

Ion–Ion Collisions Leading to Formation of C–C Bonds at Surfaces: An Interfacial Kolbe Reaction

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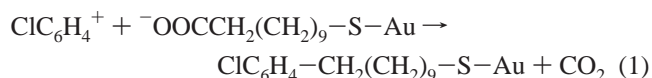
Surface modification in chemically and spatially specific ways is an important technological development.¹ Molecular self-assembly is often used to generate model surfaces to study functionalization and chemical patterning^{2–4} while low energy ion/surface collisions (typically ca. 10–100 eV) show high surface sensitivity and a chemical selectivity that allows modification of surfaces in a particularly straightforward fashion.^{5–8} Ion/surface collisions at these energies have been found to be effective in introducing atoms or small refractory groups, e.g., Br, F, OH, and CN,^{6,9,10} into surfaces. Selective incorporation of more complex molecular species using ion beams remains challenging, although progress is being made as exemplified by the fact that C₃F₅ molecular fragments can be “grafted” into a polystyrene surface.¹¹

Recently we demonstrated that intact polyatomic ions can be deposited into chemically inert SAM surfaces (fluorinated and hydrocarbon SAMs) at very low energy (ca. 10 eV).¹² The SAM matrices efficiently dissipate the kinetic energy and prevent the fragmentation of the deposited ion, allowing the molecular structure of the deposited species to be preserved. As an extension of this work we here select an ionic terminated surface, and gently deliver a polyatomic ion to it, to follow the ion/counterion collision process and seek formation of new covalent bonds. That is, a direct approach is used to create terminally functionalized SAM surfaces by reactive “soft-landing” of ions. The selective conversion of a carboxylate-terminated hydrophilic SAM surface to a phenyl-terminated hydrophobic SAM surface is demonstrated using this strategy.

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An 11-mercaptoundecanoic acid SAM surface¹³ was treated with ammonium hydroxide to convert the terminal free carboxylate to the ammonium salt.¹⁴ This ionic surface was then treated with the gas-phase cation ³⁷CIC₆H₄⁺ (*m/z* 113) (total ion dose ca. 9.0 × 10¹² per 50 mm²) at 12 eV, while a 65 eV Xe⁺ ion beam was used to monitor the surface composition before and after the attempted chemical modification. The Xe⁺ sputtering mass spectrum recorded before ion beam modification showed no peaks in the range of *m/z* 115–180, except for the phthalate contaminant at *m/z* 149, but after modification, a new peak at *m/z* 127 was observable. The chemical composition of the *m/z* 127 peak was verified by treating the ³⁷CIC₆H₄⁺ modified surface with the ³⁵CIC₆H₄⁺ cation under the same conditions (total ion dose ~9.7 × 10¹²). Xenon sputtering then revealed the expected additional feature at *m/z* 125, assigned to ³⁵CIC₆H₄CH₂⁺. The unreacted projectile ions at *m/z* 111 (³⁵CIC₆H₄⁺) and 113 (³⁷CIC₆H₄⁺) were not observed as such upon Xe⁺ sputtering of these modified surfaces, only their reaction products appeared. This is consistent with the previous conclusion^{12a} that small ions such as C₆H₅⁺, without sterically bulky substituents, have poor soft-landing efficiency in hydrocarbon and fluorocarbon SAMs. The present reaction appears to result in the formation of a new functionalized surface with aryl terminal groups, eq 1. The surface modified



by reaction with ³⁵CIC₆H₄⁺ was further characterized ex situ by time-of-flight secondary ion mass spectrometry (TOF-SIMS).¹⁵ This experiment showed the expected peak due to ³⁵CIC₆H₄CH₂⁺ (expected value, *m/z* 125.0158; measured value, *m/z* 125.0142), and also a small peak corresponding to ³⁵CIC₆H₄CH₂CH₂⁺ (expected value, *m/z* 139.0314; measured value: *m/z* 139.0306). The appearance of these product ions supports the conclusion that the intact CIC₆H₄ moiety is covalently bound to the hydrocarbon chain.

Chemical modification of the ammonium salt surface was also performed using other aryl projectile ions. As shown in Figure 1, sputtering analysis of the ammonium 11-mercaptoundecanoate surface after modification by C₆H₅⁺ revealed signals which correspond to C₆H₅CH₂⁺ (*m/z* 91) and C₆H₅CH₂CH₂⁺ (*m/z* 105). Chemical modification of the SAM was also performed using ⁷⁹BrC₆H₄⁺, and subsequent Xe⁺ chemical sputtering analysis showed the formation of ⁷⁹BrC₆H₄CH₂⁺ (*m/z* 169). Collisions of C₆H₅⁺ ions with an untreated 11-mercaptoundecanoic acid SAM surface showed no evidence of new C–C bond formation. The salt surface allows this type of surface chemical modification.

Further evidence for C–C bond formation comes from reactive scattering experiments performed at somewhat higher energies than those discussed so far. In these experiments, C–C bond formation was sought in the scattered ions rather than in the surface itself. Scattering of C₆H₅⁺ at 20 eV from the ammonium salt SAM surface showed the C–C bond formation product, C₆H₅-CH₂⁺ (*m/z* 91). Note that earlier studies showed that closed-shell ions such as C₆H₅⁺ do *not* abstract alkyl groups in reactive collisions with hydrocarbon surfaces.¹⁶ The formation of C₇H₇⁺ by collisions of C₆H₅⁺ in this case again suggests that C–C bond

(13) The preparation of the 11-mercaptoundecanoic acid SAM on gold followed the literature procedure: Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1988**, 105, 4481.

