

Structures and Reactivities of Cycloheptane, Cycloheptene, 1,3-Cycloheptadiene, and Cycloheptatriene on Pt(111)

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The structures and reactivities of various cyclic C_7 hydrocarbons (cycloheptane, cycloheptene, 1,3-cycloheptadiene, and cycloheptatriene) adsorbed on Pt(111) have been examined by means of temperature-programmed reaction, reflection–absorption infrared, and Auger electron spectroscopies. At temperatures below 200 K, cycloheptane binds weakly to the surface and exhibits vibrational mode softening consistent with the presence of agostic $C-H\cdots M$ interactions. In contrast, the cyclic alkenes cycloheptene, 1,3-cycloheptadiene, and cycloheptatriene all bind strongly (and largely irreversibly) to the surface principally by means of interactions with their π -systems. The chemistry of these adsorbates at higher temperatures has been mapped out in considerable detail. For cycloheptane, most simply desorbs but about 30% is dehydrogenated; interestingly, cycloheptene is not an intermediate in this process. Cycloheptene first loses two hydrogen atoms to give what we propose is an $\eta^3, \eta^1-C_7H_{10}$ product. 1,3-Cycloheptadiene first loses two hydrogen atoms to afford an η^5 -cycloheptadienyl product, which dehydrogenates further to give surface-bound cycloheptatriene in (apparently) high yield. Between 325 and 375 K, all of the cyclic C_7 hydrocarbons dehydrogenate further and eventually yield a planar η^7 -cycloheptatrienyl (C_7H_7) species on the surface, although for cycloheptene this conversion is inefficient. The thermolytic decomposition of the $\eta^7-C_7H_7$ species begins at about 425 K and affords surface-bound hydrocarbons that are largely undetectable by RAIR spectroscopy. At higher temperatures (>800 K), these hydrocarbons are completely dehydrogenated to form a carbonaceous overlayer. Ring contraction products, such as surface-bound benzene, are not observed as intermediates in any of the thermolytic reactions. The RAIR spectra of the η^5 -cycloheptadienyl and cycloheptatriene adsorbates both contain an unusual low-frequency vibrational band near 2770 cm^{-1} . This band is not indicative of an agostic $C-H\cdots M$ interaction, but is instead the signature of a methylene $C-H$ bond that has been perturbed by hyperconjugative drain of electron density into the adjacent π -system.

Introduction

The surface reactions of cyclic hydrocarbons on transition metal surfaces, in particular platinum, have received considerable attention.^{1,2} Numerous studies have sought to elucidate the underlying fundamental mechanisms of these reactions on single-crystalline substrates such as Pt(111).^{3–25} It is now understood that the reactivity of cyclic hydrocarbon adsorbates bound to Pt(111), and the products formed by their thermal decomposition, can vary dramatically depending on such factors as their ring size and degree of unsaturation. Many unsaturated hydrocarbons, owing to the strong π -bonding interactions that occur with the platinum surface, bind irreversibly and thus show a large propensity to dehydrogenate (and subsequently fragment) rather than desorb upon heating.^{3,5,9,10,15,17–19,22,23} Adsorbed cyclohexene and both isomers of cyclohexadiene, for example, are dehydrogenated to benzene at ~ 340 K and 230–260 K, respectively, on Pt(111).^{10,15} At high coverages of these adsorbates, an appreciable fraction of the benzene product desorbs from the surface.²⁶ In many cases, however, the primary dehydrogenation products do not desorb because they are too tightly bound to the surface (and thus are retained until they decompose). An illustrative example of the latter class of product is the pentahaptocyclopentadienyl species, $\eta^5\text{-Cp}$, which is

formed in high yield via the dehydrogenation of cyclopentene and 1,3-cyclopentadiene on Pt(111).^{3,5}

In contrast to the behavior of unsaturated cyclic hydrocarbons (which yield significant quantities of surface-bound carbon), saturated cycloalkanes (e.g., cyclopentane, cyclohexane, and cyclooctane) bind relatively weakly to the Pt(111) surface.^{4,6,12,19,20,23,24} The $C-H$ bonds in these adsorbates are more difficult to activate on Pt(111), and most of the adsorbed monolayer, in fact, desorbs molecularly when the crystal is heated. The few adsorbate molecules that do undergo $C-H$ bond cleavage do not give hydrocarbon products that desorb into the gas phase but, instead, undergo further fragmentation.

Vibrational spectroscopy has proven to be a useful tool for characterizing the molecular structures of such surface-bound molecules and intermediates and the energetics involved in their thermolytic transformation. Such data also provide valuable insights into both the orientation and organization of the surface-bound species. The vibrational spectra of bulk phases and discrete organometallic complexes provide extremely useful reference data from which the structures of reactive intermediates can be deduced.^{27–29} To characterize the molecular orientation of an intermediate, it is necessary to account for the effects of the selection rules since the spectra of organized overlayers on a metal surface exhibit significant dichroism. Several very useful methods for the quantitative analysis of such data have now been reported in the literature.^{30–33}

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It is important to note that some caution is necessary when applying such methods to the interpretation of the vibrational spectra of complex adsorbates (such as those of interest in this study). Of particular concern is that the normal modes of a surface-bound species can be significantly different from those seen in the gas phase. For example, the optical functions (and thus the vibrational spectra) of hydrocarbons adsorbed molecularly on a transition metal surface such as Pt(111) are significantly perturbed, and perhaps the most dramatic example of these perturbations is the observation of a significant red-shifting of certain C–H stretching modes.^{3,4,12–14,34–46} The low frequencies of these “soft” modes are generally believed to reflect a weakening of the C–H bond by contact interactions with the surface (C–H···M), but it is still unclear whether a correlation exists between the characteristics of the soft mode (i.e., its position, line width, and intensity) and the ease of C–H bond scission. Most generally accepted are the conclusions drawn by Raval and Chesters from studies of cyclohexane adsorbed on several transition metal surfaces:⁴⁴ large shifts in the frequency of the C–H stretching vibrations appear to be strongly correlated with the facility of the dehydrogenation process. Lamont et al., however, demonstrated that this correlation apparently does not hold for cyclohexane adsorbed on the (5 × 20) and (1 × 1) surfaces of Pt(100).⁴⁷ They observed that, even though the vibrational spectrum of cyclohexane adsorbed on the (5 × 20) surface exhibited significant mode softening, the reactivity on this surface was three to four orders of magnitude lower than that on the (1 × 1) surface (on which no soft modes were seen). How such correlations might be extended to the sequential bond activation chemistries seen in other hydrocarbon ring systems is unclear from the data currently available.

