Importance of Hydrocarbon Fragment Diffusion in the Formation of Adsorbed Alkyls via EID of Multilayers on Pt(111)

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The interactions of low-energy electrons with organic solids is of interest for a variety of processes. One particular application that we are interested in has to do with using low-energy electron induced dissociation (EID) of hydrocarbon multilayers to prepare monolayer coverages of adsorbed hydrocarbon intermediates on reactive metal surfaces under UHV conditions. To probe the mechanism of the formation of adsorbed alkyl species via EID of multilayer alkane films, we have investigated EID in a two-component, structured multilayer system on Pt(111) at 90 K. Temperature-programmed desorption (TPD) was mainly used to study the reaction products of EID of films comprised of cyclohexane-d_{12} and *n*-butane. On the basis of these results, we conclude that diffusion of the EID-produced alkyl fragments to the surface is the main channel for the formation of surface alkyl species in these types of systems. We exclude a dominant role for transfer of the alkyl fragment to the surface indirectly through abstraction of hydrogen atoms from molecules in the chemisorbed layer to produce new reactive fragments adjacent to the surface.

Introduction

Electron-induced dissociation (EID) and desorption (ESD) of adsorbed molecules has been extensively studied and both are well-known phenomena.[1−19] This is especially true in the case of weakly adsorbed molecules, because the cross sections for reactions caused by low-energy electrons are much larger for physisorbed molecules than for chemisorbed molecules. White and co-workers have effectively used the selectivity for C−H bond cleavage in EID of physisorbed molecules [18] using electron energies below 50 eV to prepare hydrocarbon intermediates on primarily Ag surfaces. This selectivity in EID using low-energy electrons to dissociate monolayers is unfortunately limited to weakly adsorbed molecules. This is simply because the metal substrate quenches excitations induced by low-energy electrons in cases of moderate and strong chemisorption. In common practice, however, the most interesting systems include moderately or strongly bonded adsorbates on reactive metal surfaces. We have recently described a simple but crucial modification of EID experiments which enables selective preparation of hydrocarbon intermediates on reactive metal surfaces containing moderately and strongly bound chemisorbed adsorbates. Instead of using monolayer coverages, we produce a multilayer. The additional layers are isolated from the substrate by the monolayer, and excitations induced by low-energy electrons have a prolonged lifetime which opens a dissociation pathway. Our first experiments produced adsorbed cyclohexyl on Pt(111) and Sn/Pt(111) surface alloys[16,20] via EID of cyclohexane multilayers. In that work, the cyclohexane multilayer had a large cross-section for EID (on the order of 10^{-15} cm^2), but the cross section for the chemisorbed monolayer was more than 1000 times smaller. Once the cyclohexyl intermediate was bonded to the surface after being formed from EID of the multilayer, the chemisorption bonding to the surface inhibited further EID due to the much smaller cross section caused by quenching by the substrate. Thus, EID of multilayer hydrocarbons is a new method to selectively prepare hydrocarbon intermediates on reactive surfaces. In the case of symmetrical alkanes and cycloalkanes, it appears that a high coverage of a single type of hydrocarbon fragment can be prepared.

There are many aspects of the mechanism of EID that need to be studied, both for fundamental reasons and for increasing our capability to use EID to prepare novel surface species. However, here we address only one important component relevant to EID of multilayer hydrocarbons. That is how the hydrocarbon fragment produced via EID in the multilayers is transferred to the surface. It could be transferred to the surface by one of two mechanisms, either (i) directly by diffusion to the surface before a second electron-induced reaction occurs or (ii) indirectly through abstraction of a hydrogen atom from another molecule in the first chemisorbed layer, forming a new reactive fragment adjacent to the surface. We will try to distinguish between these two possibilities. In addition to the appropriate control reactions, we will adsorb a monolayer of C_6D_{12} on the surface and then two layers of C_4H_{10}. This multilayer will then be subjected to electron bombardment and we will monitor what products are formed subsequently during temperature programmed desorption (TPD). If the first mechanism is operative, butene (C_4H_8) desorption will be the major product. Otherwise, benzene (C_6D_6) will be the main product. The large propensity for the formation of butene rather than benzene in this experiment illustrates the importance of hydrocarbon fragment diffusion in the formation of adsorbed alkyls via EID of alkane multilayers on Pt surfaces.