(14) The terminal carboxylic acid of 11-mercaptoundecanoic acid SAM was converted to the ammonium carboxylate by rinsing the SAM surface with concentrated ammonia solution.

(15) 15 keV Ga⁺ time-of-flight secondary ion mass spectrometry analysis was performed using a Charles Evans & Associates TFS series TOF-SIMS instrument (Redwood City, CA).

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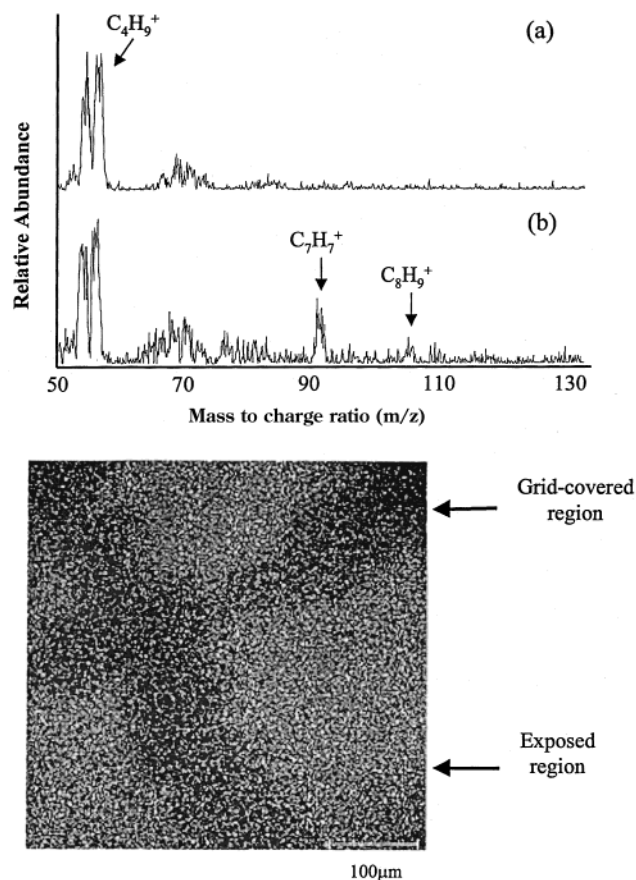


Figure 1. (Top) Scattered ion mass spectra recorded upon collision of 65 eV Xe⁺⁺ ions with the ammonium salt of 11-mercaptoundecanoic acid SAM (a) before and (b) after modification with 14 eV C₆H₅⁺. (Bottom) High-resolution TOF-SIMS C₇H₇⁺ ion image from an ammonium 11-mercaptoundecanoate SAM surface treated with 14 eV C₆H₅⁺ ions while a Ni grid (50 wires/in., wire diameter 0.00 in., 75% transparency) is placed in front of the surface. The bright regions represent higher intensity of the monitored C₇H₇⁺ ions.

formation at the surface is accompanied by facile decarboxylation of the terminal carboxylate groups. The increased collision energy means that the terminal arylhydrocarbon adsorbate formed transiently undergoes benzylic C–C cleavage to yield the observed scattered benzylic ion.

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An experiment in which a nickel grid was placed in front of the surface during the 3-h deposition of C₆H₅⁺ at 14 eV yielded a TOF-SIMS image (Figure 1, bottom) of the treated surface which showed higher C₇H₇⁺ intensity in the exposed area. The SIMS mass spectrum reconfirmed the presence of the phenyl-bonded species at *m/z* 91 and 105 (corresponding to C₆H₅CH₂⁺ and C₆H₅CH₂CH₂⁺). The patterned SAM surface has pure hydrophilic (untreated) regions as well as microscopically mixed hydrophobic/hydrophilic character in the exposed regions.

A new surface modification method, in the form of direct, reactive incorporation of molecular groups into surfaces, has been demonstrated in this study. In contrast to earlier experiments using ion treatment, in which atoms or at most small functional groups are incorporated into a surface or indiscriminate reactions were performed, reactive soft-landing of ion beams provides a means of covalently attaching intact molecular moieties to give well-defined products. The very low collision energies (<20 eV) used in these experiments prevent or reduce the fragmentation of the reactive projectiles and help preserve the molecular integrity of the ionic reagent, in a fashion similar to that previously demonstrated for soft-landing of ions. The direct chemical conversion of the terminal carboxylic acid at an ammonium salt mercaptoundecanoic acid SAM to an aryl group, linked through a stable C–C bond, also offers a very attractive opportunity to create novel monolayer surfaces which are not conveniently accessible by conventional molecular assembly methods. One implication of this study is that an additional method has been found that can be used to prepare a microscopically mixed system of hydrophobic and hydrophilic groups, a process not possible by conventional plasma and electrochemical methods. The product surface should be stable to phase segregation because of the strong bonding. It can be expected that such intimately mixed materials of opposite solvation character will confer unusual physical and chemical properties on these surfaces. Further reactions at these modified surfaces, using either ion beam or conventional methods, could be used to create new modified surfaces. For example, by selectively introducing ligating species, it might be possible to complex a catalyst onto the surface so that selective electrodeless metalization at spatially defined positions could be performed.¹⁷ The detailed mechanism of the aryl reactive soft landing is not known, although the superficial similarity to the classical Kolbe alkane synthesis from organic carboxylates¹⁸ prompts us to term this an interfacial Kolbe reaction.

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