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Heterogeneous catalysis on platinum and self-assembled monolayers on metal and metal oxide surfaces (Note a)

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Abstract – This paper describes research in two areas: heterogeneous catalysis and molecular self-assembly. The work in heterogeneous catalysis used the platinum-catalyzed hydrogenation of diolefin(dialkyl)platinum(II) complexes to generate platinum surface alkyls of known structure. The structure and reactivity of these surface alkyls were inferred from characteristic processes occurring on the surface. The incorporation of deuterium from isotopically labelled protic solvents (e.g. EtOD) was particularly useful mechanistically. The technique of self-assembly was used to form organic monolayers by coordination of a ligand to a metal or metal oxide surface. In addition to the chemisorption of alkyl thiols on gold (as alkyl thiolates, RS^-Au^+), a number of other systems were demonstrated to give ordered organic surface species.

INTRODUCTION

This paper describes our recent work in the areas of heterogeneous catalysis on platinum and self-assembled monolayers on the surfaces of metals and metal oxides. In heterogeneous catalysis, we wish to characterize the reactivities of surface alkyls (R*) on platinum. The reduction of diolefin(dialkyl)platinum(II) complexes generates R* moieties having well-defined initial structures. We infer the reactivities of these species using, as a primary tool, deuterium labelling.

In self-assembly, we wish to prepare structurally well-defined interfaces. The self-assembly of long-chain alkyl thiols (and disulfides) on the surfaces of gold and silver, and of other species on the surfaces of other metals and metal oxides, generates appropriate interfaces. We have also used differences in coordination to develop systems for the formation of interfaces patterned in the plane of the surface. This type of process provides a route to well-defined surface organometallic structures, and illustrates the similarities and differences between analogous coordination chemistries in solution and at surfaces.

HETEROGENEOUS CATALYSIS: STUDIES OF THE REACTIONS OF HYDROCARBON SPECIES ON THE SURFACE OF PLATINUM

The heterogeneous hydrogenation of olefins is one of the simplest reactions in heterogeneous catalysis; many components of the reaction are, however, not well understood. Perhaps the most fundamental (and most elusive) goal of research in heterogeneous catalysis is to understand the structure and reactivity of the hydrocarbon species (R*) that are derived from olefins, and exist as intermediates on the surface of the catalyst. We have developed a system that generates R* of known initial structure under conditions similar to those employed in heterogeneous catalysis in synthetic organic chemistry: the reduction of diolefin(dialkyl)platinum(II) complexes (DOPtR$_2$) by dihydrogen and platinum black catalyst suspended in organic solvents (eq 1) (ref. 1-6). The reaction occurs by

$$ \text{(1)} $$
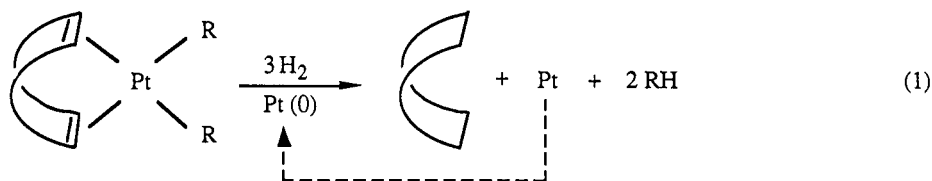
adsorption of the components of DOPtR$_2$ on the surface of platinum, with consequent generation of surface alkyls (R* and DO*). The surface alkyls react with surface hydrides and produce alkanes, and the platinum atom in the complex becomes part of the surface of the catalyst. We believe that the R* moieties produced from these complexes are related to those produced in the heterogeneous hydrogenation of olefins (Scheme 1). In addition, the hydrogenation of DOPtR$_2$ complexes can be used to generate R* that cannot be generated via the hydrogenation of olefins (e.g. methyl*, phenyl*, 1-norbornyl*).

Scheme I

Proposed Analogy between the Et* Moieties Derived from Ethylene (left) and Those Derived from $DOPtEt_2$ (right).

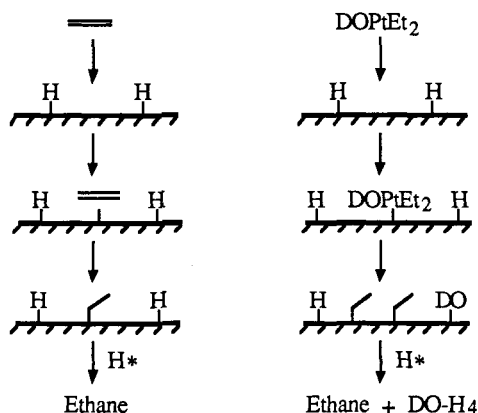**TABLE I.** Standard Conditions for Reductions under MTL and RRL Conditions