This report describes a comprehensive study of the structures and reactivities of several cyclic C₇ hydrocarbons on Pt(111). Little is known concerning the reactivity patterns of such hydrocarbons on transition metal surfaces. It has been reported that cycloheptatriene is thermally converted to benzene on Ni(100) and W(100)-(5 × 1)-C surfaces.^{17,18} Activation of cycloheptatriene on Pt(111), however, did not result in the formation of benzene.²² The production of benzene on the W(100)-(5 × 1)-C surface was shown to involve the formation of an intermediate cyclic C₇H₇ (cycloheptatrienyl) species.¹⁸

The adsorbates examined in this study include cycloheptane (CHA), cycloheptene (CHE), 1,3-cycloheptadiene (1,3-CHD), and cycloheptatriene (CHT). Our results suggest that little correlation exists between the appearance of soft modes seen in the vibrational spectra and the specific patterns of C–H bond activation that occur upon heating. We also find that the facility of C–H bond activation is not correlated with the degree of unsaturation, at least not in a simple way. This aspect notwithstanding, we find that all the unsaturated cyclic C₇ adsorbates decompose to give (in varying yields) the same cycloheptatrienyl product. This species is stable only over a modest temperature range, decomposing above 425 K via C–C and C–H bond fragmentation to give a carbonaceous overlayer.

Experimental Section

Studies were carried out in a single ultrahigh vacuum chamber with a base pressure of $< 4 \times 10^{-10}$ Torr.^{12,48} The Pt(111) crystal was purchased from Cornell Laboratories and was oriented to within 0.5° and polished to a fine mirror finish using standard metallographic techniques. The Pt(111) crystal was cleaned by heating at 950 K in the presence of 1×10^{-6} Torr of O₂ for three minutes followed by annealing in a vacuum at 1000 K for two minutes. If this treatment did not clean the

surface sufficiently, the crystal was sputtered with 1 kV Ar⁺ ions at 950 K for approximately 15 min and subsequently annealed at 1050 K. Surface cleanliness was established by Auger electron spectroscopy (detectable carbon < 0.5 atomic %). Cooling was accomplished by connecting the crystal to a liquid nitrogen reservoir with a copper braid. The crystal was directly mounted on a Varian-style button heater (Spectra Mat); the crystal temperature was controlled over the range of 95–1050 K (± 2 K) by using a Eurotherm 818P temperature programmer and a type K thermocouple spot-welded directly to the crystal.

RAIR spectra were collected on a Digilab FTS 60A spectrometer equipped with a broad-band, liquid nitrogen cooled, MCT detector. Reflection optics ($\sim f/12$) were used to collect spectra for near-grazing angles of incidence ($\sim 84^\circ$).⁴⁹ The RAIR spectra, each calculated from single-beam (sample and reference) spectra of 1024 scans taken at 4 cm⁻¹ resolution and requiring a total collection time of approximately 6 min, are presented as absorbance plots ($-\log R/R_0$).

Temperature-programmed reaction spectra (TPRS) were collected at a constant heating rate of 2 K/s. The spectra were recorded with a Vacuum Generators SXP 300 quadrupole mass spectrometer that was differentially pumped by a 45 L/s ion pump. The mass spectrometer was isolated from the chamber by an enclosing nickel aperture (1 mm, Beam Dynamics, Minneapolis, MN) which served both to shield the ionizer region of the mass spectrometer and to define the acceptance cone of the desorbing fragments.

Deuterium and hydrogen (99.995%) were purchased from Matheson and used as received. All other compounds were purchased from Aldrich and dried over alumina; gas chromatography indicated that the samples were greater than 99% pure except for cycloheptatriene, which was contaminated with $\sim 15\%$ cycloheptadiene. We were unable to separate this impurity and thus have had to take its contribution into account when drawing conclusions from studies of this molecule. All samples were degassed before being introduced into the chamber by a freeze/pump/thaw technique. Dosing was accomplished by backfilling the chamber through a variable leak valve. Coverages are given relative to a saturation coverage of the adsorbate (θ_{sat} , determined by a combination of RAIRS and TPRS).

Results

Temperature-Programmed Reaction Spectroscopy. To obtain insights into the reactions of the cyclic C₇ hydrocarbons on Pt(111), we have carried out a series of temperature-programmed reaction spectroscopy studies. In all of the TPR traces discussed below, the surface was dosed with the specified cyclic C₇ hydrocarbon at temperatures below 110 K. To observe multilayer and monolayer desorption features, the exposures were more than that required for saturation of a monolayer, but less than twice that amount ($\theta_{\text{sat}} < \theta < 2 \theta_{\text{sat}}$).

Reactivity of Cycloheptane (CHA) on Pt(111). Figure 1 presents temperature programmed reaction spectra for a variety of different m/e values ($m/e = 98, 94, 92, 78$, and 2). In the $m/e = 98$ channel (the molecular ion), the low-temperature desorption feature seen at 164 K is characteristic of multilayer desorption. A desorption feature for a more tightly bound monolayer is also seen at 243 K. Similar two-stage desorption behavior has been reported for other saturated hydrocarbons adsorbed on transition metal surfaces.^{4,6,12,20,23} In the $m/e = 96$ channel, the peaks seen at 164 and 243 K are not due to desorbing cycloheptene (CHE), but rather arise by means of electron impact induced fragmentation of the desorbing CHA.

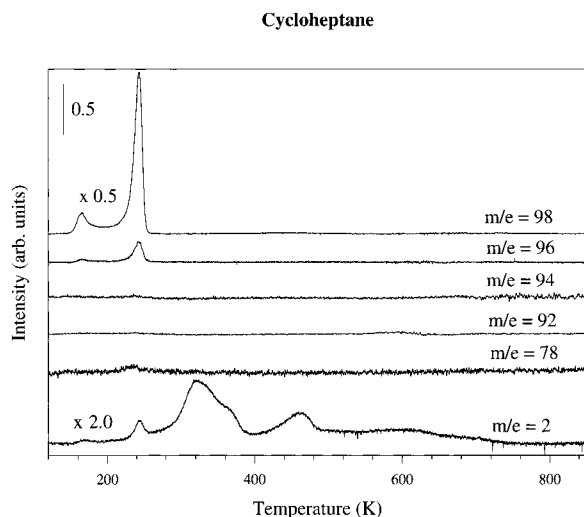


Figure 1. Temperature-programmed reaction spectra for cycloheptane adsorbed on Pt(111) at 110 K ($\theta \approx 2.0 \theta_{\text{sat}}$) for the following mass values: $m/e = 98$ (cycloheptane), 96 (cycloheptene), 94 (cycloheptadiene), 92 (cycloheptatriene), 78 (benzene), and 2 (dihydrogen).

