

Reactions of Low-energy Ions with Ferrocene Self-assembled Monolayer Surfaces

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Collisions of low-energy $\text{Cr}(\text{CO})_n^+$ ($n=0, 2, 6$) ions with self-assembled monolayer surfaces bearing covalently bound ferrocene groups result in transfer of the cyclopentadienyl ligand into the gas phase as the $\text{Cr}(\text{C}_5\text{H}_5)^+$ ion. High fluences of Cr^+ ions lead to deposition of Cr at the surface and subsequent Xe^+ collisions liberate the metal ion. The Cr atoms deposited on the surface appear to be chemically bonded to the cyclopentadienyl rings. The implications of these results for modification of surfaces using ion beams are discussed.

Collisions of low-energy (10–200 eV) polyatomic ions with solid surfaces can lead to inelastic scattering and hence dissociation of the projectile ion.¹ This surface-induced dissociation (SID) process is a means of characterizing ions in tandem mass spectrometers.² Information on the molecular structure of the surface can be obtained in the same experiment through the chemical sputtering channel. In this process, charge exchange occurs between the ion and adsorbed or covalently bound molecular groups, and leads to ejection of ionized molecular fragments.³ A third major reaction channel involves reactive scattering and is a potential source of information on the nature of the surface as well as the identity of the projectile ion.⁴ Reactive scattering is particularly facile for radical-ion projectiles, and a large number of examples have been accumulated for organic ions, metal carbonyls and such atomic ions as Xe^{++} and I^+ .^{4–6} Although fragmentation of the nascent adduct may sometimes obscure the underlying processes, well-characterized examples of reactive scattering include hydrogen atom and alkyl radical abstraction from the surface by aromatic^{4,6–9} and heteroatom-containing radical ions,^{4,10} and F atom pick-up by $\text{W}(\text{CO})_n^+$, $n=1–4$,¹¹ and by aromatic ions.^{11,12}

In this paper we report results which may be significant for the characterization of organometallics at surfaces as well as for chemical modifications of surfaces, using ion beams. The new processes include (i) abstraction of the cyclopentadienyl ligand by a suitable molecular-ion projectile in an ion/surface reaction, and (ii) chemical sputtering to release surface molecular fragments which include metal-cyclopentadienyl ions.

EXPERIMENTAL

The ion/surface scattering experiments described below were performed using a BEEQ (B = magnetic sector, E = electric sector and Q = quadrupole mass analyser) instrument designed and developed in this laboratory.¹³ The experiments were carried out at fixed scattering angles of 55° (incident) and 90° (scattered). Ion selection was performed using the first two sectors (BE) and scattered ions of a selected kinetic energy were mass analyzed using the quadrupole mass spectrometer. Projectile ions were produced by electron impact at 70 eV at a sample pressure of 1×10^{-5} Torr.

The scattering chamber was held at a vacuum better than 2×10^{-8} Torr. The target surface was prepared and characterized by C. Chidsey as described elsewhere.¹⁴ It was rinsed with hexane before use.

RESULTS AND DISCUSSION

The surface of interest in this work is a self-assembled monolayer (SAM) surface consisting of a C_{16} alkane, bound to a gold substrate through a covalent S–Au bond, and bearing a terminal ferrocene group bound through an ester linkage. The acyl group is directly attached to the cyclopentadienyl ring. When 90 eV $^{132}\text{Xe}^{++}$ ions are allowed to impinge on this surface, the major scattered product is m/z 121, i.e. $\text{Fe}(\text{C}_5\text{H}_5)^+$. The ion is assumed to be the result of chemical sputtering, i.e. charge exchange between the ion and surface, followed by fragmentation of the ionized surface-bound thioalkane.³ This fragmentation pathway can reasonably be expected to lead to $\text{Fe}(\text{C}_5\text{H}_5)^+$, a major — if high energy — product of dissociation of the gaseous ferrocene molecular ion.¹⁵ Fragments corresponding to $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)^+$, $\text{C}_5\text{H}_5\text{C}_5\text{H}_4^+$ and $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)\text{CO}^+$ are also observed in low abundance, and chemical sputtering is clearly useful in characterizing this surface-bound organometallic compound. The products of chemical sputtering and their abundances suggest that the SAM surface is well-ordered, with the cyclopentadienyl rings forming the top-most layer of the surface. Surface disorder would have resulted in cyclopentadiene fragments with alkyl chains, which are totally absent.