Experimental Methods

These experiments were performed in a stainless steel UHV chamber pumped by a 220 L/s ion pump, a Ti sublimation pump and a 170 L/s turbomolecular pump with a base pressure of 2 × 10^{-10} Torr during experiments. This chamber was equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a four-grid optics for low-energy electron diffraction (LEED), a UTI Model 100 C quadrupole mass spectrometer (QMS) for TPD, and an ion gun for Ar$^+$ ion sputtering. A stainless steel shield with an aperture of about 1 cm diameter covered the ionizer region of the QMS. In order to reduce (<60 nA) electron emission from the ionizer, two high-transparency stainless steel screens were used—one across the end of the ionizer grid (with a bias of −55 V) and one across the entrance aperture of the shield (at ground potential)—between
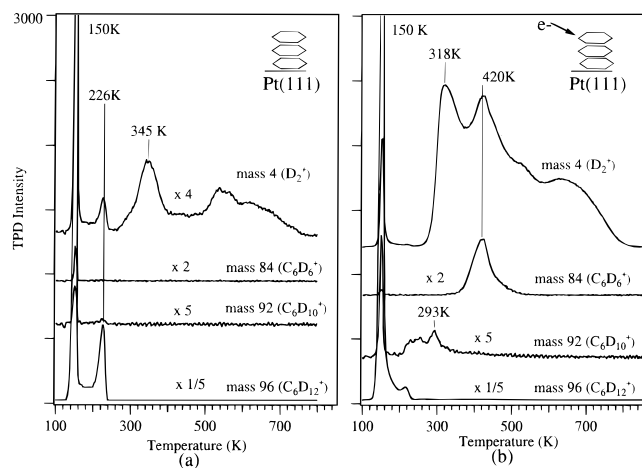
Figure 1. TPD spectra for 3 ML cyclohexane-d_{12} (C_6D_{12}) adsorbed on Pt(111) at 95 K (a) without electron exposure and (b) after electron bombardment.
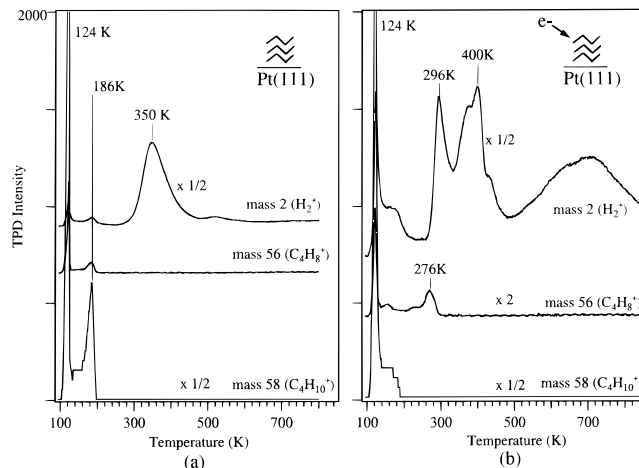

Figure 2. TPD spectra for 2.6 ML *n*-butane (C_4H_{10}) adsorbed on Pt(111) at 90 K (a) without electron exposure and (b) after electron bombardment.

the ionizer region and the sample. The TPD measurements were made with the sample placed 1 mm in front of the entrance aperture of the QMS shield, in line-of-sight with the QMS ionizer, and using a linear heating rate of 4 K s^{-1}.

A variable-energy electron gun (5–1000 eV, Kimball Physics, Model FRA-2X1-2) was used in these experiments. Low-energy EID was carried out using an incident electron beam energy of 50 eV with the sample grounded. The incident beam current was 1 μA, as measured with a sample bias of +225 V, defocused over the entire sample. The uniformity of the electron beam over the sample was checked by measurements using a faraday cup. The fwhm of the electron beam intensity at the sample position (1.0 in. from the end electron gun optics) was 9 mm diameter, compared to the Pt(111) crystal diameter of 8 mm. The corresponding electron flux was 1.2 × 10^{13} electrons/(cm^2·s).