The absence of peaks in the $m/e = 94$, 92, and 78 channels (parent ions for CHD, CHT, and benzene, respectively) suggests that the corresponding products do not desorb from the surface in significant amounts. It is possible that small amounts of these products are formed but that they are present at coverages too small to promote their desorption from the surface.²⁵

The significant intensity of the monolayer desorption feature at 243 K demonstrates that most of the adsorbed cycloheptane simply desorbs molecularly when the surface is heated. A small fraction of the monolayer, however, remains on the surface, as judged from Auger electron spectroscopy (see below).

Significant structure is seen in the dihydrogen desorption channel ($m/e = 2$). The peak at 243 K is not due to desorbing H_2 , but again reflects electron impact induced fragmentation of molecularly desorbing CHA. The broad features at 320 and 360 K, however, arise from the recombination-limited desorption of hydrogen generated by dehydrogenation of the CHA molecules that remain on the surface above the monolayer desorption temperature. Two other desorption features, at 460 and ~ 610 K, occur above the temperature range at which the recombinative desorption of hydrogen is rate limiting.⁵⁰ These desorption features must be reaction limited and mark the further decomposition of the CHA dehydrogenation product(s).

The TPRS results show that, when CHA dehydrogenates, the resulting unsaturated hydrocarbons never desorb from the surface. At higher temperatures, however, they undergo further dehydrogenation, and eventually a carbon overlayer is formed (see the Auger results below). Therefore, the total integral of the $m/e = 2$ TPD trace above 275 K must correspond to a loss of 14 hydrogen atoms per molecule of CHA that is activated. Integration of the trace suggests that about half of the hydrogen atoms are lost between 275 and 400 K, and the remaining half are lost between 400 and 800 K. Accordingly, the chemical composition of the species present on the surface at 400 K is approximately C_7H_7 . The RAIR results (to be discussed below) support the conclusion that, at 400 K, a molecule with this composition is in fact present on the surface.

Reactivity of Cycloheptene (CHE) on Pt(111). The TPR spectra obtained after the Pt(111) surface is exposed to CHE ($m/e = 96$, Figure 2) demonstrate that, unlike CHA, only a small fraction of the monolayer desorbs molecularly. This result is consistent with numerous studies of other cycloalkenes adsorbed

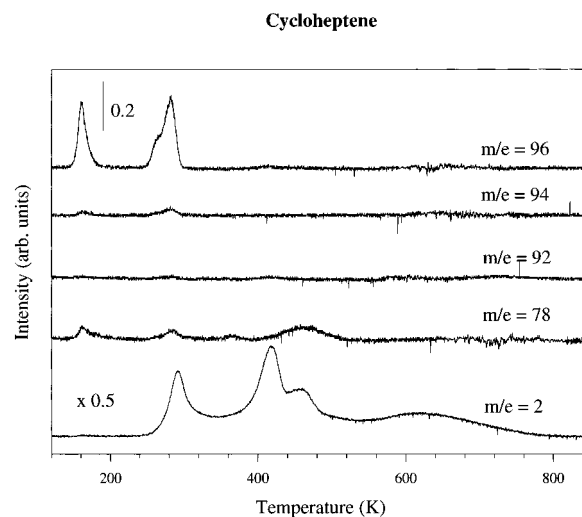


Figure 2. Temperature-programmed reaction spectra for cycloheptene adsorbed on Pt(111) at 110 K ($\theta \approx 2.0 \theta_{\text{sat}}$) for the following mass values: $m/e = 96$ (cycloheptene), 94 (cycloheptadiene), 92 (cycloheptatriene), 78 (benzene), and 2 (dihydrogen).

on a variety of transition metal surfaces.^{3,5,9-12,14,18,22-24} The peak seen in the $m/e = 96$ channel near 160 K is a multilayer desorption feature. The peak(s) at 283 K mark the desorption of a small quantity of a more tightly held monolayer (less than 10% the monolayer desorbs as judged from the Auger results; see below). The small peaks seen in the $m/e = 94$ channel are due to electron impact induced cracking of CHE.

Interestingly, benzene desorbs from the surface in a peak at 460 K (Figure 6, $m/e = 78$). We will show below that the quantity of benzene desorbing into the gas phase is very small. Thus, a significant fraction of the CHE (or species derived from it) must remain on the surface and eventually decompose.

The TPR spectra for dihydrogen ($m/e = 2$) contain an interesting low-temperature feature at 290 K; this peak is large and thus cannot be due solely to a cracking fragment of the coincidentally desorbing CHE. (This H_2 desorption process is recombination limited, but the desorption temperature is lower than seen for CHA, probably because the surface has a higher coverage of hydrocarbon.) This result reveals that a significant quantity of the CHE is activated (i.e., undergoes C–H bond scission) on the Pt(111) surface at or below 290 K. Integration of the 290 K peak suggests that two of the hydrogen atoms of CHE are lost to generate a species of stoichiometry C_7H_{10} . The other features in this trace at 420, 460, and ~ 610 K are due to reaction-limited recombination of hydrogen on the surface, as the C_7H_{10} species undergoes further dehydrogenation.

From a comparison of the $m/e = 2$ TPR traces obtained upon heating Pt(111) surfaces dosed with CHA and CHE, it is clear that the species present on the surface between 250 and 440 K are not the same. Above 440 K, the traces are identical, however, and at these temperatures some correspondences must exist between the surface species that are present.

Reactivity of 1,3-Cycloheptadiene (1,3-CHD) on Pt(111). The TPR spectrum of 1,3-CHD on Pt(111), monitored at $m/e = 94$, shows two low-temperature desorption features (Figure 3). The peak at 180 K is due to desorption from a multilayer whereas the weak feature at 322 K corresponds to the desorption of a small quantity of 1,3-CHD from the monolayer. Corresponding features are seen in the $m/e = 78$ and $m/e = 92$ channels, which track major electron impact induced cracking fragments of 1,3-CHD. A weak desorption feature for benzene also is seen at 457 K in the $m/e = 78$ channel.

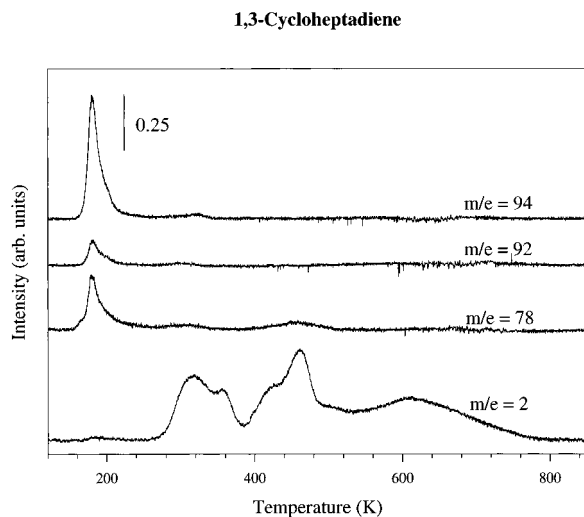


Figure 3. Temperature-programmed reaction spectra for 1,3-cycloheptadiene adsorbed on Pt(111) ($\theta \approx 2.0 \theta_{\text{sat}}$) at 110 K for the following mass values: $m/e = 94$ (CHD), 92 (CHT), 78 (benzene), and 2 (dihydrogen).