Figure 1(a) shows a portion of the scattered ion spectrum recorded when the Xe^+ projectile is replaced by $^{52}\text{Cr}^+$ at 190 eV. It can be seen that the chemical sputtering product, $\text{Fe}(\text{C}_5\text{H}_5)^+$, is accompanied by an abundant $^{52}\text{Cr}(\text{C}_5\text{H}_5)^+$ ion ($m/z=117$). When $^{53}\text{Cr}^+$ is used as the projectile, the ion at m/z 117 disappears and an ion at m/z 118, corresponding to $^{53}\text{Cr}(\text{C}_5\text{H}_5)^+$, appears (Fig. 1(b)). The peak at m/z 117 appears in the mass spectrum when the Cr^+ beam is replaced by either $\text{Cr}(\text{CO})_6^+$ or $\text{Cr}(\text{CO})_2^+$. In both cases the $\text{Cr}(\text{C}_5\text{H}_5)^+$ feature at m/z 117 first appears at a lower collision energy of 60 eV. In the experiments with $\text{Cr}(\text{CO})_6^+$ and $\text{Cr}(\text{CO})_2^+$, the ion at m/z 117 is accompanied by an ion, m/z 145, in low abundance, attributed to $\text{Cr}(\text{C}_5\text{H}_5)\text{CO}^+$. Clearly, chromium ion beams are capable of picking up cyclopentadienyl ligands from the surface. The mechanism by which this occurs is not

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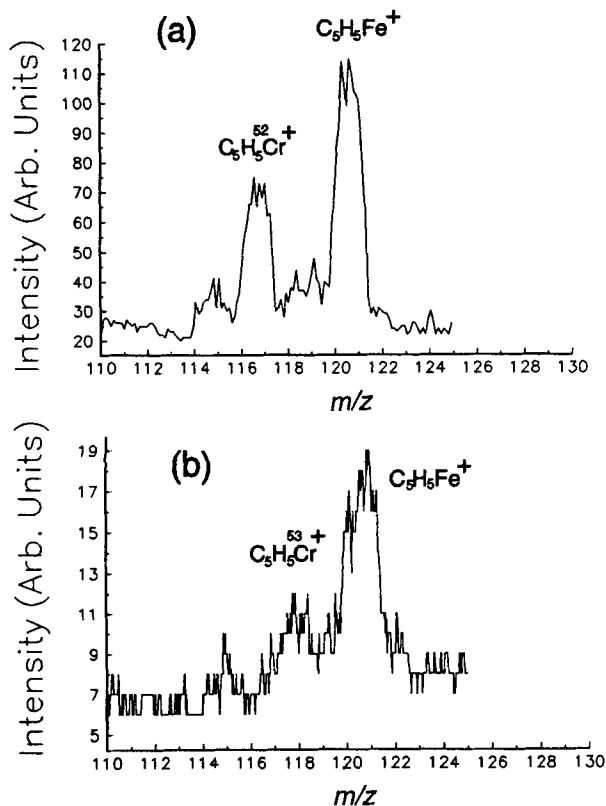


Figure 1. Mass spectra of the ions scattered when (a) $^{52}\text{Cr}^+$ and (b) $^{53}\text{Cr}^+$ beams of 190 eV impinge on the ferrocene self-assembled monolayer surface. The peaks of interest are labeled.

known, but it is significant to note that other metal ions such as $\text{Fe}(\text{CO})_5^+$, $\text{Mo}(\text{CO})_6^+$ and $\text{W}(\text{CO})_6^+$ do not give corresponding products in observable amounts. The ability to abstract ligands clearly suggests the possibility of a capability to recognize chemical modifications to surface-bound organometallics. The possibility that the ion/surface reaction occurs through an intermediate double-decker sandwich structure such as $(\text{CO})_x\text{Cr}^+(\text{Cp})\text{Fe}(\text{Cp})\text{CO}-\text{O}-\text{C}_{15}\text{H}_{31}-\text{CH}_2-\text{S}-\text{Au}$ must be entertained. In the case of Cr^+ impact, it appears more likely that the high translational energy is used to chemically sputter $\text{Fe}(\text{C}_5\text{H}_5)^+$ with sufficient internal energy to cause dissociation to C_5H_5^+ which is captured by the neutralized Cr.