The Pt(111) single crystal (Atomergic, 5N purity) was cleaned using a standard procedure reported previously.[21] AES and LEED were used to check the Pt(111) surface prior to each experiment. A substrate temperature of 85–1200 K could be achieved with resistive heating through two Ta wires spot-welded to the crystal in direct contact with a Cu block that served as a liquid nitrogen reservoir. The sample temperature was monitor by a chromel–alumel thermocouple spot-welded on the edge of the crystal.

The gases used in these experiments included cyclohexane-d_{12} (C_6D_{12}, Cambridge Isotope Laboratories, 99.7% D) and n-butane (C_4H_{10}, Matheson, 99.9%). Cyclohexane was used after several cycles of freeze–pump–thaw to remove dissolved air, and butane was used as received in a lecture bottle without further purification. The purity of all of the gases were checked in situ using the QMS.

Results

Figure 1a shows TPD spectra following adsorption of a 3-monolayer (ML) film of cyclohexane-d_{12} on Pt(111) at 90 K. Signals from the QMS at 2, 3, 4, 20, 32, 36, 60, 64, 84, 92, 95, 96, 164, and 188 amu were monitored during TPD. These masses were chosen to elucidate possible products including H$_2$, HD, D$_2$, CD$_4$, C$_2$D$_x$, C$_4$D$_x$, C$_6$D$_x$, and C$_{12}$D$_{10}$ (biphenyl from dimerization of C$_6$D$_5$). On Pt(111), molecular C$_6$D$_{12}$ desorbs in peaks at 226 and 150 K due to the chemisorbed monolayer and physisorbed multilayer, respectively. The coverage of the cyclohexane monolayer is about 0.19 ML,[22] and about 31% of the monolayer desorbs molecularly during TPD,[23] and

so the area of the cyclohexane TPD peak at 226 K corresponds to 0.06 ML. D$_2$ (4 amu) resulting from cyclohexane dehydrogenation desorbs in a major peak at 345 K. This D$_2$ evolution is desorption rate-limited on Pt(111) and cyclohexane dehydrogenation is initiated at about 180–195 K.[24, 25] The structure in the D$_2$ TPD spectra above 400 K, and thus the average C:D stoichiometry of surface species differs slightly from the analogous H$_2$ TPD spectra resulting from cyclohexane dehydrogenation.[20,23] In separate experiments using C$_6$H$_{12}$, we obtained good agreement with the previously reported H$_2$ TPD results,[20, 23] and so the differences must correspond to kinetic isotope effects on the dehydrogenation kinetics. The peaks at 150 and 226 K for all of the TPD spectra are due to cracking fractions of C$_6$D$_{12}$ in the QMS ionizer. As we will see below, benzene (C$_6$D$_6$) and cyclohexene (C$_6$D$_{10}$) are the key products of EID of multilayer cyclohexane on Pt(111), but desorption of these products is not observed in the TPD spectra in Figure 1a without electron influence.[16, 20]

Prior to the TPD spectra shown in Figure 1b, a 3 ML cyclohexane-d_{12} film on Pt(111) at 90 K was subjected to an electron bombardment of 3.6 × 10^{15} electrons/cm^2. Comparison to the TPD results in Figure 1a shows that the C$_6$D$_{12}$ monolayer desorption peak at 226 K was nearly eliminated and desorption of C$_6$D$_6$ and C$_6$D$_{10}$ now occurs in peaks at 420 and 293 K, respectively, after EID. D$_2$ desorption occurs with a much larger yield with peaks at 318 and 420 K, along with a broad feature that extends to about 800 K in Figure 1b. No mass 56 (C$_4$D$_4$), except the cracking fraction expected from C$_6$D$_{12}$ at 150 K and C$_6$D$_6$ at 420 K was observed. This is very important since the 56 amu intensity corresponds to the key product following EID of multilayer *n*-butane, which we are going to use in the two-molecule systems reported on below. This is also the reason why we selected cyclohexane-d_{12} rather than the perhydrido-cyclohexane for these experiments.