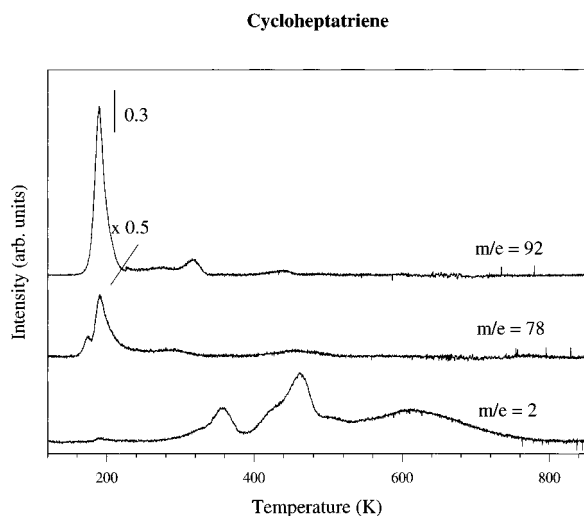


Figure 4. Temperature-programmed reaction spectra for cycloheptatriene adsorbed on Pt(111) at 110 K ($\theta \approx 2.0 \theta_{\text{sat}}$) for the following mass values: $m/e = 92$ (CHT), 78 (benzene), and 2 (dihydrogen).

A complex envelope of desorption peaks is seen for dihydrogen ($m/e = 2$). This result suggests that 1,3-CHD is extensively dehydrogenated on the surface. TPR features due to both recombination-limited (315 and 360 K) and reaction-limited (460 and ~ 610 K) desorption of H₂ are seen. Integration of the $m/e = 2$ TPR trace suggests that three of the 10 hydrogen atoms of 1,3-CHD are lost between 280 and 390 K. At the latter temperature, therefore, the average composition of species present on the surface is C₇H₇. Between 390 and 800 K, the remaining seven hydrogen atoms are lost. Comparisons show that the TPR traces for CHA and 1,3-CHD are essentially identical above 390 K, thus suggesting that the same C₇H₇ product is generated from both adsorbates.

Reactivity of Cycloheptatriene (CHT) on Pt(111). TPR profiles for CHT on Pt(111) show several low-temperature features in the $m/e = 92$ channel (Figure 4). The multilayer desorbs near 190 K, and several weak features are seen for the desorption of material present in a more strongly bound monolayer (271, 317, and 440 K). Exceedingly weak desorption features for benzene ($m/e = 78$) are also seen at 282 and 460 K; the lower temperature peak is due to an electron induced cracking fragment of CHT.

The TPR profile monitoring the desorption of dihydrogen ($m/e = 2$) is similar to that seen when 1,3-CHD is dosed on the surface except that the low-temperature H₂ desorption feature at ~ 315 K is now largely absent. Integration suggests that the peak at 360 K corresponds to the loss of one of the eight hydrogen atoms of CHT, so that the composition of the product is C₇H₇. Above 400 K, the TPR trace is essentially identical to that seen for CHA and 1,3-CHD, which suggests that the same C₇H₇ product is common to all three decomposition pathways.

Auger Electron Spectroscopy. We have used AES to estimate the amount of carbon that remains on the surface after a monolayer of each cyclic C₇ compound is heated to ~ 850 K. We find the following approximate values, expressed as a fraction of a monolayer of carbon (θ_c):²⁰ CHA (0.19), CHE (0.75), 1,3-CHD (0.87), and CHT (0.87). Control experiments verified that carbon deposition via the outgassing of the Auger electron spectrometer was minimal. The information provided by AES is instructive, because the amount of carbon remaining after a substrate bearing a near saturation coverage is heated provides a measure of the dissociation/desorption branching ratio. For the cyclic C₇ hydrocarbons, the following qualitative conclusions can be drawn: CHA desorbs molecularly to a significant degree, whereas CHE, 1,3-CHD, and CHT mostly undergo extensive dissociation and fragmentation reactions upon heating.

Reflection–Absorption Infrared Spectroscopy. Reflection–absorption infrared spectroscopy (RAIRS) is useful for establishing both the structures and the orientations of surface-bound adsorbates.^{51,52} The identification of an adsorbed species is best accomplished by comparing an experimental spectrum with that of a suitable model species of known structure. For metal surfaces, information about the orientation of adsorbed molecules can be obtained by virtue of the surface-dipole selection rule,^{53–56} which states that, to be observable, a vibration must have a nonzero projection of its transition dipole moment onto the surface normal. In more quantitative terms, the intensity of a vibrational mode will be proportional to $\cos^2\theta$, where θ is the angle formed between the transition moment vector and the surface normal.⁵⁷

The following RAIRS spectra were obtained from overlayers of various cyclic hydrocarbons at or approaching monolayer coverages on Pt(111). Brief descriptions of the RAIR spectra measured for multilayer coverages of the adsorbates on Pt(111) are presented in the Supporting Information. The assignments of the bands seen in the multilayer spectra are based on literature assignments and assist in making assignments for the features seen in the monolayer spectra discussed below.

Cycloheptane (CHA) on Pt(111). Temperature-dependent RAIR spectra for near saturation coverages (~ 1 monolayer) of CHA adsorbed on Pt(111) are shown in Figure 5; the corresponding mode assignments are presented in Table 1 along with those for gas-phase samples of CHA.⁵⁸ The high-frequency region of the RAIR spectra (2300–3000 cm^{−1}) contains two sets of bands for distinct types of C–H stretching vibrations: there is a set of sharp bands in the normal C–H stretching region between 2800 and 3000 cm^{−1}, and there is a broad band (fwhm ~ 300 cm^{−1}) near 2630 cm^{−1}. The low-frequency feature at ~ 2630 cm^{−1} (a so-called “soft” mode) arises from C–H oscillators experiencing direct C–H...M interactions with the platinum surface; we hereafter refer to these C–H bonds as lying proximal to the surface (C–H_{proximal}).^{40,42,44} The appearance of the soft mode (both its line shape and its frequency) closely resembles that seen for cyclohexane on Pt(111) and other metal surfaces.^{16,34,36–39,41,43–45}

TABLE 1: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of Cycloheptane on Pt(111)

assignment	110 K	150 K	200 K	250 K	300 K	350 K	400 K	450 K	gas phase ^a
CH ₂ ν_a (C–H) ^b			2924	2930	2935				
CH ₂ ν_a (C–H) ^c	2907	2906	2907						2925
CH ₂ ν (C–H _{distal}) ^c	2882	2883	2889						
CH ₂ ν_s (C–H) ^{c,d}	2845	2845	2849	2848					2860
CH ₂ ν (C–H _{proximal}) ^c	2630	2630	2710						
CH ₂ bend ^b			1452	1447					
combination band ^b			954	955					

^a Assignments taken from gas-phase infrared spectrum of cycloheptane (see Supporting Information).⁵⁸ ^b Contains at least a partial contribution from an adsorbate resulting from the dehydrogenation of cycloheptane. The structure of this intermediate is presently not known (see text). ^c From adsorbed cycloheptane. ^d At 250 and 300 K, this feature primarily arises from the adsorbed intermediate whose identity is presently unclear.

