of the organic functional groups present at an interface. A large variety of reactive ions can be chosen as probes, and this chemical method of surface characterization may prove to be complementary to conventional physical methods which employ electron, photon, or atom beams as probes.[19]

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Polyatomic Ion/Surface Collisions at Self-Assembled Monolayer Films

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The chemical and physical properties of ordered molecular monolayers and thin films have been extensively investigated because of their technological potential.[1-11] In solution, 1-alkanethiols are known to spontaneously form highly ordered, covalently bound monolayer films on gold[4-11] or silver.[8] These films have been described in numerous publications[4-10] and are stable, easy to prepare, and useful as electrochemical barriers[4,9-11] in solution. In this report, we discuss the ion/surface chemistry that is detected when gas-phase polyatomic ions, of well-defined mass, structure, and collision energy, collide with a self-assembled monolayer of alkanethiol on gold at collision energies of 10-80 eV.

The experiments described here were performed in a tandem mass spectrometer in which two quadrupole mass analyzers were placed at 90°, with a surface placed to intersect the ion optical path of each quadrupole[12] (angle of incidence 50° with respect to the surface normal). The pressure in the collision region was 10^{-7} Torr. Surfaces utilized include stainless steel, gold, ethanethiol on gold, and octadecanethiol on gold. Gold foil (0.05-0.1 mm thick) was allowed to react with an alkanethiol in ethanol (20 mM) for 15 min[6,9] to produce the self-assembled monolayers.

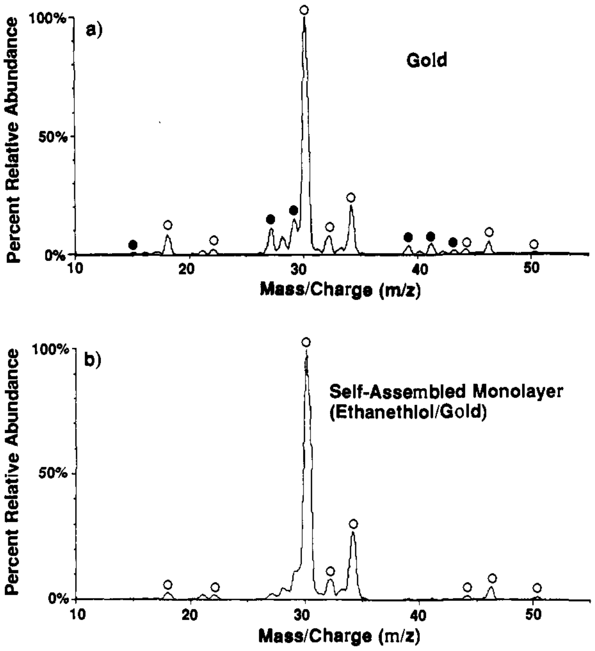

Figure 1. (a) Product ions detected when mass-selected $CD_3CD_2OD^{\bullet+}$ (m/z 52) collides with a gold surface at a collision energy of 60 eV. (b) Product ions detected when mass-selected $CD_3CD_2OD^{\bullet+}$ collides with an ethanethiol/gold surface at a collision energy of 60 eV. For both a and b, the peaks labeled with open circles are direct dissociation products of ethanol-d_6. The peaks labeled with filled circles are sputtered hydrocarbon ions, not dissociation products of ethanol-d_6.

Several processes can occur when mass-selected polyatomic ions collide with a surface at collision energies in the electronvolt range.[12-22] These include *surface-induced dissociation* (SID) of the mass-selected projectile ion,[13-18] *chemical reaction* between the projectile and surface adsorbates,[13,19,20] and *chemical sputtering*,[13,16,21] i.e., charge exchange between the mass-selected projectile ion and surface adsorbates with the release of ionized adsorbates from the surface. Previously, collisions of mass-selected polyatomic ions with metal surfaces have been investigated primarily by using surfaces that have not been intentionally modified (e.g., stainless steel, gold, silver, and platinum).[13-16,19-22] These reports suggest, however, that adventitious hydrocarbons (e.g., from pump oils) are present at the metal surfaces and that the hydrocarbon adsorbates at the surface can be ionized by charge transfer from certain projectile ions, such as perfluorinated molecules. The spectra recorded in these cases contain chemical sputtering peaks corresponding to typical hydrocarbon ions (CH_3^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, ...) and cannot be attributed simply to fragmentation of the incoming projectile ion.

The presence of chemical sputtering products along with diagnostic fragmentation products is illustrated for collision of ethanol-d_6 with an untreated gold surface (Figure 1a). The spectrum indicates product ions that are clearly surface-induced dissociation products of $C_2D_5OD^{\bullet+}$ because they contain combinations of C, D, and O. However, it also shows $C_nH_m^+$ ions that indicate that charge exchange has occurred from the projectile ion to the hydrocarbon adsorbates, with the release of ionized adsorbates.