The results presented in parts a and b of Figure 1 are fully consistent with our previous studies of C$_6$H$_{12}$ on Pt(111).[16,20] Furthermore, we determined that the *total* EID cross section for these cyclohexane multilayers was about 1.0 × 10^{-15} cm^2, as measured by the decrease in the cyclohexane monolayer desorption peak area. This value is similar or higher than in previous reports of EID cross-sections for hydrocarbon films using electron energies in the range 30–55 eV.[10,13,16,18,26]

Figure 2a shows the TPD spectra of 2.6 ML *n*-butane adsorbed on Pt(111) at 90 K. The *n*-butane (C$_4$H$_{10}$) desorbs in peaks at 186 and 124 K from the monolayer and multilayer film, respectively. This is consistent with our previous

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results, [27] and we can estimate the monolayer coverage to be about 0.21 ML.[22] The C_4H_8 yield is only due to a cracking fraction of butane, and the H_2 yield above 250 K is due to coadsorbed hydrogen from the background; very little thermal decomposition of *n*-butane occurs [27] and AES after TPD experiments showed no carbon present. The amount of coadsorbed H ($\Theta_H \leq 0.1$ ML) is much higher than in our normal experiments but was necessitated by the longer cooling times required to achieve the lowest possible temperatures (85−90 K) that we used to stabilize the butane multilayers. This coadsorption does not affect in any way the conclusions that we will reach about hydrocarbon transport in these films.

TPD spectra after electron bombardment of a 2.6 ML *n*-butane film on Pt(111) at 90 K are given in Figure 2b. The electron exposure was 3.6×10^{15} electrons/cm^2. The desorption of *n*-butane in the monolayer peak at 186 K is strongly reduced after this electron bombardment. In addition, H_2 TPD showed the sharp peaks and features that are characteristic of sequential dehydrogenation of surface hydrocarbons on Pt(111), and this desorption continued out to about 950 K. Butene (C_4H_8) desorption at 230 and 270 K in Figure 2b constitutes a primary product in TPD. No other products were observed. The low-temperature peaks in both the H_2 and C_4H_8 spectra are due to cracking fractions of butane. We do not expect a single type of surface bound species to be produced by EID of *n*-butane multilayers, since there are two kinds of C−H bonds in the molecule—primary and secondary C−H bonds. Assuming no propensity for the dissociation of one type of bond, we should produce both butyl and isobutyl groups on the surface. This is of little consequence in these studies. We only rely on the selectivity to produce butene from EID of butane and benzene from EID of cyclohexane.

We also note that the small molecular desorption yield of cyclohexane or butane following electron bombardment is not due to insufficient electron dose to form a monolayer equivalent of alkyl groups. Additional electron exposures do not produce smaller molecular desorption peaks. Thus, we conclude that this yield is due to low-temperature facile rehydrogenation of surface-bound hydrocarbon fragments.

Figures 1 and 2 set the stage to investigate the role of hydrocarbon fragment diffusion in the alkyl formation mechanism for EID of multilayer hydrocarbons on transition metals. In the following, we investigate using TPD the products from "structured" hydrocarbon multilayer films using a two-molecule system of $C_6D_{12} + C_4H_{10}$ exposures.

We know that the cross-section for EID of the hydrocarbon in the chemisorbed monolayer is much less (about 3 orders of magnitude) than that for EID of hydrocarbons in physisorbed multilayers, both from our previous studies[16] and as confirmed in this work.