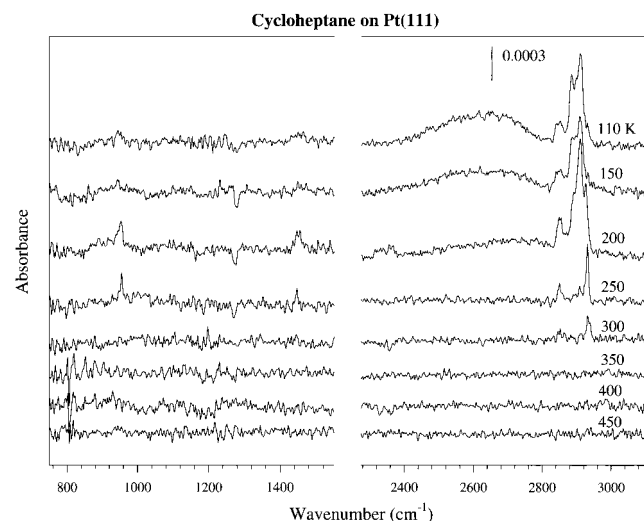


Figure 5. Reflection-absorption infrared spectra for a monolayer of cycloheptane adsorbed on Pt(111) taken after annealing at the following temperatures: 110, 150, 200, 250, 300, 350, 400, and 450 K.

The intense bands at 2907, 2882, and 2845 cm⁻¹ are assigned to the C–H stretching vibrations of C–H bonds that are not involved in C–H...M contacts. We expect one band for the C–H_{distal} bond of the methylene group(s) whose C–H_{proximal} bond is responsible for the soft mode at 2630 cm⁻¹. Other bands (possibly at 2907 and 2845 cm⁻¹) are expected for the antisymmetric and symmetric C–H stretching modes of the methylene groups that are not involved in strong interactions with the surface. These mode assignments are tentative, however, because the bands in this region are not well resolved and appear to contain multiple components. In addition, the line widths of the bands seen at 110 K are larger than we might expect, which suggests that the spectra may reflect the presence of nonequilibrium organizational structures.

When the CHA-dosed surface is heated to higher temperatures ($T > 200$ K), the spectra change markedly. The soft mode blue-shifts and becomes less intense, and eventually disappears when the sample is heated above 250 K. These changes are accompanied by decreases in the intensities of the other bands seen at 100 K and the growth of new bands at 2930, 1447, and 955 cm⁻¹.⁵⁹ The spectra obtained after the 250 K anneal resemble those seen at this temperature for cycloheptene adsorbed on Pt(111) (see below). We cannot, however, conclude that CHA converts to CHE, because the TPR spectra clearly show that different species are present at this temperature. Irrespective of the identity of this thermolysis product, the overall intensities of the new bands suggest that the coverage of this species is low, an observation that is consistent with the fact that most of the CHA desorbs molecularly (as demonstrated by the TPR results).

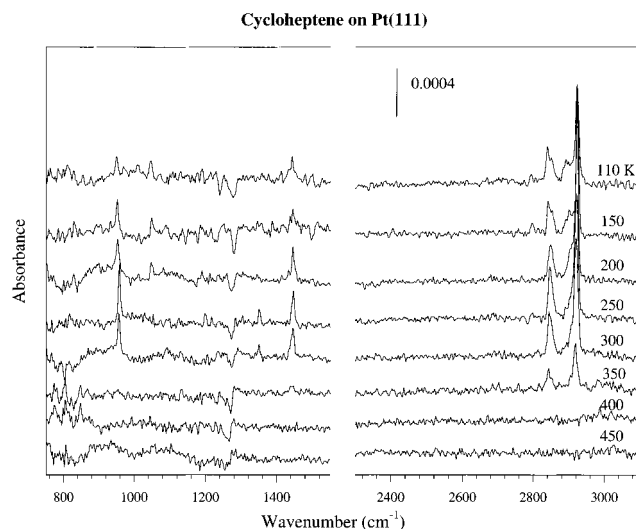


Figure 6. Reflection-absorption infrared spectra for a monolayer of cycloheptene adsorbed on Pt(111) taken after annealing at the following temperatures: 110, 150, 200, 250, 300, 350, 400, and 450 K.

Above 350 K, the RAIR spectra of the CHA-dosed surface are featureless.

cis-Cycloheptene (CHE) on Pt(111). The temperature-dependent RAIR spectra of CHE are shown in Figure 6. The mode assignments for these spectra are given in Table 2. We first note that the spectra are essentially identical between 110 and 300 K. In each instance, the spectrum is dominated by four bands at ~2920, 2845, 1444, and 955 cm⁻¹. The first two bands are assigned to the antisymmetric and symmetric stretches of the methylene groups of surface-bound CHE. The latter two low-frequency modes correspond to a CH₂ scissor deformation and a combination band, respectively (see Table 2).

When a metal-bound adsorbate contains a C=C bond that is not interacting with the surface, olefinic C–H stretching modes above 3000 cm⁻¹ are usually observed in the RAIR spectrum.¹⁴ In Figure 6, the absence of bands above 3000 cm⁻¹ is consistent with our expectation that CHE is bound to the Pt(111) surface by means of its C=C bond. When the C=C bond of an olefinic species binds to a metal surface, there is a rehybridization of the olefinic carbons (sp²) to greater sp³ character.⁶⁰ The stretching mode for such a rehybridized olefinic C–H bond appears as a weak feature between 2885 and 2925 cm⁻¹ for a variety of Pt(111)-bound alkenes including ethylene, cyclopentene, cyclohexene, and cyclohexadiene.^{3,10,15,61–67} In Figure 6, a poorly resolved shoulder at ~2900 cm⁻¹ is probably assignable to this olefinic C–H stretch, but we note that the distal C–H stretches of methylene groups in contact with a Pt(111) surface also occur in this region.^{40,42}

Subtle changes in the RAIR spectrum occur upon heating the CHE-dosed surface to 250 K. The shoulder at ~2900 cm⁻¹ either disappears or moves to higher frequency. These changes

TABLE 2: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of Cycloheptene on Pt(111)

assignment	110 K	150 K	200 K	250 K	300 K	350 K	400 K	450 K	neat ^a
CH ₂ ν_s (C–H)	2920	2922	2920	2920	2919	2918			2921
CH ν (C–H)	2890	2899							
CH ₂ ν_s (C–H)	2837	2840	2847	2845	2844	2844			2839, 2850
CH ₂ bend	1443	1444	1455	1446	1445				1446
combination band	951	953	953	958					
C–H out-of-plane bend ^b							774, 848		

^a Assignments taken from the neat IR spectrum of cycloheptene (see Supporting Information). ^b From the η^7 -cycloheptatrienyl intermediate.

