

Ion-Surface Reactions Involving Isotopically Labeled Langmuir-Blodgett Films

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Recent research on low-energy (tens of eV) ion-surface reactions^{1–10} has utilized self-assembled monolayer surfaces (SAMs) of alkanethiols or their substituted derivatives on gold as well-defined model surfaces of varying chemical composition.^{2–3,5–8} For example, perdeuterated SAMs were used to confirm the occurrence of alkyl and hydrogen (deuterium) abstraction from target surfaces by projectile ions as well as to confirm the chemical compositions of ion-surface reaction products.^{2,3,5} The research described in this Communication utilizes isotopically labeled Langmuir-Blodgett (L-B) films as the reaction partners of low-energy polyatomic ions and shows that predominantly the terminal groups or atoms of L-B films react with the incoming ions. The information obtained from *low-energy ion-surface reactions* is distinct from the sputtering results that are obtained with the established method of kiloelectronvolt ion-surface collisions (i.e., secondary ion mass spectrometry, SIMS¹¹).

Various mechanisms for alkyl and/or hydrogen abstractions from surfaces have been proposed in the literature, including sputtered ion mechanisms for alkyl abstractions^{2,6,12,13} or direct abstractions via the Eley–Rideal mechanism.^{5,10,14} In order to improve understanding of the mechanisms of alkyl abstractions as well as to explore the potential of ion-surface reactions for surface characterization, it is desirable to perform the ion-surface reactions on surfaces that are isotopically labeled only at the terminal methyl groups. Unfortunately, the materials for preparation of the appropriately labeled alkanethiolate SAMs are not available, so other alternatives were considered.

Four different Langmuir-Blodgett (L-B)¹⁵ films, another type of well-studied ordered organic surface, were chosen for this study. The L-B films were prepared from n-octadecanoic (stearic) acid (99%, Aldrich) or stearic acids isotopically labeled

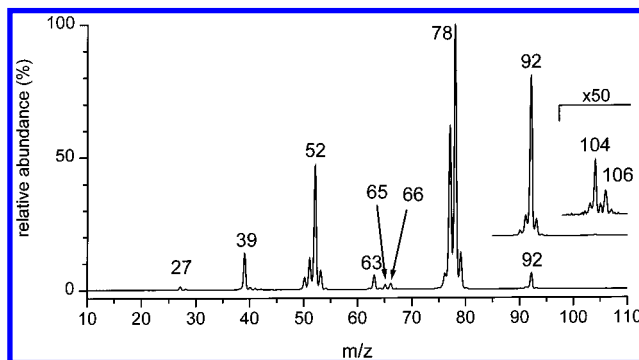


Figure 1. Product ion spectrum acquired when benzene molecular ions (m/z 78) collide with the three-layer L-B film of $^{13}\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ at 30 eV collision energy.

(Cambridge Isotope Lab., MA) either at the terminal methyl group, $^{13}\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ (^{13}C , 99%) or $\text{CD}_3(\text{CH}_2)_{16}\text{COOH}$ (D, 98%), or along the whole chain, $\text{CD}_3(\text{CD}_2)_{16}\text{COOH}$ (D, 98%). The L-B films were prepared in a NIMA (Type-611, England) Langmuir-Blodgett trough. The subphase used was 5×10^{-4} M Cd^{2+} (CdCl_2) in pure water (18M Ω ·cm, NANOpure). Stearic acids were spread onto the aqueous subphase as a 10^{-3} M solution in HPLC grade chloroform. L-B films of stearate were dipped onto a clean evaporated gold surface at a dipping speed of 3 mm/min with a compressing pressure of 32 mN/m. All films used in this study are three-layer Y-type¹⁵ with methyl groups as the terminal groups. The instrument used for investigating ion-surface reactions is a custom tandem mass spectrometer equipped with two Extrel (Pittsburgh, PA) 4000u quadrupoles set at 90° with the surface bisecting the two quadrupoles at roughly 45°. The organic projectile ions were generated by an electron impact ionization (EI) source, mass selected by the first quadrupole analyzer, and then collided with the L-B films. The product ions were analyzed by the second quadrupole.