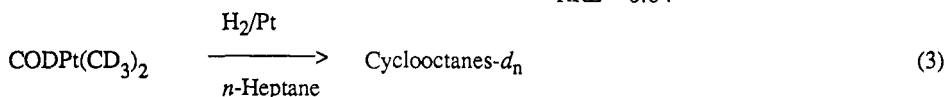| Parameter	MTL	RRL	Remarks
Substrate (mg)	15 - 30	15-60	
Solvent (mL)	3	3	ethyl alcohol or *n*-heptane
Vessel (mL)	20	20	glass pressure tube
P_{H_2} (atm)	0.17	2.4	
T (°C)	40	-20	
Catalyst (mg)	40	30	platinum black
S_{Pt} (μg-atom)	20	15	established by H_2/O_2 titration
Stirring (RPM)	1800	1800	rate of rotation of magnetic stir bar (10 x 6 mm)

The kinetics of the reductions of $DOPtR_2$ complexes are characterized by two distinct regimes: mass-transport limited (MTL) and reaction-rate limited (RRL) (ref. 1,6). Table I gives the reaction conditions employed in each regime. In the MTL regime, the rate of delivery of H_2 to the surface of the catalyst limits the rate of reaction. In the RRL regime, the rate of an unspecified reaction on the surface of the catalyst limits the rate of reaction. The rate of C-H bond activation of R* moieties relative to the rate of reductive elimination as alkane is faster under MTL than under RRL conditions.

Three pieces of evidence characterize this reaction as heterogeneous rather than homogeneous. First, the rate of reduction is negligible in the absence of platinum catalyst (ref. 1). Second, the reduction stops when typical

$$(DCPD\text{-}d_{12})PtMe_2 \xrightarrow[\text{n-Heptane}]{H_2/Pt} \text{Methanes-}d_n \qquad (2)$$
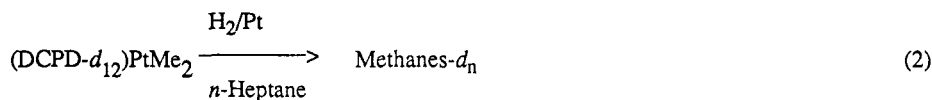
D found in methanes
MTL 0.50
RRL 0.04

$$CODPt(CD_3)_2 \xrightarrow[\text{n-Heptane}]{H_2/Pt} \text{Cyclooctanes-}d_n \qquad (3)$$

D found in cyclooctanes
MTL 1.25
RRL 0.08

poisons (e.g. group V and VI Lewis bases, Hg(0), mercury compounds) are added to the catalyst (ref. 1). Third, transfer of deuterium occurs between DO* and R* when the catalyst is suspended in hydrocarbon solvents: the hydrogenation of (dicyclopentadiene-d_{12})dimethylplatinum(II), $(DCPD\text{-}d_{12})PtMe_2$, produces methanes that contain deuterium (eq 2), and the hydrogenation of (1,5-cyclooctadiene)(dimethyl-d_3)platinum(II), $CODPt(CD_3)_2$, produces cyclooctanes that contain deuterium (eq 3) (ref. 6). The transfer of deuterium described in eq 2 and 3 undoubtedly occurs on the surface of the catalyst.

We designed two experiments to clarify the mechanism by which $DOPtR_2$ complexes adsorb on the surface of the catalyst. Equations 4 and 5 show that the reduction of norbornadiene (NBD) by D_2 incorporates deuterium

(4)