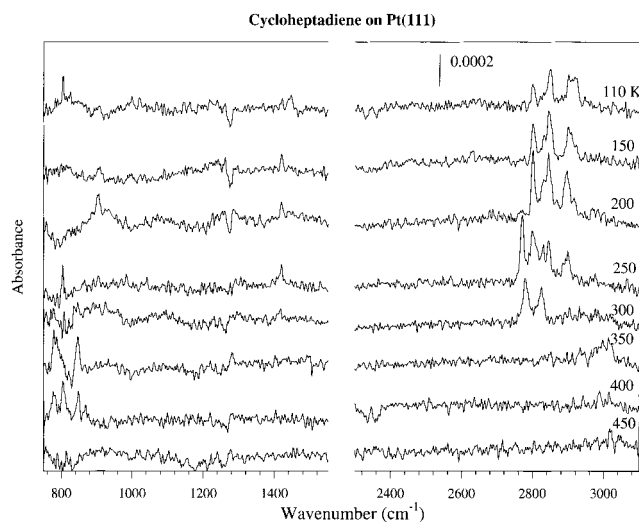


Figure 7. Reflection-absorption infrared spectra for a monolayer of 1,3-cycloheptadiene adsorbed on Pt(111) taken after annealing at the following temperatures: 110, 150, 200, 250, 300, 350, 400, and 450 K.

occur in a temperature range in which dehydrogenation of CHE is taking place, as shown by the TPR studies.

The RAIR spectrum of CHE changes markedly at temperatures above 350 K: the modes for surface-bound CHE decrease in intensity and disappear entirely by 400 K. At this temperature, new (but extremely weak) bands are observed at 774 and 848 cm⁻¹.⁶⁸ It is likely that all of the features seen in the low-frequency region are due to the out-of-plane C–H bending motions of a CHE dehydrogenation product. The absence of any modes of significant intensity in the C–H stretching region (2800–3100 cm⁻¹) suggests that this species is probably planar and bound in an orientation in which the C–H bonds are parallel to the plane of the surface.

1,3-Cycloheptadiene (1,3-CHD) on Pt(111). The temperature-dependent RAIR spectra of 1,3-CHD on Pt(111) are shown in Figure 7. Mode assignments are summarized in Table 3.⁶⁹ The free 1,3-CHD molecule adopts a conformation of C_s symmetry in which the four olefinic carbons and two allylic carbons all lie in the same plane; the homoallylic carbon is displaced out of this plane by ~60°. The absence of significant C–H stretching modes with frequencies >3000 cm⁻¹ is consistent with a binding mode in which the π -system remains coplanar and both C=C bonds interact with the surface.¹⁵ In organometallic complexes, the allylic methylenes are lifted out of the plane of the π -framework; similar structural changes are expected to occur here as well.

The bands at 2799 and 2849 cm⁻¹ are assigned to the symmetric and antisymmetric stretching modes, respectively, of the allylic methylene groups.⁷¹ We assign the broad band at ~2900 cm⁻¹ (located at 2908 cm⁻¹ in the 100 K spectrum) to the antisymmetric stretch of the homoallylic methylene. The corresponding band assignable to the symmetric stretch of this

group appears to be weak and/or poorly resolved from other components.

The low-frequency region shows only one weak band at approximately 1420 cm⁻¹ (it is most noticeable in the 150 K spectrum); we assign this band to a CH₂ scissors mode.

As the temperature is increased, only minor changes are noted in the spectra until ~250 K, at which point bands due to reaction products become evident. In the 250 K spectrum, diagnostic bands are seen in the C–H stretching region at 2830, 2783, and 2770 cm⁻¹. The band at 2770 cm⁻¹ appears first, and it subsequently loses intensity as the bands at 2830 and 2783 cm⁻¹ continue to grow in. We believe that the 2770 cm⁻¹ band is the vibrational signature of an η^5 -cycloheptadienyl species (C₇H₆) formed by the activation of a single C–H bond of the diene, whereas the two higher frequency modes signal the formation of a further dehydrogenation product, cycloheptatriene (see below). To form an η^5 -cycloheptadienyl species, one of the allylic C–H bonds (next to a C=C bond) of 1,3-CHD must be cleaved preferentially.^{2,10,15}

In the η^5 binding mode, the olefinic C–H stretches of the C₇H₆ unit would have their transition dipoles oriented nearly parallel to the surface, and consequently they should not be easily detectable by RAIRS. The signature of this species, the 2770 cm⁻¹ band, is sufficiently low in frequency to suggest (at first glance) that it is a soft mode arising from an agostic C–H...M interaction. Two facts argue against this interpretation, however. First, the band is unusually sharp (fwhm ~10 cm⁻¹); in contrast, soft modes have line widths of at least 50 cm⁻¹ (and often ~300 cm⁻¹).⁴⁰ Second, cyclodienyl ligands in organometallic complexes are known to exhibit a highly characteristic IR band between 2730 and 2830 cm⁻¹ arising from the stretching motions of the exo C–H bond of the methylene unit(s) adjacent to the π -system.^{72,73} In organometallic complexes, the shifting of the exo C–H stretch to lower frequencies has been attributed to hyperconjugative drain of electron density into the adjacent π -system. We believe that the band at 2770 cm⁻¹ is best ascribed to analogous exo C–H stretching motions of the methylene groups of a surface-bound η^5 -cycloheptadienyl fragment.

In the RAIR spectrum, the absence of a band due to the endo C–H bonds of the methylene groups can be explained. The geometry of the η^5 -cycloheptadienyl fragment is likely to be very similar to that seen for the organometallic complex (η^5 -C₇H₉)Fe(CO)[P(OPh)₃]Me.⁷⁴ In this mononuclear species, the carbon atoms of the two methylene groups form a dihedral angle of approximately 45° with respect to the five π -bonded carbon atoms. For a surface-bound η^5 -cycloheptadienyl group, this would mean that the endo C–H bonds of the two methylene groups would be nearly parallel to the surface, and thus their stretching modes (which should be largely decoupled from the endo C–H stretching modes owing to the frequency difference of ~100 cm⁻¹)^{72,73} should be unobservable owing to the RAIR selection rule.