The L-B films perform well as collision targets for surface-induced dissociation (SID^{1,6,8,16b}) in MS/MS with efficiency and energy deposition characteristics similar to those recorded⁵ for SAM surfaces such as $\text{CH}_3(\text{CH}_2)_{17}\text{SAu}$. However, this paper will focus on the ion-surface reaction products formed with isotopically labeled L-B films and not on the performance for SID. The product ion spectrum recorded when benzene molecular ions (m/z 78) collide at 30 eV kinetic energy with the $^{13}\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ L-B film is shown in Figure 1. The ion at m/z 92 in Figure 1 is an ion-surface reaction product corresponding to the abstraction of one carbon unit from the film ($[\text{C}_6\text{H}_6 + ^{13}\text{CH}_3 - \text{H}_2]^+ \rightarrow ^{13}\text{CC}_6\text{H}_7^+$, m/z 92). Its fragments produced by loss of acetylene ($^{13}\text{CHCH}$ or CHCH) are observed at m/z 65 and 66. Figure 2 gives the expanded C_1 adduct ion regions, for four different L-B films, for benzene molecular ion (m/z 78, the left column) or benzene- d_6 molecular ion (m/z 84, the right column). When the terminal CH_3 - group on the L-B film is ^{13}C -labeled, the product peaks shift to higher mass by 1 amu (Figure 2 a vs b, e vs f). For example, the peak at m/z 91 (C_7H_7^+ , Figure 2a or as reported before^{1,5,17}) for an unlabeled surface shifts to m/z 92 ($^{13}\text{CC}_6\text{H}_7^+$, Figure 2b) for the $^{13}\text{CH}_3$ - $(\text{CH}_2)_{16}$ - film. Furthermore, both $\text{CD}_3(\text{CH}_2)_{16}$ - and $\text{CD}_3(\text{CD}_2)_{16}$ - L-B films give similar ion-surface reaction patterns (Figure 2c,d,g,h), whether the L-B film is deuterium-labeled at the methyl group or along the whole alkyl chain. C_1 abstractions were also investigated by using two other projectile ions,

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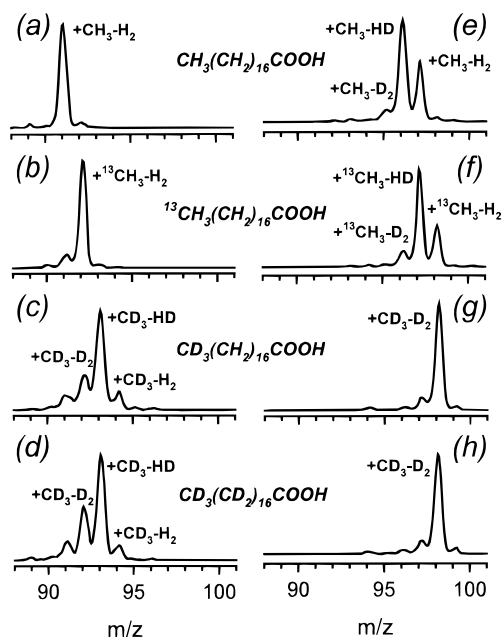


Figure 2. Expanded adduct ion regions for 30 eV collisions of benzene molecular ion (m/z 78, **a–d** in left column) or benzene- d_6 molecular ion (m/z 84, **e–h** in right column) incident on the L-B film of (**a, e**) $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, (**b, f**) $^{13}\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, (**c, g**) $\text{CD}_3(\text{CH}_2)_{16}\text{COOH}$, and (**d, h**) $\text{CD}_3(\text{CD}_2)_{16}\text{COOH}$.

pyrazine (m/z 80) and acetone- d_6 (m/z 64) molecular ions, for which the methyl additions with SAM surfaces have been reported.^{14,18} In Figure 3, portions of the product ion spectra of these two projectiles at 20 eV collision energy on $^{13}\text{CH}_3(\text{CH}_2)_{16}$ - or $\text{CD}_3(\text{CH}_2)_{16}$ - L-B films are shown. In the C_1 adduct ion regions, the predominant peaks correspond to the addition of the terminal methyl group, $^{13}\text{CH}_3$ (Figure 3a,c) or CD_3 (Figure 3b,d). Some minor peaks that appear in the C_1 adduct ion regions of pyrazine spectra can be partially assigned as H loss (m/z 95 in Figure 3c) or D loss (m/z 96 in Figure 3d) from intact $^{13}\text{CH}_3$ or CD_3 adduct ions, respectively.