(5)
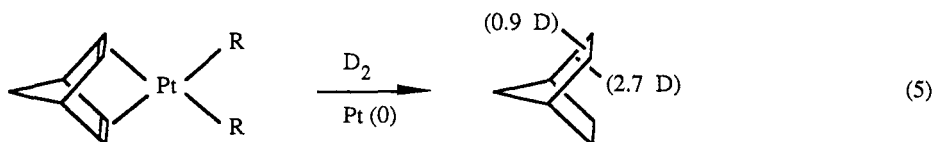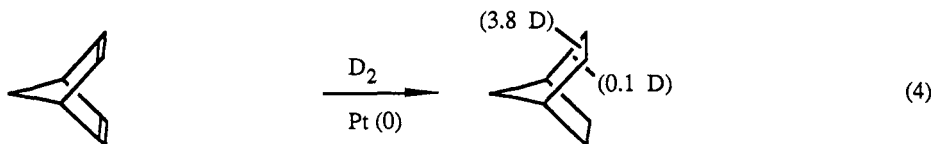
predominantly into the *exo* positions of norbornane; analogous reduction of (norbornadiene)dimethylplatinum(II) (NBDPtMe$_2$) incorporates deuterium predominantly into the *endo* positions of norbornane (ref. 2). Similarly, eq 6 and 7 show that the reduction of homohypostrophene (HOP) by D$_2$ incorporates deuterium into the *exo*
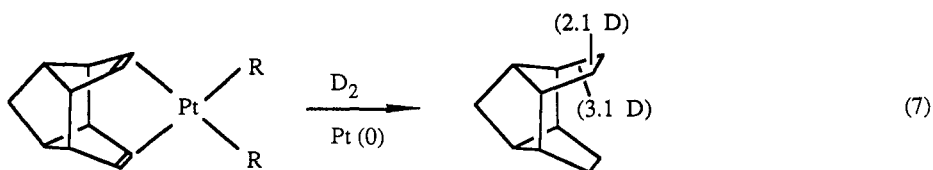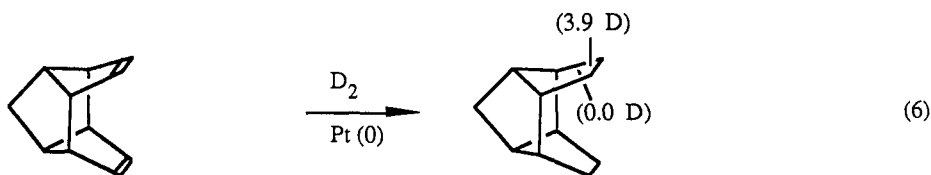
positions of homohypostrophane (HOPH), but analogous reduction of (homohypostrophene)neopentyl(2-norbornyl)platinum(II) complexes incorporates deuterium predominantly into the *endo* positions of HOPH (ref. 6). These results argue that the adsorption of DOPtR$_2$ complexes occurs by initial adsorption of the platinum atom in the complex.

Adsorption of DOPtR$_2$ on the surface of platinum occurs without loss of the regiochemistry initially defined by the bonding of R to platinum in the soluble organometallic complex. The following experiments summarize the support for this conclusion (ref. 2). The reduction of propylene by D$_2$ incorporates deuterium into the 1 and 2 positions of propane. In contrast, the reduction by D$_2$ of CODPt(n-propyl)$_2$ produces exclusively 1-propane-d_1, and that of CODPt(iso-propyl)$_2$ produces predominantly 2-propane-d_1.

APPLICATIONS

We used this system to explore the relative rates of α, β, γ, δ, ϵ and ζ C-H bond activation of surface alkyls (ref. 3). We synthesized a series of platinum complexes, CODPt(CD$_3$)$_2$, CODPt(CH$_2$CD$_3$)$_2$, CODPt(CH$_2$C(CD$_3$)$_3$)$_2$, CODPt(CH$_2$C(CH$_3$)$_2$(CH$_2$)$_n$CD$_3$)$_2$ (n = 1-3), and hydrogenated them under MTL conditions over platinum black in *n*-heptane. The extent of incorporation of deuterium into the cyclooctanes provided a measure of the rates of α, β, γ, δ, ϵ, and ζ C-H bond activation of surface alkyls relative to the rate of reductive elimination as alkanes. The following order of rates was observed: $\alpha \gg \beta > \delta > \gamma \approx \epsilon \approx \zeta$. This order contrasts with that observed for C-H bond activation in homogeneous platinum(II) complexes in solution: $\beta > \delta > \gamma \approx \epsilon \gg \alpha$ (not observed) (ref. 7-10). The relative orders on the surface and in solution are similar except for α C-H bond activation. This difference probably arises from the fact that facile α activation on platinum requires more than one metal center.

With this system, we were able to provide the most definitive description currently available of the stereochemistry of reduction of C* bonds (ref. 5). Previous studies of this reaction focussed, for example, on the hydrogenation of olefins. In these studies, however, the initial stereochemistry of bonding of the olefin to the surface was not known; thus, the stereochemistry of the reduction of C* bonds in these reactions could be determined only by inference. Since the reduction of DOPtR$_2$ complexes generates R* of *known initial* stereochemistry, these reductions provide a direct determination of the stereochemistry of the reduction of C* bonds.

We synthesized samples containing predominantly (homohypostrophene)neopentyl(*exo*-2-norbornyl)platinum(II) (**Exo**), and those containing predominantly (homohypostrophene)neopentyl(*endo*-2-norbornyl)platinum(II) (**Endo**). Equations 8 and 9 summarize the results from the reductions of these samples by D$_2$. Equation 8

Exo   Endo
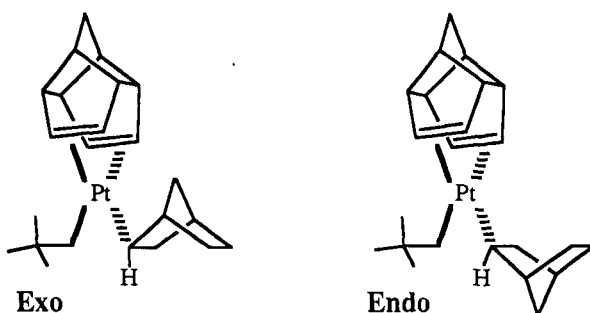
describes, for example, the reduction of a mixture of 90% **Exo** and 10% **Endo**. In summary, the reduction of **Exo** incorporates deuterium into the *exo* position of norbornane; reduction of **Endo** incorporates deuterium predominantly into the *endo* position of norbornane. These results argue that the reduction of C* bonds occurs with predominant retention of configuration.