The η^5 -cycloheptadienyl species has only a modest thermal stability. By 300 K, the RAIRS band at ~2770 cm⁻¹ disappears,

TABLE 3: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of 1,3-Cycloheptadiene on Pt(111)

assignment	110 K	150 K	200 K	250 K	300 K	350 K	400 K	450 K	neat ^a
CH ₂ ν_a (C–H) ^b (homoallylic)	2908	2900	2895	2898					2905
CH ₂ ν_a (C–H) ^b (allylic)	2849	2845	2843	2843					2963
CH ₂ ν_a (C–H) ^c				2830	2824				2966
CH ₂ ν_s (C–H) ^b (allylic)	2799	2799	2800	2798					2830
CH ₂ ν_s (C–H) ^c				2783	2781				2838
CH ₂ ν (C–H _{exo}) ^d				2770					
CH ₂ bend ^e	1421, 1447	1420	1420	1420					1430–1448
C–H out-of-plane bend ^f						782, 847	778, 849		

^a Assignments taken from the neat IR spectra of 1,3-cycloheptadiene and cycloheptatriene (see Supporting Information).^{69,76} ^b From adsorbed cycloheptadiene. ^c From adsorbed cycloheptatriene. ^d From the η^5 -cycloheptadienyl intermediate. ^e In the RAIR spectra taken at 100, 150, or 200 K this feature arises from adsorbed cycloheptadiene, while at 250 K this feature largely arises from the η^5 -cycloheptadienyl intermediate. ^f From the η^7 -cycloheptatrienyl intermediate.

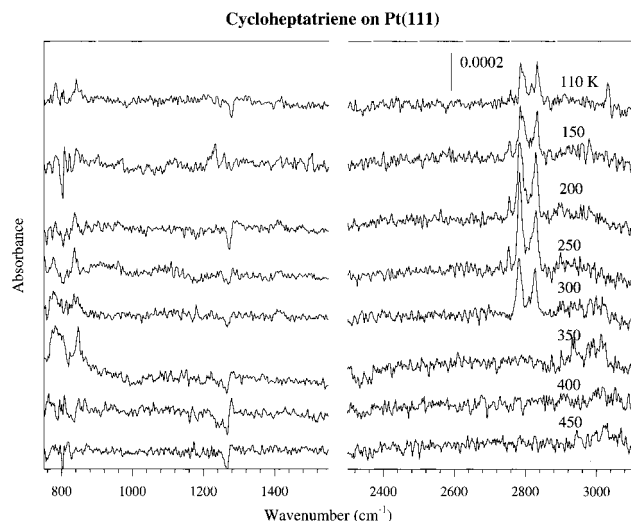


Figure 8. Reflection-absorption infrared spectra for a monolayer of cycloheptatriene adsorbed on Pt(111) taken after annealing at the following temperatures: 110, 150, 200, 250, 300, 350, 400, and 450 K. Note: the band at 2753 cm⁻¹ arises from the presence of small amounts of cycloheptadiene (CHD) in the sample of CHT used to dose the surface (see Experimental Section).

and only the peaks at 2824 and 2781 cm⁻¹ due to the adsorbed cycloheptatriene product remain. This latter assignment is strongly supported by comparing the data in Figure 7 to a low-temperature spectrum of a monolayer prepared directly from the triene (Figure 8, see below).

At 350 K, the adsorbed cycloheptatriene decomposes to yield another species that exhibits two bands at 782 and 847 cm⁻¹,⁷⁵ which we believe are the out-of-plane bending modes of a planar C₇H₇ species. As before, the absence of any significant intensity for C–H stretches in the 2800–3100 cm⁻¹ region suggests that all of the C–H bonds in this species are essentially parallel to the surface. This C₇H₇ species persists, with little change seen in the RAIR spectra, until temperatures greater than 400 K are reached. At this point, the RAIR spectrum becomes featureless. This result is consistent with the decomposition of the planar C₇ species in this temperature range.

Cycloheptatriene (CHT) on Pt(111). Calculations suggest that the lowest-energy conformation of free CHT is that of a distorted boat.⁷⁶ If CHT retains the same geometry when adsorbed on Pt(111), strong olefinic C–H stretches (> 3000 cm⁻¹) should appear in the RAIR spectra. From the data shown in Figure 8 (for which assignments are given in Table 4),⁷⁶ it is evident that some other geometry must characterize the bound state of the molecule, at least at temperatures above 110 K.⁷⁷ Because little or no intensity is observed at frequencies higher than 2850 cm⁻¹, we suggest that the three π -bonds must be coplanar (or nearly so) and must lie parallel to the surface.

The two bands at 2830 and 2784 cm⁻¹ seen in the RAIR spectra at low temperatures are assigned to the antisymmetric and symmetric stretches of the single methylene unit in CHT.⁷⁸ If equivalent oscillator strengths are assumed for these modes, the relative intensities of the bands suggest that the methylene carbon must form a dihedral angle of $\sim 45^\circ$ with respect to the surface (and thus with respect to the other six atoms of the ring). For comparison, the dihedral angle in the corresponding cycloheptatrienyl complex (η^6 -C₇H₈)Mo(CO)₃ is $\sim 50^\circ$.⁷⁹ Like the 2770 cm⁻¹ band of the η^5 -C₇H₉ species discussed above, the 2784 cm⁻¹ band has an unusually low frequency for a methylene C–H stretch but is far too narrow to be a soft mode arising from an agostic C–H \cdots M interaction. We suggest a similar assignment of this band to the stretching mode of the methylene exo C–H bond, which is significantly perturbed by hyperconjugative interactions with the adjacent π -system of the surface-bound CHT molecule.

When the CHT-dosed surface is heated, few changes are noted in the spectra until the annealing temperature approaches 350 K. At this latter temperature, the C–H stretching bands largely disappear, and the only significant features observed lie in the low-frequency region between 750 and 850 cm⁻¹. The pattern seen (bands near 789 and 847 cm⁻¹) closely resembles that found for the other adsorbed cyclo-C₇ molecules except that the bands are more intense when CHT is used as the precursor. On the basis of the arguments presented above, we conclude that a planar η^7 -cycloheptatrienyl species has been formed via a C–H bond activation reaction.⁸⁰

Discussion

The studies described above allow us to construct a unified view of the structures and reactivity patterns seen for these cyclic C₇ hydrocarbons on Pt(111). In the following sections, we comment on different aspects of the underlying mechanisms and energetics.