The experimental results discussed above indicate that predominantly the terminal methyl groups are involved in the C_1 abstractions from these surfaces. At this point, it is unclear whether some minor reaction peaks are due to the involvement of underlying methylene carbons rather than the terminal methyl carbons in the C_1 additions, e.g., the minor peak at m/z 91 vs the predominant peak at m/z 92 with the $^{13}\text{CH}_3(\text{CH}_2)_{16}$ - film (Figure 2b). However, the contribution of adventitious hydrocarbons (e.g., contaminants in the vacuum chamber at 10^{-7} – 10^{-6} Torr pressure or contamination during film preparation) may, at least partially, explain these minor reaction peaks. For example, if benzene- d_6 were to be collided on a “perfect” perdeuterated film, all the reaction products would occur at even m/z values. Therefore, the minor peak at m/z 97 in Figure 2h must be due to adventitious hydrocarbons. The same peak has been previously reported for the perdeuterated SAM surface.⁵ This suggests that the minor peak at m/z 91 in Figure 1b is, at least partially, due to adventitious hydrocarbons.

The C_2 addition products formed by collision of benzene molecular ion with the $^{13}\text{CH}_3(\text{CH}_2)_{16}$ - L-B film are shown in

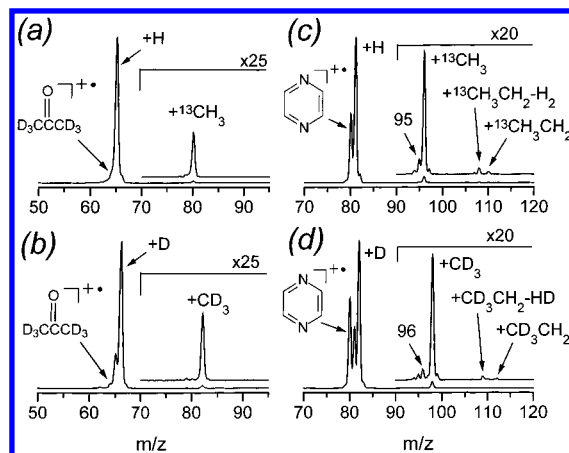


Figure 3. The molecular ion and adduct ion regions of the product ion spectra of acetone- d_6 (m/z 64, **a** and **b**) or pyrazine (m/z 80, **c** and **d**) incident on the L-B film of (**a, c**) $^{13}\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ and (**b, d**) $\text{CD}_3(\text{CH}_2)_{16}\text{COOH}$.

the Figure 1 inset, which was acquired with a higher gain on the electron multiplier detector. Two major peaks corresponding to the C_2 adduct ions occur at m/z 104 and 106. On unlabeled $\text{CH}_3(\text{CH}_2)_n$ - surfaces, the peaks corresponding to the major C_2 adduct ions occur at m/z 103 (C_8H_7^+) and 105 (C_8H_9^+) (spectra not shown). A 1 amu shift to higher mass occurs due to the terminal methyl ^{13}C -label. For pyrazine molecular ion colliding with the $^{13}\text{CH}_3(\text{CH}_2)_{16}$ - L-B film, the two major C_2 adduct ions detected (Figure 3c) correspond to $[\text{C}_4\text{H}_4\text{N}_2 + ^{13}\text{CH}_3\text{CH}_2]^+$ (m/z 110) and $[\text{C}_4\text{H}_4\text{N}_2 + ^{13}\text{CH}_3\text{CH}_2-\text{H}_2]^+$ (m/z 108). Note that predominantly the terminal labeled carbon and one unlabeled carbon, presumably the terminal ethyl group, on the surface are involved in the C_2 additions. No incorporation of two ^{13}C -labeled carbons was detected in C_2 additions, which is consistent with the report that the two carbons in C_2 addition are not from different chains on a mixed SAM surface of $\text{CH}_3(\text{CH}_2)_{15}\text{S-Au}$ and $\text{CD}_3(\text{CD}_2)_{15}\text{S-Au}$.¹⁴

For the $\text{CD}_3(\text{CH}_2)_{16}$ - L-B film, deuterium additions occur as the major H/D addition products by the projectiles (Figure 3b,d). The relatively higher H addition with the $\text{CD}_3(\text{CH}_2)_{16}$ - L-B film of pyrazine versus acetone- d_6 (Figure 3 d vs b) will be investigated by using deuterated pyrazine.

In summary, the range of amphiphilic compounds available for the preparation of L-B films as well as the ease of variation in the numbers of layers suggests that L-B films will serve as a useful complementary set of model organic surfaces, in addition to alkanethiolate SAM surfaces, for the studies of ion-surface interactions at low collision energies. The ion-surface reaction results presented above indicate that predominantly the uppermost groups or atoms are involved in these low-energy ion-surface reactions. This supports the use of low-energy ionic projectiles to probe the uppermost groups or atoms on organic surfaces. Based on the results reported here, mechanisms proposed for alkyl abstractions in the future must account for the fact that predominantly the terminal alkyl groups are involved.

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