$$\text{Pt (0.90) / Pt (0.10)} \xrightarrow[\text{Pt}]{D_2} \text{D (1.1) / D (0.1)} \qquad (8)$$

$$\text{Pt (0.03) / Pt (0.97)} \xrightarrow[\text{Pt}]{D_2} \text{D (0.4) / D (1.0)} \qquad (9)$$
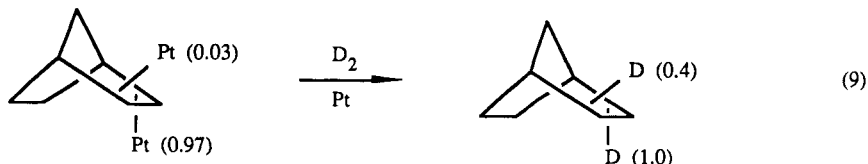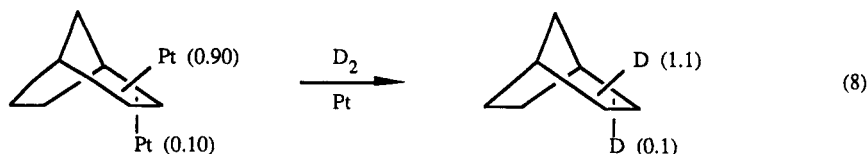
REDUCTIONS IN PROTIC SOLVENTS

Our initial investigations of the reduction of $DOPtR_2$ complexes in protic solvents demonstrated that the isotopic exchange of H/D between the OH(D) group of the solvent and H(D)* was fast (eq 10) (ref. 6). For example, when the hydrogenations described in eq 2 and 3 were carried out in ethyl alcohol (EtOH) rather than *n*-heptane,

$$H* \quad + \quad ROD \quad \rightleftharpoons \quad D* \quad + \quad ROH \qquad (10)$$

neither the methanes (eq 2) nor the cyclooctanes (eq 3) contained deuterium. The mechanism of the exchange shown in eq 10 has not been resolved.

To demonstrate the utility of the rapid exchange of isotopes of hydrogen between the protic solvent and the surface of platinum, we reduced, under MTL conditions (75 °C rather than 40 °C), a series of unsubstituted cycloolefins using H_2 as the reductant and D_2O/THF (1:1, v:v; $pH(D)_{D_2O} = 1$) as the solvent (ref. 5). Figure 1 summarizes the results. We use d_{av} to describe the average content of deuterium in alkanes (eq 11). It is remarkable that

$$d_{av} = 1/100 \sum_{n=1}^{m} n \, (\% \text{ alkane-} d_n) \qquad (11)$$

extensive incorporation of deuterium can be achieved using dihydrogen to reduce cycloolefins over platinum black in a deuterated solvent (ROD). The content of deuterium in the cycloalkanes provides a measure of the rate of C-H bond activation of the intermediate cycloalkyl* moieties relative to the rate of reductive elimination as cycloalkanes. Interestingly, the rate of C-H activation (as measured by d_{av}/d_{max}) correlates with the strain energies of the cycloalkanes: the greater the strain energy of a cycloalkane, the faster the rate of C-H bond activation (relative to the rate of reductive elimination from the surface).

The rapid isotopic exchange between H(D)* and ROH(D) was a useful tool in comparing the surface ethyl moieties (Et*) derived from ethylene with those derived from $CODPtEt_2$ (ref. 6). The isotopic distributions of the ethanes produced from the reductions of ethylene and $CODPtEt_2$ by D_2 in EtOD under RRL conditions and MTL conditions are shown in Figure 2. Under RRL conditions, the distribution of ethanes obtained from the reduction of ethylene appears to be shifted by one additional deuterium to that obtained from the reduction of $CODPtEt_2$. These results suggest that, under RRL conditions, the relative rates of C-H bond activation and reductive elimination are similar for the Et* moieties derived from these two substrates.
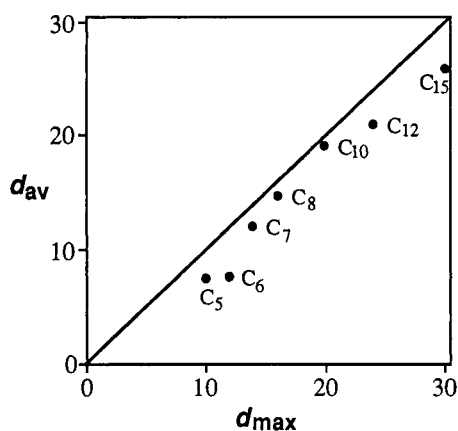