In an effort to gain further insights into these processes, the surface was irradiated with a 2 nA beam of $^{52}\text{Cr}^+$ at 190 eV for a period of 2 h and then Xe^+ was used to examine the surface constituents by chemical sputtering. Depending on the Xe^+ ion energy, the spectra showed Cr^+ and $\text{Cr}(\text{C}_5\text{H}_5)^+$ ions but not the Cr-for-Fe substitution product $(\text{C}_5\text{H}_5)\text{Cr}(\text{C}_5\text{H}_4)^+$, even when $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)^+$ was abundant. The Cr^+ ion was considerably more abundant than Fe^+ , indicating the deposition of atomic chromium at the surface (Fig. 2). Analogous deposition of atomic iodine using iodine-containing beams has been reported,⁵ as has the incorporation of N^+ ¹⁶ and other species into surfaces. When the surface was interrogated by Xe^+ bombardment after Cr^+ bombardment, the intensity of the ion at m/z 117 was found to be much higher than that of m/z 121. The sputtered products also contained $\text{Cr}(\text{CO})_x^+$ ($x = 1, 2$) supporting the sandwich structure mechanism discussed above. No Cr-for-Fe substitution products

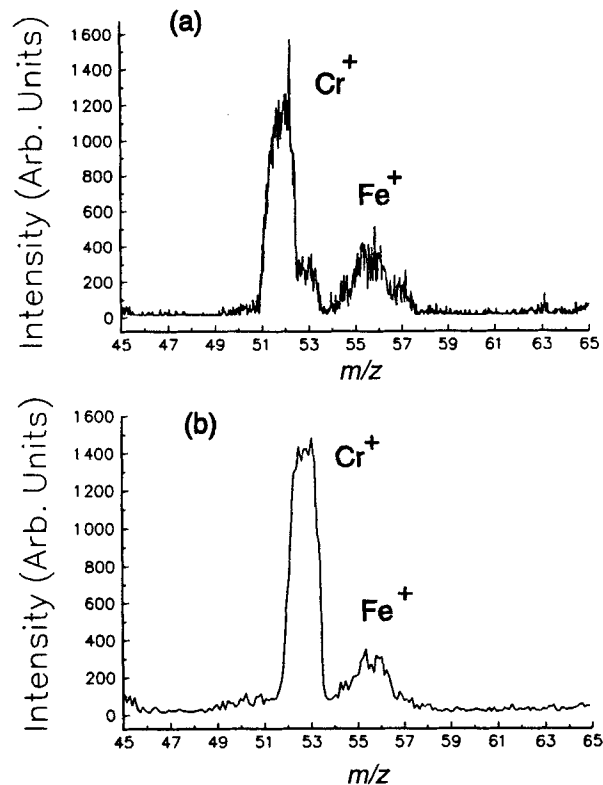


Figure 2. (90 eV) Xe^+ ion-induced secondary-ion mass spectra for the ferrocene self-assembled monolayer surface after exposure to (a) both $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$ and (b) $^{53}\text{Cr}^+$ alone.

were observed. This indicates that the Cr ions left on the surface are chemically bound and are not labile, and explains the absence of substitution products. The chromium–cyclopentadienyl bond formation seems to be driven by the kinetic energy of the projectile ion and it is apparently a single-step event. It does not seem to be facilitated by the subsequent Xe^+ bombardment. It may be pointed out that the intensity of the peak at m/z 117 increases as a function of Cr exposure.

The complex surface chemistry associated with low-energy metal-ion bombardment of organometallic surfaces deserves continuing scrutiny. The metal-atom-exposed surface could be chemically modified further, opening up exciting areas of research in clusters, catalysts, low dimensional solids and electronic materials.

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