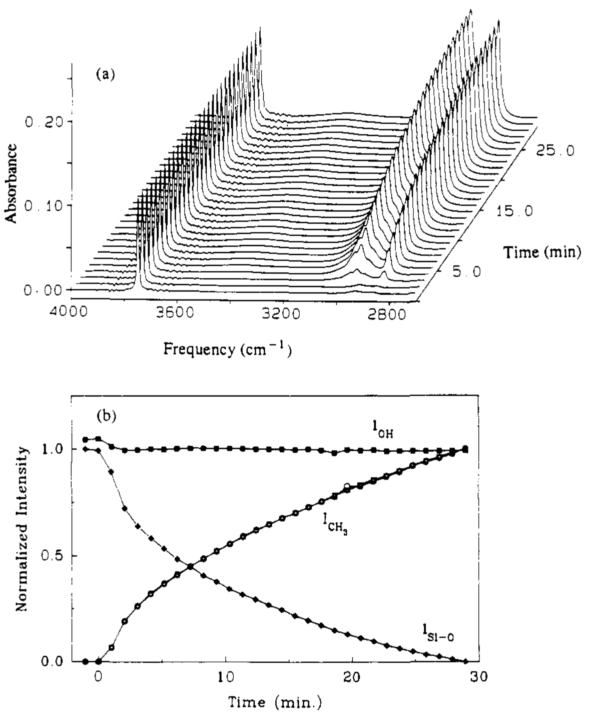
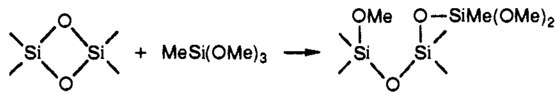


Figure 1. Infrared spectra recorded as a function of time upon exposure of a dehydroxylated silica surface to 4 mTorr of methyltrimethoxysilane at 330 K (a). Intensities of the methoxy CH_3 (asym: Δ, 2960 cm^{-1}; sym: ▽, 2978 cm^{-1}), $SiCH_3$ (asym: ○, 2978 cm^{-1}), Si–O (◆ ~906 cm^{-1}), and O–H (■, 3749 cm^{-1}) stretching vibrations normalized to 1 plotted as a function of time (b).

as shown by the data in Figure 1a,b. We have also found that the reactivity of the silica surface toward MTMSi *decreases* with increasing concentration of surface hydroxyl groups and *increases* with the severity of the dehydroxylation.[10] These results provide unequivocal evidence that alkoxysilanes can react directly with the highly strained rings on the dry silica surface.

The products of this reaction should be



(3)

by analogy with the reactions of water and methanol with these same highly reactive sites.[2,3,5] We expect cleavage to occur at one of the Si–O bonds of the MTMSi[11] by reaction of the basic oxygen of the adsorbate with an electron-deficient (and therefore highly Lewis acidic) surface silicon site.[5,12] This leaves two stable adsorbates: $MeSi(OMe)_2O$ and MeO. The driving force for this reaction must be the release of the ring strain energy since the bonds in the resulting siloxane and alkoxide products should be the same as those in the incident MTMSi (the vibrational spectrum of the products is virtually identical to that of the gas-phase reactant[10]). No additional surface chemistry is taking place since the intensities of all of the hydrocarbon stretching vibrations increase at an identical rate (Figure 1b).

The surface alkoxides and alkylsiloxanes resulting from the reaction in eq 3 are thermally stable: the surface can be heated to 600 K with minimal loss in intensity of the infrared bands.[10] These reaction products are also stable in the presence of water vapor ($\lesssim$1 Torr) at 330 K.[10]

Finally, we have explicitly tested for the reactivity of strained siloxane bonds with several of the R′ groups found in conventional silane coupling agents. We find no significant adsorption of either mercaptans (propanethiol) or epoxides (propylene oxide) under our typical experimental conditions (4 mTorr gas pressure, 330 K sample temperature, 30 min).[13] Thus, these groups are still free to bind into the polymer network.

In conclusion, this work provides a new mechanism by which silane coupling agents can bond to silica surfaces: the nucleophilic attack of an alkoxysilane on a highly strained siloxane ring of the substrate.[14] The extent of this reaction scales *inversely* with the surface hydroxyl concentration and *increases* with the dehydroxylation temperature (and therefore the number of strained siloxane bonds), explicitly showing that surface hydroxyl groups are *not* involved in the reaction. The use of this novel concept to actually improve polymer–surface adhesion remains to be exploited.

Acknowledgment. We thank E. A. Chandross for several helpful discussions and R. W. Filas for the loan of many of the alkoxysilanes used in this study.

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(12) The Lewis basic surface oxygen atoms may also be playing a role in the reaction, although it is expected to be small.[5] In either case, the products are the same.