Regarding the structure of these mixed films, extensive intermixing of the butane and cyclohexane layers does not seem to occur during deposition at 90 K. This is supported by the related work of Raval and Cooper [28] using FTIR to study cyclohexane multilayers on Ni(111), and also by the results shown in Figure 3. Here, we exposed the Pt(111) surface to form 1 ML cyclohexane-d_{12} followed by two layers of n-butane at 90 K. TPD spectra from this sample are consistent with only minimal intermixing and consistent with the layered molecular structure depicted schematically in the top right corner for this two-molecule system. We observed a large chemisorbed cyclohexane peak, no physisorbed cyclohexane peak, and a large HD yield with a peak at 350 K which is characteristic for cyclohexane thermal decomposition. No desorption peak at 186 K characteristic of butane in the first monolayer is observed.
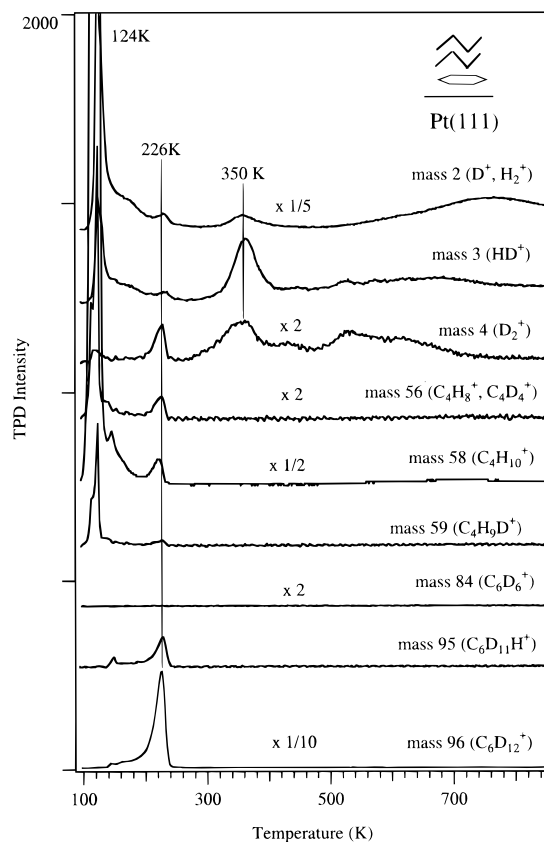

Figure 3. Thermal desorption spectra from TPD after preparation of the multilayer on Pt(111) at 90 K by the procedure preadsorbed 1 ML cyclohexane-d_{12} followed by a 2 ML dose of *n*-butane.

The peaks at 226 K for masses 56 and 58 are due to a C_4D_4 and C_4D_5 crack of cyclohexane. This TPD experiment provides a "worst-case" scenario since the multilayer film is heated during TPD and intermixing is much more facile at these elevated temperatures than at 90 K. However, this particular structure with the more strongly adsorbed hydrocarbon (C_6D_{12}) in the monolayer also effectively decreases intermixing since it is more difficult to displace cyclohexane from the monolayer compared to that for butane in the reverse structure that we will discuss later.

Figure 4 shows the TPD results after electron bombardment (3.6×10^{15} electrons/cm^2), with the sample at 90 K, of the same structured multilayer film as used for Figure 3. In this case, a large decrease in the cyclohexane monolayer peak and a large increase in the cyclohexane multilayer peak occurs, due to displacement of cyclohexane from the monolayer during EID. The loss of the cyclohexane monolayer is not due mainly to EID of cyclohexane since no benzene is formed (mass 84) and the D_2 TPD peak area is greatly decreased. In contrast to Figure 3, we now see a peak at 276 K for mass 56 due to butene (C_4H_8) formation and a large H_2 evolution characteristic of the decomposition of surface butyl species. A small amount of $C_6D_{11}H$ desorption is observed, accompanied by some HD and a very small amount of D_2 desorption, since displacement of cyclohexane from the monolayer into the physisorbed layers by butyl fragments bonding to the surface now allows efficient EID of physisorbed cyclohexane and the associated subsequent chemistry on the surface.

