

Site-Selective Abstraction in the Reaction of 5–20 eV O⁺ with a Self-Assembled Monolayer

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Steric effects exert significant control over many chemical reaction pathways, yet it remains an experimental challenge to study a bimolecular reaction under conditions where one reactant encounters the other with a specific angle of attack. In both gas-phase and solution environments, the relative orientation of two approaching molecules is isotropic. On the other hand, when a beam of reactants is targeted at an array of molecules adsorbed to a solid surface, the approach geometry is severely constrained. In the present study, an O⁺ beam is directed at an alkanethiolate self-assembled monolayer (SAM), and the relative rate of hydrogen abstraction is measured as a function of the position, along the hydrocarbon chain, from which the hydrogen atom is removed.

When a hyperthermal energy (3–500 eV) particle strikes a surface, it can activate a wide variety of chemical process at the gas/surface interface, including abstraction, elimination, insertion, implantation, and oxidation.¹ In low-earth orbit (LEO), a spacecraft is continuously exposed to a flux of energetic neutral atoms/molecules, ions, electrons, and photons that threaten to erode and degrade the vehicle's external surfaces. The most abundant neutral and ionic species in LEO are O and O⁺; not only are they chemically reactive, but they typically impact the RAM surfaces of a spacecraft with 5 eV of translational energy. Next-generation satellites could be partially fabricated with lightweight, low-cost polymeric materials, if a strategy is developed to inhibit the degradation of organic films in the corrosive environment of LEO.

Alkanthiolate molecules bound to Au(111) comprise the most thoroughly characterized SAM system.^{2,3} The densely packed, stand-up phase serves as a model for polymeric films such as polyethylene. Studying the reaction of hyperthermal energy O⁺ with a hydrocarbon SAM may uncover some of the erosion mechanisms suffered by polymers in LEO.

Qin et al. monitored ion-induced modifications of a decanethiolate SAM by employing X-ray photoelectron spectroscopy (XPS) in vacuo at different stages of exposure to 5 eV O⁺.⁴ The etch rate caused by 5 eV O⁺ was four orders-of-magnitude higher than Fairbrother and co-workers observed using only thermal oxygen atoms.⁵ George and co-workers utilized an oxygen plasma to erode a decanethiolate SAM and concluded that oxygen ions, rather than the majority neutral species in the plasma, were principally responsible for the film's decay.⁶

Hydrogen abstraction near the vacuum/SAM interface is a major pathway by which SAMs are degraded. Once a chain is compromised, further reactions with O⁺ can quickly consume the remaining molecule.⁷ Of interest is the precise location where an impinging O⁺ will first remove a hydrogen atom from the hydrocarbon chain. Gu and Wysocki found that 30 eV pyrazine and acetone ions preferentially abstract hydrogen atoms from the terminal methyl group of an isotopically labeled Langmuir–Blodgett film.⁸ To

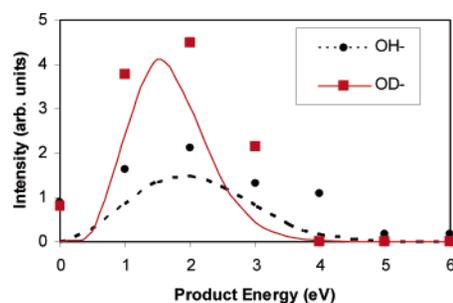


Figure 1. Outgoing energy distributions of scattered OH⁻ and OD⁻ products resulting from 5 eV O⁺ reacting with C-12 SAM (incident angle = 45°; exit angle = 65°). Deconvolution of the instrument response function from the experimental data (solid points) yields corrected energy distributions (curves).

determine the detailed site-dependence to abstraction in the present system, we utilize labeled SAMs in which all the hydrogen atoms bound to the 10th, 11th, or 12th carbon atom of 1-dodecanethiol are selectively substituted with deuterium atoms.

The three isotopically labeled dodecanthiols (C-10, C-11, and C-12) are synthesized through methods described in Supporting Information. An isotopomeric SAM is prepared by immersing a Au(111) crystal in the corresponding 1 mM dodecanethiol ethanolic solution for 24 h. The surface is transferred to a customized ultra-high vacuum (UHV) chamber where it is held at ground potential and room temperature.⁹ A monoenergetic beam of mass-filtered O⁺ is directed at the SAM, 45° to the surface normal. Incident O⁺ efficiently neutralizes close to the SAM. When abstraction occurs, the nascent OH species adopts a partial negative charge on the low work-function surface ($\Phi = 3.7$ eV).¹⁰ If the product departs rapidly from the surface, there is a finite probability that it will escape nonadiabatically and appear as OH⁻. For each of the three isotopomeric SAMs, the yields of OD⁻ and OH⁻ are compared.

Figure 1 shows the energy distributions of scattered OH⁻ and OD⁻ products resulting when 5 eV O⁺ is incident on a C-12-labeled SAM. The detector is positioned 65° from the surface normal at the angle where the scattered signal is at its maximum. The overall intensity of OD⁻ is approximately double that of OH⁻. This result indicates that 5 eV O⁺ preferentially abstracts D from the labeled position (the topmost carbon of the SAM) in comparison to all other unlabeled H positions combined.