(13) In addition, previous studies have shown that neither vinyl (ethylene) nor methyl (methane) groups are reactive toward the strained siloxane bonds found on dehydroxylated silica surfaces.[3]

(14) The dissociative adsorption of alkoxysilanes is *not* limited to trifunctional adsorbates, as we have observed a similar series of vibrational spectra after exposing a clean, dehydroxylated silica surface to 4 mTorr of bifunctional dimethyldimethoxysilane and methyldimethoxysilane and monofunctional trimethylmethoxysilane at 330 K. Ethoxysilanes (including methyltriethoxysilane and trimethylethoxysilane) and silanols (triethylsilanol) are also effective at cleaving strained Si–O–Si bonds. All of these adsorbates have thermal and hydrolytic stability similar to that of MTMSi.[10]

Effect of Adsorbate Coverage and Ion Beam Exposure Time on Reactive Ion–Surface Collisions: $C_5H_5N^+$ Reactions with C_5D_5N/Ag(111)

Qinyuan Wu and Luke Hanley*

University of Illinois at Chicago
Department of Chemistry, m/c 111
Chicago, Illinois 60607-7061

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Much experimental effort has been applied to the study of the scattered ions which are produced in molecular ion–surface collisions.[1-12] These experiments have been developing surface-induced dissociation as a practical method of fragmenting organic ions in tandem mass spectrometry and have sought to understand on a fundamental level both dissociative and reactive ion–surface collisions. However, most experiments studying molecular ion–surface interactions have been limited by the lack of well-characterized surfaces and/or the ability to control in situ the adsorbates under ultrahigh vacuum (UHV) conditions. By application of UHV surface science methods to the study of reactive ion–surface collisions for the pyridine/Ag(111) system, it is shown here that scattered ion yields can be strongly dependent

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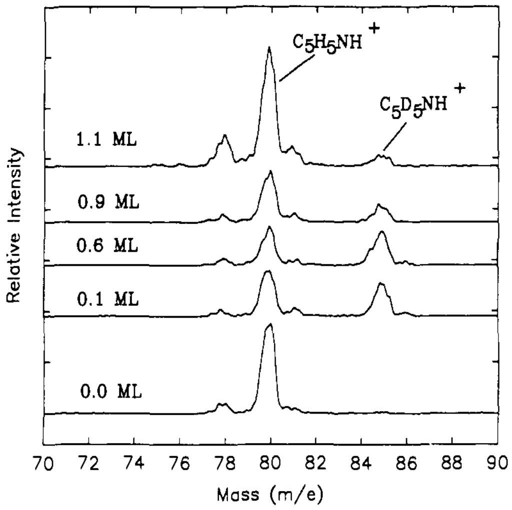

Figure 1. Scattered ion spectra resulting from 32-eV $C_5H_5N^+$ (79 *m/e*) collisions with clean and C_5D_5N-coveraged Ag(111) surfaces at 100 K. Initial C_5D_5N coverages are given in monolayers (ML). Both $C_5H_5NH^+$ and $C_5D_5NH^+$ intensities vary with initial adsorbate coverage.

upon adsorbate coverage and that this coverage can be altered during the time scale of the experiment by primary ion bombardment.

The UHV chamber used here is equipped with an energy- and mass-selected ion beam and has a base pressure of 3×10^{-10} Torr with the electron impact ion source running. Scattered ions were collected at 90° with respect to the incident beam by a quadrupole mass spectrometer set to pass 3 ± 2 eV ions. A 10 ± 2 nA/cm^2, 32 ± 2 eV beam of $C_5H_5N^+$ was directed onto the Ag(111) surface ($T_{surface} = 100$ K) at an incident angle of 55° off normal. The Ag(111) crystal was aligned and polished to within 0.3° and then cleaned by 500-eV Ar^+ sputter–anneal cycles until Auger electron spectra were free of elemental impurities and a sharp hexagonal pattern was obtained from low-energy electron diffraction. The monolayer (ML) coverages of pyridine-d_5 were determined by 2 K/s thermal desorption spectroscopy (TDS) and infrared reflection absorption spectroscopy. Pyridine has been shown previously to chemisorb weakly and nondissociatively on the Ag(111) surface and is completely desorbed when the crystal is heated above 350 K.[13-18]

Scattered ion mass spectra from 70 to 90 *m/e* are shown in Figure 1: Both the incoming $C_5H_5N^+$ ions (79 *m/e*) and the sputtered pyridine-d_5 (84 *m/e*) abstract hydrogen to form $C_5H_5NH^+$ (80 *m/e*) and $C_5D_5NH^+$ (85 *m/e*), respectively. The intensities of $C_5H_5NH^+$ and $C_5D_5NH^+$ both depend upon the initial adsorbate coverage. The 78 *m/e* peak most likely results from loss of H_2 from the $C_5H_5NH^+$ to form $C_5H_4N^+$ whereas the 81 *m/e* peak results predominantly from pickup of a D atom from the adsorbate.