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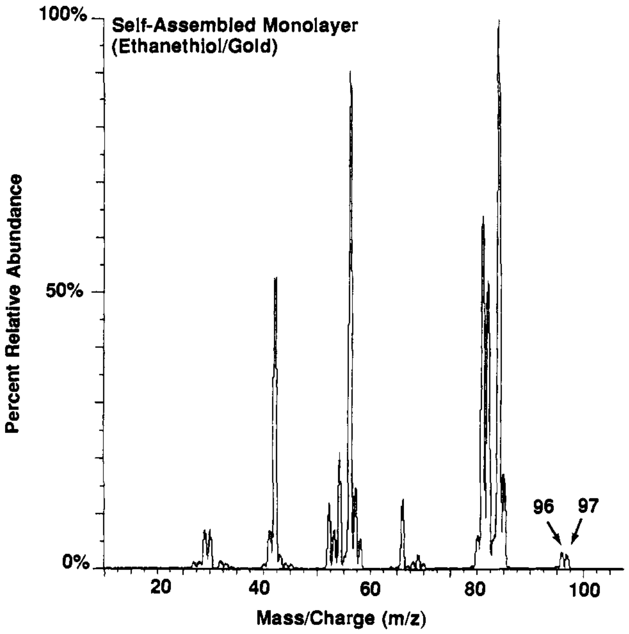

Figure 2. Product ions detected when ionized benzene-d_6 (m/z 84) collides with an ethanethiol/gold surface at a collision energy of 30 eV. The ions higher in mass than the colliding projectile ion are the result of reactions at the surface.

Figure 1b illustrates that the use of a self-assembled monolayer of ethanethiol on gold, rather than bare gold, greatly reduces chemical sputtering. This spectrum was obtained by allowing ionized ethanol-d_6 (m/z 52) to collide with an ethanethiol/gold surface at a collision energy of 60 eV. The spectrum is simple and consists mainly of peaks corresponding to combinations of C, D, and O, as expected from fragmentation of a $C_2D_6O^{\bullet+}$ ion.[23,24] For ethanethiol-modified gold, this decrease in chemical sputtering was observed for time periods as long as 1 month, even after the surface had been bombarded with numerous projectile ions (alcohols, benzene, pyridine, peptides) and continuously bathed with isobutane (10^{-5} Torr) for 72 h. When long-chain alkanethiols, such as octadecanethiol, are used to prepare the self-assembled monolayers, sputtering products ($C_nH_m^+$) are detected in the surface-induced dissociation spectrum of ethanol-d_6, although they are of decreased abundance compared to the sputtering products obtained from untreated gold.[25] In future work, a series of alkanethiols of varying chain length or deuterated[26] alkanethiols will be used to determine whether the sputtering products result solely from ionization and fragmentation of the long alkanethiolate chain or also from ionization and fragmentation of hydrocarbons adsorbed on the monolayer surface.

Although *chemical sputtering* is greatly reduced at the ethanethiol-modified gold surface, *ion/surface reactions*[19] such as addition of hydrogen or methyl still occur, as they do from the untreated metal surfaces on which hydrocarbons are adsorbed. This type of reaction would account for the product ion of m/z 21 (HD_2O^+) in Figure 1b.[24] Another example of an ion/surface reaction product is the ion of m/z 91 that results upon collision of ionized benzene with untreated metal surfaces. This product has been suggested[19,20] to arise from addition of methyl followed by loss of H_2. Our results for benzene-d_6 both on untreated metal surfaces and on alkanethiol surfaces (Figure 2) support this view, because ions corresponding to addition of methyl followed by loss of H_2 and loss of HD are detected (m/z 97 and m/z 96, respectively). For the self-assembled monolayer surfaces of ethanethiol on gold, *ion/surface reaction products* are detected even when *chemical sputtering* products are not detected. This suggests that the ion/surface abstraction reactions may involve the alkanethiolate.[26]

The reactions between self-assembled monolayers and ions with kinetic energies in the electronvolt range may be related to neutral molecular beam work at single crystal surfaces,[27] since our reactions of projectile *ions* with alkanethiol-treated surfaces show a similar dependence on collision energy (i.e., highly unsaturated adducts containing an increasing number of carbon atoms are detected as the collision energy is increased). By using model systems in which the exposed tail group (terminal functional group remote to the sulfur) of the alkanethiolate is varied (e.g., substitute OH for CH_3),[28] it should be possible to systematically explore both charge transfer and reactive ion/surface collisions as a function of projectile ion, collision energy, and surface type. These experiments could be useful in the characterization of both projectile ion and surface properties.[26]

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(23) On the basis of comparison of the ionic products formed from both ethanol and ethanol-d_6, the major fragmentation pathways indicated in Figure 1 correspond to (i) α-cleavage by methyl radical loss (product ion at m/z 34; CD_2OD^+) and (ii) formation of $C_2D_3^+$ (m/z 30).

(24) Ions of odd m/z ratios (21, 29, 33) that do not decrease in abundance when results from the untreated gold surfaces are compared with those from the self-assembled monolayer on gold are ascribed to dissociation of an initial H addition product, $(CD_3CD_2OD + H)^+$, or to H/D scrambling at the surface.

(25) Projectile ions, such as CF_3^+, with a strong propensity for charge transfer to hydrocarbon adsorbates, produce sputtering spectra even on the ethanolthiol/gold surface. However, the total ion current detected is significantly lower than that produced when CF_3^+ is allowed to collide with adventitious hydrocarbons on a metal surface.

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Use of Intramolecular Coulombic Interactions To Achieve "Impossible" Reactions. Photochemical Cleavage of 4-Nitrophenyl Ethers

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Reactive intermediates electronic distribution largely determines the outcome of a chemical or photochemical reaction. Therefore, its coulombic disturbation can lead to previously unknown processes of wide importance. This approach has been tested with success in the present work achieving the photoreductive cleavage of some 4-nitrophenyl ethers, circumventing the spin regioconservation principle.[1]

The reductive cleavage of diaryl ethers and alkyl aryl ethers is well-known.[2] Nevertheless 4-nitrophenyl ethers are not active in this kind of reaction.[1,3-5] We advanced that by altering (through coulombic interactions)[6] the electronic density of the

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