In order to verify and provide a cross check on these results, we repeated these experiments but with the order of the hydrocarbon exposure reversed to form the reversed structure—a chemisorbed monolayer of n-butane with two additional physisorbed layers of cyclohexane-d_{12} on Pt(111) at 90 K. TPD
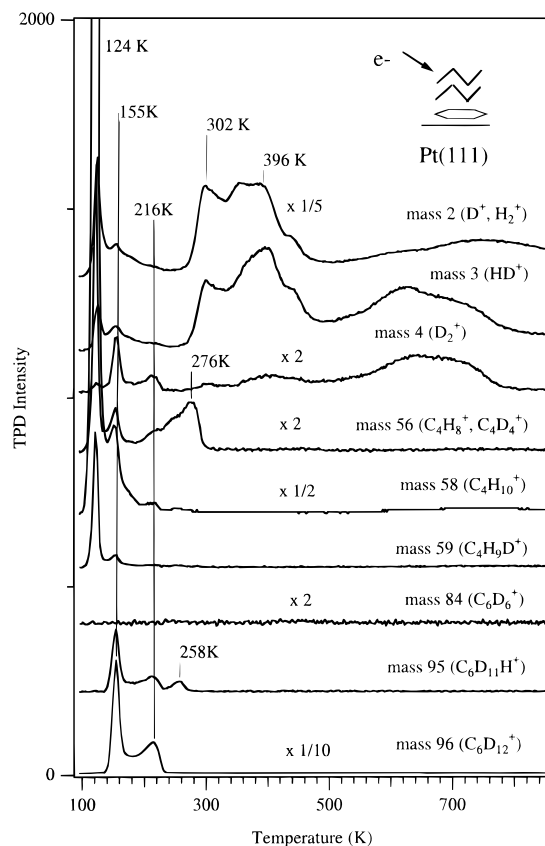
Figure 4. TPD spectra following EID of the multilayer on Pt(111) at 90 K prepared by the procedure preadsorbed 1 ML cyclohexane-d_{12} followed by a 2 ML dose of *n*-butane.

Figure 5. Thermal desorption spectra from TPD after preparation of the multilayer on Pt(111) at 90 K by the procedure preadsorbed 1 ML *n*-butane followed by a 2 ML dose of cyclohexane-d_{12}.

results from this multilayer film with no electron bombardment are shown in Figure 5. In this case, extensive intermixing occurs, but this happens mainly at temperatures higher than 90 K that are encountered during TPD based on the TPD spectra after EID at 90 K shown later in Figure 6. In Figure 5, butane desorption mainly occurs from a multilayer state and a large desorption of cyclohexane-d_{12} is seen from both monolayer and multilayer states. A large D_2 desorption is seen due to decomposition of cyclohexane, with a characteristic peak at 350 K.

Electron bombardment (3.6×10^{15} electrons/cm^2) of the same preadsorbed structured molecular film as probed in Figure 5 on Pt(111) at 90 K produced the TPD results shown in Figure 6. The most important observations are the formation of a benzene (C_6D_6) peak at 420 K and very little butene (C_4H_8) formation in a peak near 276 K. The peak for mass 56 at about 420 K is a cracking fraction of C_6D_6 in the QMS ionizer. In Figure 6 we also see a high yield of D_2 desorption with a characteristic profile for EID of physisorbed cyclohexane, as shown in Figure 1b. Thus, the same surface bound intermediate is indicated for both experiments.

Discussion

The current understanding of EID of physisorbed hydrocarbons at 50 eV incident electron energies is that impact ionization occurs, this process is highly selective for breaking a C−H bond compared to a C−C bond, and only one C−H bond is broken.[16,18] For physisorbed monolayers, it is fairly obvious that bonding of the reactive fragment from EID to the metal surface should readily occur. It is this strong bonding to the surface that decreases subsequent EID reactions of the chemisorbed species and greatly protects the fragment from further decomposition. An outstanding question is how the reactive
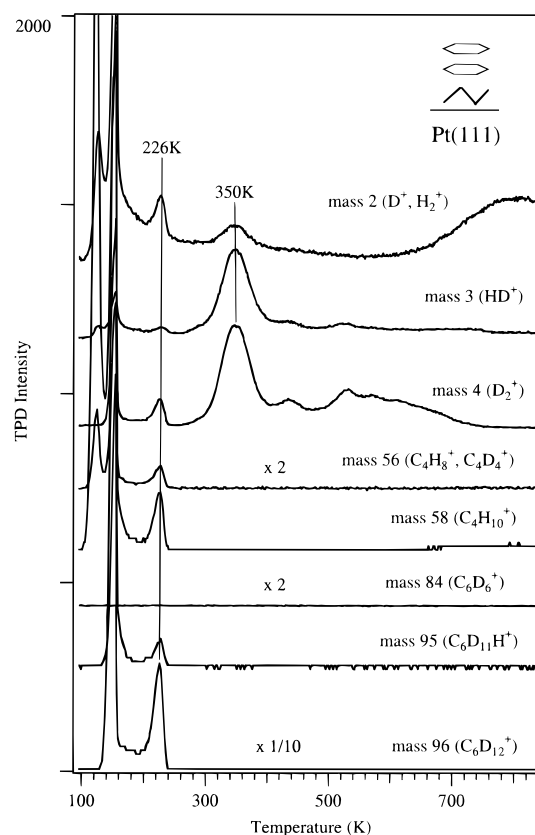
fragments produced by EID of hydrocarbon *multilayers* are transferred to the surface. Two mechanisms for saturated hydrocarbons are feasible: (i) direct transfer of the hydrocarbon fragment to the surface by diffusion, accompanied by displacement of any weakly bound surface species; and (ii) indirect transfer through abstraction of a H(D) atom from another molecule in the first chemisorbed layer (by either product of the impact ionization, i.e., H(D) or the hydrocarbon fragment) producing another reactive fragment in the monolayer which binds to the surface. If the multilayers contain unsaturated bonds, e.g., C=C, N=O, etc., then addition reactions could also occur, but this is not the case here.