FIGURE 1. A plot of d_{av} vs d_{max} for the cyclooalkanes produced in the heterogeneous reduction of unsubstituted cycloolefins using H_2 and D_2O/THF (1:1, v:v; $pD_{(D_2O)} = 1$).
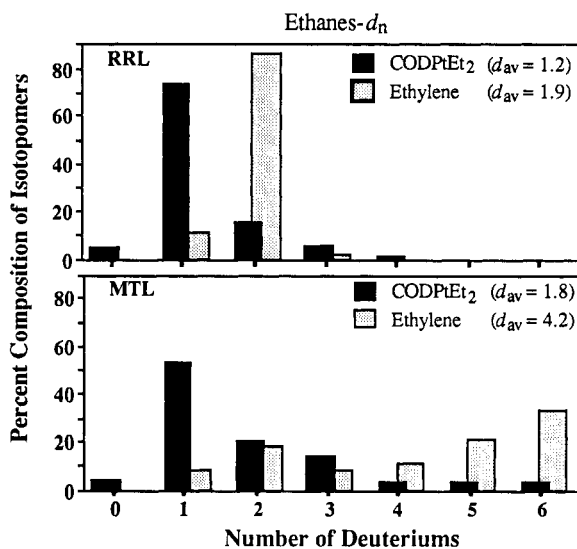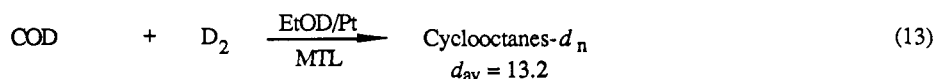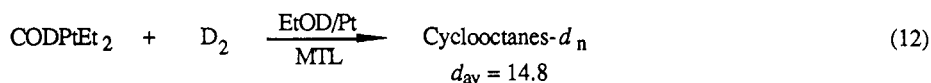

FIGURE 2. The ethanes produced under RRL conditions (top) and MTL conditions (bottom) from the reductions of $CODPtEt_2$ and ethylene using D_2 and EtOD.

Under MTL conditions, however, the ethanes produced from ethylene and CODPtEt$_2$ are markedly different. This difference probably arises from the presence of the coadsorbed cyclooctyl* moieties in the reduction of CODPtEt$_2$. Under MTL conditions, the concentration of H(D)* is low relative to that under RRL conditions. We hypothesize that the cyclooctyl* moieties provide a source H(D)* that increases the rate of reductive elimination for Et* moieties derived from CODPtEt$_2$ relative to that for Et* moieties derived from ethylene. Supporting evidence for this hypothesis is summarized in eq 12 and 13. The content of deuterium in the cyclooctanes produced in the

$$\text{CODPtEt}_2 \quad + \quad \text{D}_2 \quad \xrightarrow[\text{MTL}]{\text{EtOD/Pt}} \quad \text{Cyclooctanes-}d_n \qquad (12)$$
$$d_{av} = 14.8$$

$$\text{COD} \quad + \quad \text{D}_2 \quad \xrightarrow[\text{MTL}]{\text{EtOD/Pt}} \quad \text{Cyclooctanes-}d_n \qquad (13)$$
$$d_{av} = 13.2$$

reduction of CODPtEt$_2$ is greater than that produced in the reduction of COD; this difference probably corresponds to loss of H from cyclooctyl* moieties to coadsorbed Et* moieties in the reduction of CODPtEt$_2$.

FUTURE

These studies have demonstrated a new paradigm for determining the mechanisms of heterogeneous catalytic reactions by using a combination of organometallic chemistry and catalysis to generate surface alkyls of known structure. This type of investigation should be directly applicable to studies of a wide range of hydrogenation reactions. To what extent it can be applied to other reactions of substantial interest---Fischer-Tropsch catalysis, Ziegler-Natta polymerization, reforming---remains to be established.

ORGANIC MONOLAYER FILMS

Interest in structurally well-defined organic monolayer films supported on surfaces has been accelerated by advances in surface analytical instrumentation, and focussed by interest in adhesion and wetting and by relevance to electronic device fabrication (ref. 11). There are currently two methods commonly used for generating organic monolayers: Langmuir-Blodgett and self-assembly (Figure 3). The Langmuir-Blodgett method involves the careful transfer of a monolayer from the liquid-air interface onto a solid support, using a relatively slow,