Various experiments indicated that the absence of $C_5H_5N^+$ in the scattered ion spectra off clean Ag(111) is attributable to its thermodynamically driven perference to pick up a H atom at the surface:[1] Electrostatic reflection of the $C_5H_5N^+$ ions into the quadrupole without surface collision yielded mass spectra which were over 90% 79 *m/e* ions, indicating that the H atom addition otherwise observed occurs on the surface. Addition of a D atom occurs following $C_5D_5N^+$ surface collisions with either a pyridine-d_5 layer at 100 K or the nominally clean surface at 650 K. It is clear that addition of a D or H atom can derive from either adsorbates on the surface or fragmentation of the ion beam itself.[19] H atom coverages as low as 10^{-4} ML have been previously observed to lead to proton transfer to hyperthermal beams of a N-containing cyclic organic.[20]

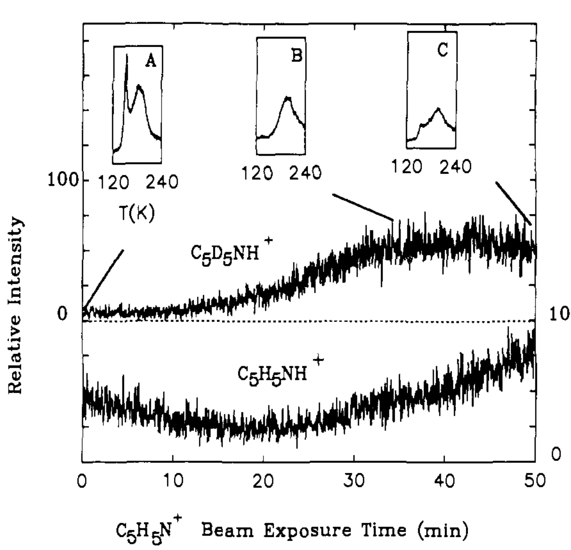

Figure 2. Time dependence of $C_5H_5NH^+$ (80 *m/e*) and $C_5D_5NH^+$ (85 *m/e*) scattered ions when 32-eV $C_5H_5N^+$ bombards Ag(111) covered with 1.1 ML of C_5D_5N adsorbate at 100 K. The inset thermal desorption spectra of C_5D_5N (84 *m/e*) show that the C_5D_5N adsorbate is sputtered off the surface by the incident ion beam.

Figure 2 shows that $C_5H_5NH^+$ and $C_5D_5NH^+$ ion signals from the 1.1 ML pyridine-d_5 covered surface change with the incident $C_5H_5N^+$ exposure time. Thermal desorption spectra (TDS) of C_5D_5N (84 *m/e* peak) for the unexposed surface (0 min in A) and ion beam exposed surface (35 min in B and 50 min in C) shown in the inset boxes indicate a significant adsorbate sputtering. Each incident ion leads to the disappearance of 2 ± 1 adsorbed pyridine molecules, predominantly by desorption and also by dissociation.[21] Each spectrum in Figure 1 was collected in less than 5 min to avoid ion beam exposure effects.

As the pyridine coverage drops from 1.1 to 0 ML, the surface work function increases ~1.8 eV.[22,23] This may explain the increases in the $C_5D_5NH^+$ signal from 10 to 35 min and the $C_5H_5NH^+$ signal from 10 to 50 min since a higher work function leads to less neutralization of scattered ions by the metal surface. The decreased numbers of adsorbed C_5D_5N molecules available for sputtering may offset the continued work function increase above 35-min exposure, leading to the slow decrease in the $C_5D_5NH^+$ signal.[24]

In conclusion, it has been demonstrated that the scattered ion yields resulting from $C_5H_5N^+$ collisions off clean and pyridine-d_5-covered Ag(111) depend strongly upon the adsorbate coverage and the ion beam exposure time. In particular, sputtering of the

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adsorbate leads to formation of $C_5D_5NH^+$ ions which can be nearly as intense as the scattered $C_5H_5NH^+$ ions. Furthermore, primary ion fluxes $>10^{13}$ cm^{-2} lead to observable changes in the scattered ion signal; this ion flux is similar to that which defines the boundary between the static and dynamic regimes of secondary ion mass spectrometry.[25]

Acknowledgment. The authors acknowledge financial support by the University of Illinois at Chicago, the National Science Foundation, and the donors of the Petroleum Research Fund. The authors thank Mike Trenary for many helpful discussions.