We have used EID of structured hydrocarbon multilayers of cyclohexane and butane to address this important question. EID of the individual component films leads to easily identifiable different products. EID of physisorbed cyclohexane layers using 50 eV electrons leads to surface bound cyclohexyl fragments that dehydrogenate to produce cyclohexene and benzene in a subsequent TPD experiment. A large D_2 desorption is also seen in TPD due to D evolution from the initial EID process and decomposition of cyclohexene and benzene. When physisorbed butane layers are subjected to electron bombardment at 50 eV, EID leads to surface bound butyl or isobutyl fragments that dehydrogenate to produce butene and liberate H_2 in a subsequent TPD experiment. A large difference is also observed in the peak temperatures and shape of the H_2 desorption in this case compared to the D_2 desorption from EID of cyclohexane.

Schematic drawings of two possible mechanisms for transfer of reactive hydrocarbon fragments to the surface in EID of multilayer films are shown in Figure 7 for the two-component structured multilayer films that we utilized. Ionization of a top layer butane molecule is shown for simplicity, but any physisorbed molecule, including those in the interfacial layer between
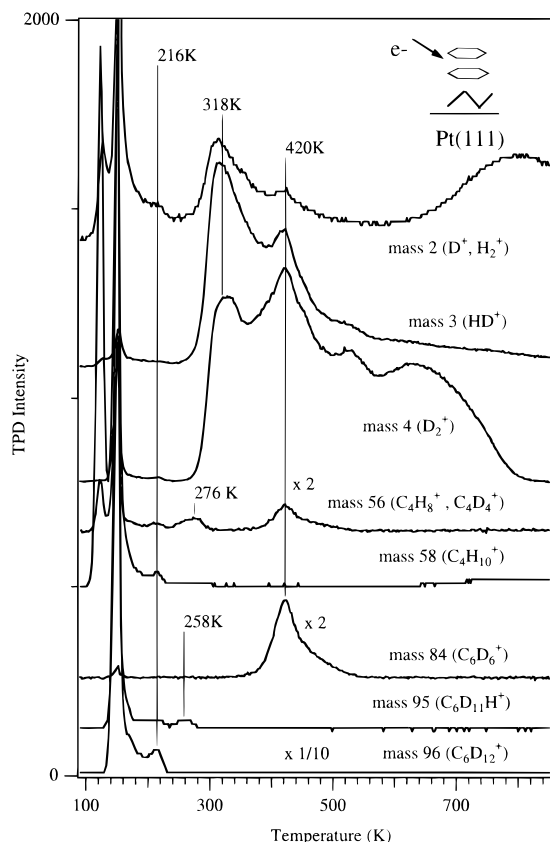
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Figure 6. TPD spectra following EID of the multilayer on Pt(111) at 90 K prepared by the procedure preadsorbed 1 ML *n*-butane followed by a 2 ML dose of cyclohexane-d_{12}.
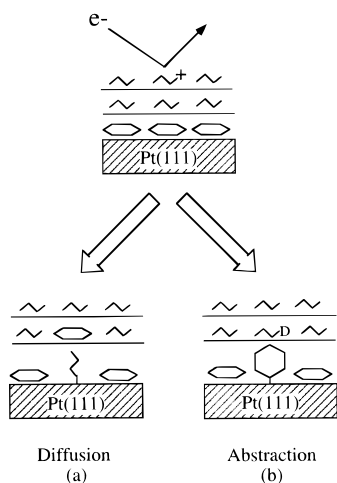