Langmuir-Blodgett   **Self-Assembled**

M = Au, Ag, Cu,   ———□ = RSH, RSSR, RNC, R$_3$P
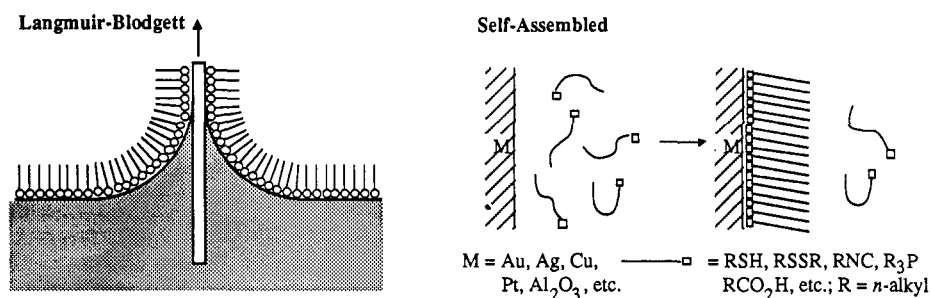Pt, Al$_2$O$_3$, etc.   RCO$_2$H, etc.; R = n-alkyl

FIGURE 3. Two methods of formation of supported organic monolayers.

mechanical dipping process. Langmuir-Blodgett films are generally attached to the substrate solely by physisorption. It is difficult to make crack-free monolayers from systems that crystallize easily using Langmuir-Blodgett techniques. The technique of self-assembly relies on a chemical reaction between the surface and the adsorbate, requires no specialized apparatus, and provides a rapid, forgiving route to robust, chemisorbed films. A wide range of self-assembling systems have been developed: dialkyl sulfides and disulfides on gold; alkyl thiols on copper, silver, and gold; alkanoic acids on alumina; alkyl trichlorosilanes on silica; amines on chromium; isonitriles on platinum (ref. 12).

SELF-ASSEMBLED ORGANOSULFUR MONOLAYERS ON GOLD

The most thoroughly studied of the self-assembly processes has been the adsorption of alkyl thiols and disulfides on gold. Under ultra-high vacuum (UHV) conditions, exposure of the (111) face of single crystal gold (Au(111)) to an alkyl thiol generates a weakly adsorbed layer of the thiol; this process is reversible at low temperature (eq 14). Exposure of Au(111) to a dialkyl disulfide results in cleavage of the sulfur-sulfur bond and formation of a strongly bound alkanethiolate species on the surface (eq 15) (ref. 13). In contrast, monolayers formed from either thiols or disulfides in solution attach to the surface via a common species, the thiolate (eq 16). Neither the mechanism of conversion of alkanethiols to gold(I) alkanethiolates, nor the species that desorbs at elevated temperatures in solution---thiol, disulfide, or gold(I) thiolate---has been identified. On gold, thiols are preferred over disulfides (~75:1) (ref. 14), even though the rates of formation of monolayers formed from either thiols or disulfides from solution are comparable (ref. 15).

UHV

$$(14)$$

$$(15)$$

SOLUTION

$$(16)$$
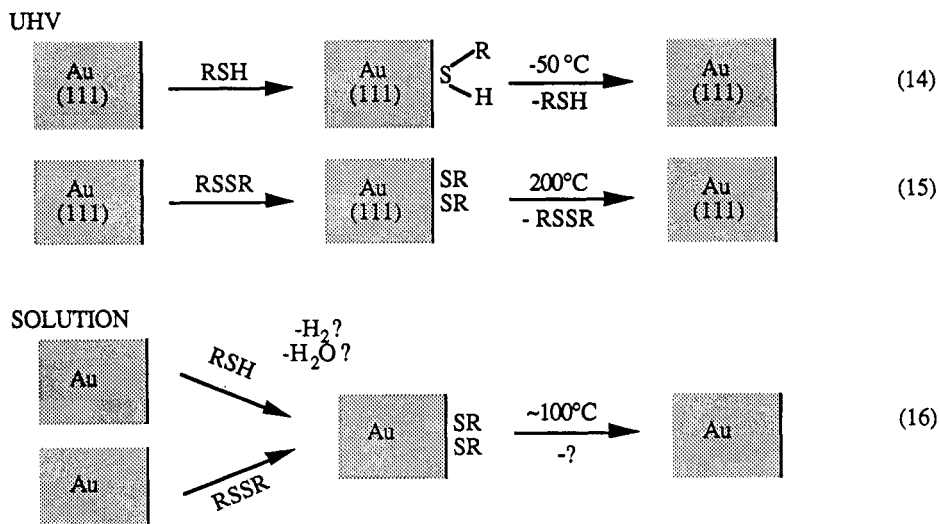
The structure of long-chain alkanethiolate monolayers on gold has been probed by a wide range of techniques including IR, XPS, and electron and helium diffraction (ref. 12). The conclusions that emerge from these studies are: the alkanethiolate monolayer forms a $\sqrt{3} \times \sqrt{3} R30°$ epitaxial layer on the gold surface; the hydrocarbon chains are densely packed with a cant of ~30° relative to the surface normal; the chains are largely trans zig-zag extended; the few gauche interactions that exist are located predominantly near the air-monolayer interface (Figure 4).

