5075. (g) Martin, C. R.; Nishizawa, M.; Jirage, K.; Kang, M. *J. Phys. Chem. B* **2001**, *105*, 1925.
- (2) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.
- (3) (a) Grönbeck, H.; Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **2000**, *122*, 3839. (b) Grönbeck, H.; Curioni, A.; Andreoni, W. *Int. J. Quantum Chem.* **2000**, *80*, 598.
- (4) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216.
- (5) (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801. (b) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.-H.; Poon, C. D.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, D.; Falvo, M.; Johnson, C. S.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537. (c) Badia, A.; Singh, S.; Demers, L. M.; Cuccia, L. A.; Brown, G. R.; Lennox, R. B. *Chem. Eur. J.* **1996**, *96*, 2657. (d) Badia, A.; Cuccia, L.; Demers, L.; Morin, F. G.; Lennox, R. B. *J. Am. Chem. Soc.* **1997**, *119*, 2682. (e) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17. (f) Templeton, A. C.; Chen, S. W.; Gross, S. M.; Murray, R. W. *Langmuir* **1999**, *15*, 66. (g) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782. (h) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27. (i) Kohlmann, O.; Steinmetz, W. E.; Mao, X.-A.; Wuelfing, W. P.; Templeton, A. C.; Murray, R. W.; Johnson, C. S., Jr. *J. Phys. Chem. B* **2001**, *105*, 8801.
- (6) Li, X.-M.; de Jong, M. R.; Inoue, K.; Shinkai, S.; Huskens, J.; Reinhoudt, D. N. *J. Mater. Chem.* **2001**, *11*, 1919.
- (7) In this case of replacement by a compound of identical chain length it is impossible to judge whether replacement of the thiol by disulfides occurs with retention of the hydrogen on the displaced thiol chain or with transfer to the incoming disulfide leaving a thiolate on the surface and a free thiol molecule derived from the disulfide. Preliminary experiments in which adsorbed benzyl mercaptan was replaced by dodecyl disulfide indicate that the former is the case, i.e., free benzyl mercaptan is formed.

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