Figure 7. Schematic drawing of two possible mechanisms for the transport of EID-derived fragments in hydrocarbon multilayers on metals, illustrated for one of the structured two-component multilayers studied. (a) Diffusion produces hydrocarbon fragments bound to the surface that are derived from the multilayer species. (b) Abstraction of D(H) produces hydrocarbon fragments bound to the surface that are derived from the monolayer species.

the two components, may contribute to this process. In scheme a, butyl fragments produced in the physisorbed layers diffuse and bond to the surface as adsorbed butyl species, displacing the more weakly adsorbed molecular cyclohexane. Sufficient electron bombardment of these films leads to a chemisorbed monolayer of butyl species that form butene and H_2 in subsequent TPD spectra. In this case, the physisorbed cyclohexane produced by displacement during EID can also undergo EID to produce cyclohexyl fragments that then diffuse to the surface. In scheme b, butyl fragments produced in the phys-

isorbed layers abstract D from adsorbed molecular cyclohexane-d_{12} to produce a cyclohexyl species which immediately bonds to the surface. In this process the surface becomes covered with a chemisorbed monolayer of cyclohexyl species that form benzene and D_2 in subsequent TPD spectra. If this mechanism is operative to an appreciable degree, one would also expect less selective preparation of surface alkyls since abstraction reactions presumably would not discriminate between adsorbed cyclohexyl and molecular cyclohexane, as do the EID cross sections, leading to surface species with several C−H bonds broken.

All the TPD results confirm that a direct process via diffusion to the surface of the hydrocarbon fragments from EID in multilayers is the dominant mechanism for producing surface bound alkyl groups. The key observations come from comparing Figures 4 and 6. When *n*-butane was initially present only in the top two physisorbed layers, as for Figure 4, we observed butene desorption and an H_2 TPD spectrum characteristic of the decomposition of surface butyl groups. For this case too, no benzene desorption and a relatively small amount of D_2 desorption was observed. If abstraction was an important channel we would have also seen a large feature at mass 59 (C_4H_9D) which was not observed. On the other hand, we observed benzene desorption and a D_2 TPD spectrum characteristic of the decomposition of surface cyclohexyl groups when cyclohexane was initially present only in the top two physisorbed layers as for Figure 6. In this latter case, a relatively small amount of butene and H_2 desorption was observed. We also did not observe a large feature at mass 95 ($C_6D_{11}H$) that would be expected if abstraction was an important channel.

Several possibilities exist to explain the low temperature diffusion of the hydrocarbon fragments formed from EID. First, excitation leading to C−H bond cleavage leaves the resulting fragment in a highly excited state, and diffusion within the multilayer can occur by coupling of this internal energy of the fragment to translational energy. Translational velocities away from the surface potentially lead to desorption, while an encounter with the surface during this motion would likely lead to trapping and chemisorption with an efficiency near unity. Second, to the extent that fragment *ions* are formed from EID, attraction to the surface by the image charge interaction increases the propensity for diffusion of the fragment ion to the surface.

Conclusions

We have investigated the mechanism by which the reactive hydrocarbon fragments formed from EID in alkane multilayers on metal surfaces are transferred to the surface to form chemisorbed alkyl groups. We used two-component hydrocarbon films grown layer by layer on Pt(111) at 90 K, in which one component initially comprises the adsorbed monolayer and the other component is only present initially in the physisorbed bilayer on top of the monolayer. The system investigated was cyclohexane-d_{12} + *n*-butane. All of the TPD results allow us to conclude that the dominant mechanism for the formation of surface alkyl groups is for the hydrocarbon fragment from EID to diffuse to the metal surface rather than abstracting hydrogen (or deuterium) atoms from adjacent molecules.

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