Au (111) • AuSR
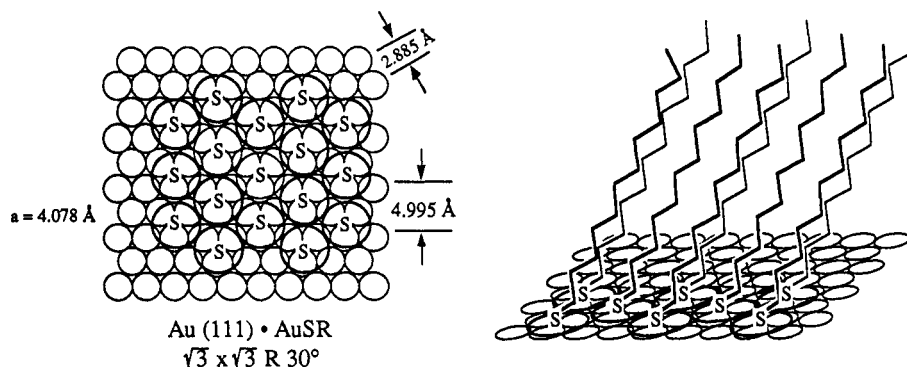$\sqrt{3} \times \sqrt{3} R\ 30°$

FIGURE 4. Structure of n-alkanethiolate monolayers formed on Au(111). The adsorbed alkanethiol forms an epitaxial layer on gold (left) generating a densely packed hydrocarbon layer that is canted ~30° from the surface normal (right).

One noteworthy attribute of the organosulfur chemistry on gold is its ability to accommodate both polar and non-polar tail groups, and to permit formation of interfaces with a range of functionalities: organic groups that can be presented at the surface include carboxylic acids, amides, and alcohols and many non-polar groups. These surfaces have served as substrates for many studies of wetting (ref. 16).

The formation of the monolayer is rapid (exposure of clean gold to a 1 mM solution of octadecanethiol in ethanol results in the formation of a complete monolayer in less than five seconds) (ref. 17). When a complete monolayer is immersed in a solution containing a different thiol or disulfide, the monolayer exchanges its components for those in solution. The mechanism of this exchange is complex and remains unresolved. Exchange appears to occur rapidly at first and then more slowly, never going to completion (ref. 15,18,19). This observation suggests that exchange may be occurring predominantly at grain boundaries or defect sites.

SELF-ASSEMBLED MONOLAYERS ON COPPER AND SILVER

We and others have extended these studies to silver and copper (ref. 20). Silver and copper (especially) oxidize more rapidly than gold on exposure to oxygen. The resulting oxide surfaces remain active toward thiols (although much less so toward disulfides). The mechanism of formation of these monolayers is not clear, but does occur with a reduction in the amount of oxide on the metal surface. Whether this decrease is due to displacement or reduction of the surface oxide by thiol has not been established mechanistically, and is probably not important: the final surface species is almost certainly RSM(I) for gold, silver, and copper. Monolayers on copper and silver exhibit many similarities to those formed on gold: they are ordered and densely packed; the surface species is a thiolate; both non-polar and polar tail groups can be accommodated to generate surfaces spanning a wide range of wettabilities; the monolayer will exchange with thiols in solution. The most important difference is that the alkyl chains of monolayers on copper and silver are oriented almost perpendicular to the surface.

ORTHOGONAL SELF-ASSEMBLED MONOLAYERS: BACKGROUND AND EXAMPLES

Many substrates other than copper, silver, and gold are able to support the formation of ordered, self-assembled monolayers. Considering the chemistry occurring at the interface between the monolayer and the support in terms of coordination chemistry, a wide range of other self-assembling systems can be imagined. We believed that differences in coordination chemistries between various ligands and surfaces could be used to generate interfaces patterned on the molecular level. With this goal in mind, we have recently begun a study of the self-assembling chemistries of various surfaces, noting trends and preferences, and looking for hints towards new metal/ligand combinations. We wished 1) to identify organic ligands that would form ordered monolayers on important surfaces and predict appropriate ligands for new ones, and 2) to design "orthogonal" self-assembling systems; that is, systems in which two ligands RL_1 and $R'L_2$ present in the same solution would associate spontaneously and selectively with two substrates S_1 and S_2 (eq 17). The technique of orthogonal self-assembly is potentially valuable in replicating photolithographically-formed patterns in the plane of the surface in the monolayer adsorbed