The integrated intensities, I_{OH} and I_{OD} , are calculated by integrating the OH⁻ and OD⁻ signal intensities, respectively, over all outgoing energies depicted in Figure 1. Equation 1 defines P_{OD} , the percentage of all abstracted H/D that originates from the labeled position in the SAM.

$$P_{OD} = \frac{I_{OD}}{I_{OH} + I_{OD}} \times 100\% \quad (1)$$

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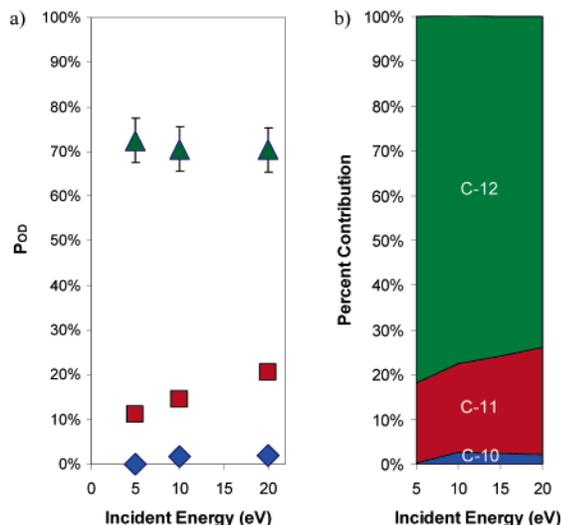


Figure 2. (a) Dependence of P_{OD} on the incident O^+ energy and on the labeled position (triangles, C-12; squares, C-11; diamonds, C-10) of 1-dodecanethiol. (b) Relative contribution of scattered hydroxide signal, arising from abstraction at the top three carbon atoms, as a function of the incident O^+ energy. The latter data have been corrected for velocity-dependent charge-transfer rates along the outgoing trajectory.

P_{OD} depends strongly on the O^+ dose, because ion-induced damage of the SAM alters the layer's structure and chemical composition. Consequently, we present only P_{OD} values recorded at low doses ($<10^{13}$ ions/cm²) before the SAM becomes damaged. Figure 2a shows the dependence of P_{OD} on the incident O^+ energy for SAMs labeled at the C-10, C-11, and C-12 positions. P_{OD} is vanishingly small for abstraction originating from C-10 and presumably is negligible for positions below C-10. Although experimental protocols were employed to minimize contamination from any unlabeled molecules, the sum of P_{OD} contributions for C-10, C-11, and C-12 is 7–16% less than the expected value of 100%. One possible explanation for this deficit is a kinetic isotope effect, through which D is abstracted less readily than H, all else being equal. Classical trajectory calculations predict only a 3.5% kinetic isotope effect for $O(^3P)$ abstracting H versus D from propane;¹¹ hence, there is little reason to believe that a kinetic isotope effect will adequately account for the missing intensity in the present experiment. A more plausible explanation for the shortfall in the OD^- signal relative to the OH^- signal involves the nonadiabaticity of charge transfer. Figure 1 illustrates that OH^- leaves the surface with slightly more kinetic energy than does OD^- . Overall, the mean velocity of OH^- appears to be $\sim 10\%$ faster than that for OD^- . Consequently, a nascent OD^- product is more likely to adiabatically transfer its electron back to the surface than is a quicker OH^- product. As described in Supporting Information, the data in Figure 2a can be corrected for charge transfer along the outgoing trajectory to yield the relative contributions to abstraction shown in Figure 2b. These adjusted contributions sum to $100 \pm 3\%$. At least 3/4 of the scattered abstraction signal arises from the terminal methyl group in the SAM, and $<2.5\%$ originates from H/D bonded to the C-10 position. This site preference is strongest at low incident energies.

Troya and Schatz developed a hybrid quantum mechanical/

molecular mechanical model to realistically simulate the reaction of 5 eV $O(^3P)$ with an octanethiol SAM.¹² A comparison between the simulation of neutral scattering at 45° incidence and our ion-scattering experiment is not completely unreasonable, because in the latter, the incident $O^+(^4S)$ ions neutralize to become $O(^3P)$ immediately prior to impact with the SAM.¹³ The simulations predict that hydrogen abstraction is the dominant reaction channel and that abstraction occurs only at the top three carbon atoms in an alkanethiol chain, in qualitative agreement with the results presented in Figure 2b. Furthermore, the trajectories show a 4-fold preference for abstraction from the methylene rather than the methyl hydrogens, when $O(^3P)$ approaches the SAM in the direction opposite to the SAM tilt orientation. In contrast, the experimental data indicate a much stronger preference for abstraction occurring from primary rather than secondary carbon sites. Although the experiments cannot resolve the scattering from a single orientational domain, the discrepancy in site selectivity between simulation and experiment is quantitatively significant. The simulations track only the adiabatic channel leading to neutral OH, whereas the experiment detects OH^-/OD^- emerging nonadiabatically. The nascent OH^- product formed deep within the SAM layer will have a difficult time retaining its negative charge as it passes between the chains on escape. Hence, the detection of only negative ions in the experiment may weight the distribution shown in Figure 2b in slight favor of abstraction sites close to the vacuum interface.

In summary, the reaction of hyperthermal (5–20 eV) O^+ with an isotopically labeled self-assembled monolayer demonstrates that hydrogen abstraction is strongly site-specific. At 5 eV incident energy, abstraction of hydrogen from the terminal methyl group is favored by a factor of 4.6 over abstraction from the methylene group just below it.

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Supporting Information Available: Synthesis procedures and characterization of C-10-, C-11-, and C-12-labeled 1-dodecanethiols and charge transfer corrections to anionic product yields (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) $O(^3P)$ is formed rather than $O(^1D)$ or $O(^1S)$, because the quartet to singlet spin-flip would require an improbable two-electron rearrangement.

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