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Fullerene Self-Assembly onto $(MeO)_3Si(CH_2)_3NH_2$-Modified Oxide Surfaces

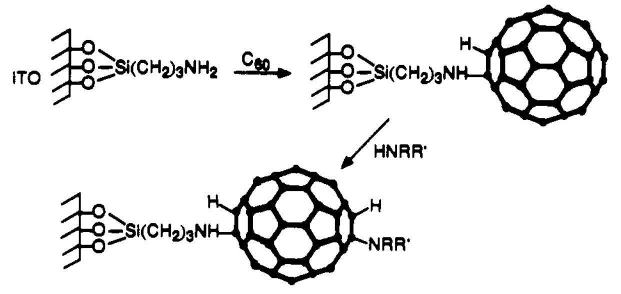
Kaimin Chen, W. Brett Caldwell, and Chad A. Mirkin*,†

Department of Chemistry
Northwestern University
Evanston, Illinois 60208

Received December 2, 1992

Physisorbed, multilayer fullerene films formed via Langmuir-Blodgett (LB) techniques,[1] solution evaporation,[2] and thermal evaporation of solid-phase fullerenes[3] have exhibited interesting mechanical, electrical, electrochemical, and optical properties. Developing synthetic methodology for the self-assembly of fullerenes into organized, *covalently bound* two-dimensional structures is the first step toward developing robust, rationally designed mono- and multilayered structures from fullerenes. Herein, we report the first self-assembled monolayer (SAM) of C_{60}, its spectroscopic and electrochemical characterization, and initial chemistry with respect to its further modification, Scheme I.[4] The latter demonstration is significant since it illustrates the potential for growing covalently bound three-dimensional structures from fullerenes in a stepwise fashion via the self-assembly process.[5]

Scheme I. Synthetic Scheme for the Modification of Oxide Surfaces with C_{60}[a]



[a] SAMs of C_{60} may be further modified with amine reagents, Table I.

Table I. Contact Angles for H_2O

surface	contact angle, deg
base-treated ITO	20
ITO treated with $(MeO)_3Si(CH_2)_3NH_2$	46
SAMs of C_{60}	72
$HN(CH_3)CH_2CH_3$	63
$H_2N(CH_2)_2CH_3$	60
$HN(CH_3)CH_2CH_2OH$	42
p-ferrocenylaniline	67

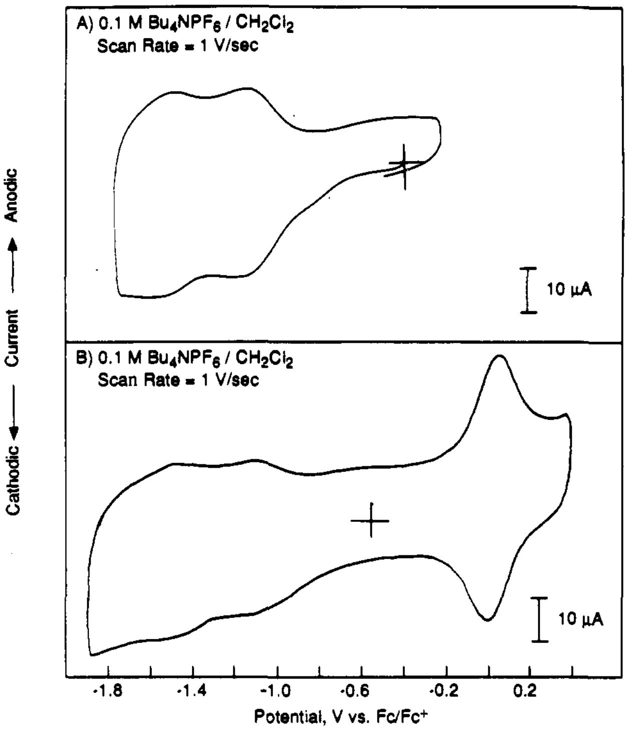


Figure 1. (A) Cyclic voltammetry of a SAM of C_{60} on $(MeO)_3Si(CH_2)_3NH_2$-treated ITO (0.5 cm^2) in CH_2Cl_2/0.1 M Bu_4NPF_6. (B) Cyclic voltammetry of a SAM of C_{60} on $(MeO)_3Si(CH_2)_3NH_2$-treated ITO (0.8 cm^2) after refluxing in a 5 mM benzene solution of *p*-ferrocenylaniline for 2 days.

Two approaches may be taken towards fullerene self-assembly onto surfaces. Either a fullerene can be modified in solution with functionalities that allow for self-assembly, or a surface may be chemically modified with a reagent that undergoes a bond-forming reaction with a fullerene in solution. Herein, we report success via the latter approach. Others have shown that primary and secondary amines undergo N–H addition reactions across the C=C bonds in C_{60} which fuse two six-membered rings.[6] Accordingly, the immobilization of $(MeO)_3Si(CH_2)_3NH_2$ onto oxide substrates[7] results in surfaces that undergo spontaneous reactions

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* Address correspondence to this author.

† Beckman Young Investigator and Dreyfus Distinguished New Faculty Awardee.

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