(17)
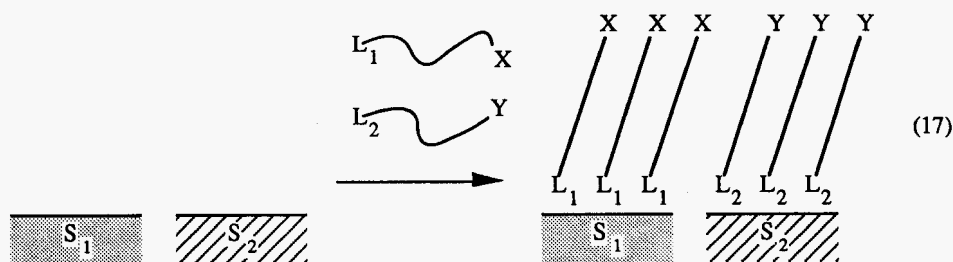
on these patterns. Table 2 summarizes the results from our study (ref. 21). In general, the results follow the Hard Soft Acid Base (HSAB) classification: carboxylic and phosphonic acids adsorb on any metal oxide; thiols and isonitriles adsorb on soft metals (Cu, Ag, Au, Pt). Surprisingly, phosphines, generally considered soft ligands, form monolayers on all of the surfaces surveyed. This result may reflect conversion of phosphine to phosphine oxide in many circumstances. Figure 5 illustrates the application of the information from these surveys of relative strengths of adsorption in a representative orthogonal system: a perfluorinated acid adsorbing on alumina and an alkanethiol on gold, respectively, on a microlithographed array (Figure 5) (ref. 22).

We are now exploiting other differences in coordination chemistry. One example is based on the fact that, upon exposure to air, silver oxidizes and gold does not. This difference makes it possible to adsorb thiols onto silver and disulfides onto gold selectively (ref. 23). While the degree of segregation is not as high as that observed in the gold/alumina system, this system has the important characteristic that it permits the wettability of the monolayers formed on silver and gold to be individually tailored by changing the tail groups of the thiol and disulfide, respectively. The ability to make interfaces containing areas differing in polarity and wettability by water will be useful in fundamental studies of wetting and of adhesion. Another example is based on differences in the adsorption of thiols or disulfides and isonitriles on gold and platinum. Gold exhibits a high affinity for organosulfur compounds. Platinum is less discriminating, but shows some preference for isonitriles. We have prepared orthogonal monolayers on gold and platinum, and characterized the segregation by wetting, electrochemistry, and XPS (ref. 19). This system should be widely useful in electrochemistry.

The gold/alumina example is not unique. Many hard metal oxides (zirconia, silica, etc.) can be substituted for alumina as substrates for carboxylic acids. Although carboxylic acids and thiols will each adsorb on the native oxide surfaces of copper and silver, a pure monolayer of the alkanethiol is formed when copper or silver is exposed to a solution containing *both* ligands. Thus, it is possible to obtain orthogonal monolayers of the type illustrated in Figure 5, by exposing any combination of a soft metal (or metal oxide) and a hard metal oxide to a solution containing a thiol and a carboxylic acid (ref. 19).
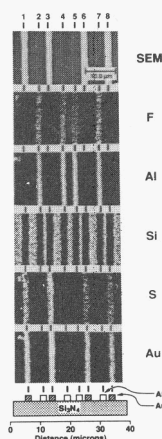
FIGURE 5. SEM and Auger elements maps for a microlithographed array of gold and alumina strips in Si_3N_4 exposed to a solution of $HS(CH_2)_{11}Cl$ and $CF_3(CF_2)_8CO_2H$. The data show that the thiol is localized solely on the gold wires, the acid on the alumina, and neither present on the Si_3N_4.

TABLE II. Adsorption of Various Alkylated Ligands onto Various Metal and Metal Oxide Surfaces

Metal	RSH	RSSR RSR	PR_3''	RNC	$R'CO_2H$ RPO_3H_2	ROH RNH_2 $R'CONH_2$
Zr, Nb, Cr, Mo, Fe, Ni, Al	−a	−	+b	+	+	+
Pt	+	−	+	+	+	c
Cu, Ag	+	−	+		+	
Au	+	+	+	+	−	−
Zn	+	−	+	+	+	+

$R = C_{18}H_{37}$, $R' = C_{17}H_{35}$, $R'' = C_8H_{17}$ b + = stable monolayer formed
a − = no monolayer formed   c blank space = no data currently available

FUTURE

Orthogonal self-assembly is an important step towards the development of nanostructures, and provides new systems with which to study wetting and electron transfer. *The design of these systems, we stress, has been based on analogies drawn from solution coordination chemistry.* This technique is still in its infancy, and many issues remain to be resolved. Thus, in the last two examples of orthogonal systems, the *kinetics* of exchange are important to the selectivity. Rates of formation and of exchange are crucial to designing (and optimizing) orthogonal systems, and our understanding of these kinetic features is very limited. Comparisons between rates of exchange (on surfaces) and rates of substitution (in solution) may clarify the selectivities in these systems and the design of other orthogonal combinations.

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