Soft Modes and C–H Bond Scission: Is there a Correlation? Raval et al. have postulated that the appearance of a soft mode is indicative of an attractive interaction between the adsorbate and the surface, and that this interaction lowers the activation energy for C–H bond scission.⁴⁴ Of all the cyclic C₇ hydrocarbons we have studied, only CHA exhibits a “soft” mode (resulting from a C–H \cdots M interaction) of appreciable intensity when adsorbed on a Pt(111) surface. Despite this fact, however, CHA does not begin to dehydrogenate at a temperature significantly lower than for the other cyclic C₇ hydrocarbons we studied. Furthermore, the C–H \cdots M interaction implied by the appearance of the soft mode cannot be particularly effective in promoting C–H bond cleavage, in view of the observation that about 70% of the CHA simply desorbs when the surface is heated. Thus, the present data do not support the contention

TABLE 4: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of Cycloheptatriene on Pt(111)

assignment	110 K	150 K	200 K	250 K	300 K	350 K	400 K	450 K	neat ^a
CH ν (C—H)	3029								3015–3060
CH ₂ ν_a (C—H)	2830	2830	2827	2825	2824				2966
CH ₂ ν_s (C—H)	2784	2784	2781	2780	2780				2838
unknown		2754	2753	2752					
C—H out-of-plane bend ^b						789, 847	778, 849		

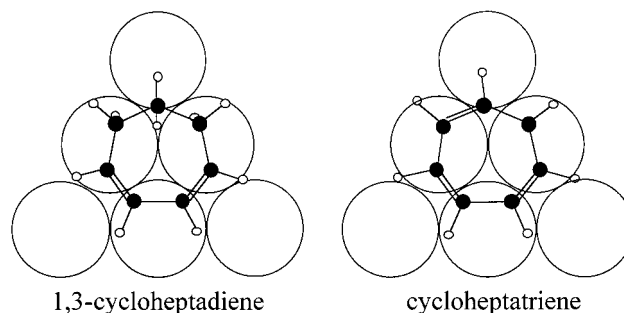
^a Assignments taken from the neat IR spectrum of cycloheptatriene (see Supporting Information).⁷⁶ ^b From the η^7 -cycloheptatrienyl intermediate.

that the appearance of soft modes is correlated with more facile C—H bond activation.

It is difficult to ascertain the exact contribution of C—H...M interactions to the ease of C—H bond activation because other factors are also doubtlessly important. Such factors include the relative stabilities of the reactants and the geometries with which their C—H bonds are presented to specific potentially reactive sites on the surface. We consider these possible geometries in the following section. Before doing so, we feel it is important to note that mode softening is a parameter determined spectroscopically. The selection rules that operate in RAIRS strongly weight those modes whose transition moments are directed most closely along the surface normal. The difficult issue this presents, vis-à-vis the correlation between the C—H...M interaction and the ease of C—H bond activation, is that the mode that will appear most prominently in the RAIRS spectrum is one whose C—H bond is orthogonal to the surface; this geometry is transverse to that presumed to be important in the transition states of the C—H bond cleavage steps.

The Structures of Cyclic C₇ Alkenes on Pt(111). Although CHE, 1,3-CHD, and CHT exhibit no indications of mode softening on Pt(111), this behavior is not generally representative of alkenes bound to Pt(111). We have previously shown, for example, that the unsaturated cyclic hydrocarbons norbornene and norbornadiene exhibit soft modes of significant intensity in their RAIR spectra.^{13,14} We believe that the differing behavior seen here arises from differences in the bonding geometries of the adsorbates. It is generally believed that the C=C bonds of alkenes preferentially occupy bridging sites on the Pt(111) surface and bind in a di- σ fashion.^{14,60,62,63,81} In this bonding mode, the adsorbate is pinned on the surface in a highly specific way, and the locations of the remaining atoms of the alkene with respect to the underlying atoms of the (111) surface can be defined more or less accurately depending on the rigidity of the hydrocarbon skeleton. Depending on the structure of the alkene, C—H bonds from other carbons might be located directly over a high-symmetry (and possibly reactive) site (such as an atop site) or might not. Obviously, the conformational dynamics of the system will allow the adsorbate to explore a range of interactions to a degree commensurate with the relative energies involved. We have shown elsewhere that adsorbate–substrate interactions involving high-symmetry, dipole-active C—H...M contacts can give soft modes of significant intensity in the C—H stretching region of the RAIR spectra.^{14,40,82} The models shown in Scheme 1 suggest that none of the unsaturated cyclic C₇ hydrocarbons studied here can form such high-symmetry interactions with the Pt(111) surface when the olefins are bound in a preferred high-symmetry site (i.e., in a di- σ fashion in which the center of the C=C bond resides over a bridge site).

For monolayer coverages of CHE and 1,3-CHD, we expect that the C=C double bonds will lie essentially parallel to the surface. For 1,3-CHD, geometric models (Scheme 1) suggest that the two conjugated C=C double bonds can bind simultaneously to the surface, albeit with some distortion from perfect bridging symmetry. This η^4 -diene structure is analogous to the

SCHEME 1. Possible Binding Geometry for 1,3-Cycloheptadiene and Cycloheptatriene on Pt(111)

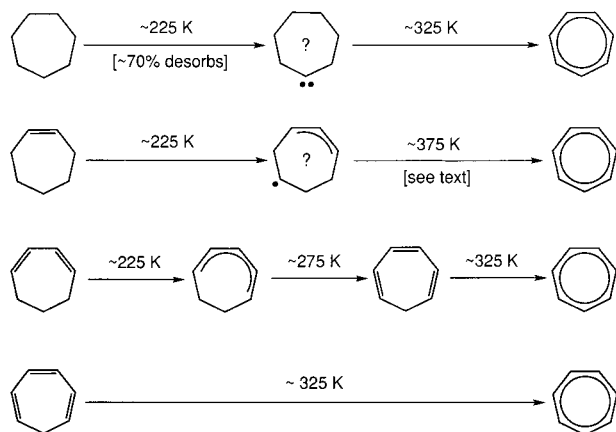
η^4 -CHD and η^4 -CHT bonding motifs observed in discrete organometallic complexes.^{83,84}

For CHT, the geometry adopted by the free molecule is not optimal for binding to a surface. The boat conformation is the lowest energy form of the free CHT molecule; in this geometry the double bonds are not coplanar (only the two “opposite” double bonds lie in the same plane). If CHT were bound to Pt(111) in the boat conformation, then at least one of the C=C double bonds would be projected away from the surface because this geometry does not permit all three C=C double bonds to bind to a Pt(111) surface simultaneously.⁷⁷ The absence of significant intensity for olefinic C—H stretches in the RAIR spectrum of CHT on Pt(111) argues against this conformation as a model for the bound state (see Figure 8).

In analogy with the discussion above, we believe that the CHT binds to the surface via a planar arrangement of its π -system. Only two of the conjugated π -bonds, however, can bind to the surface at high-symmetry sites (producing an η^4 structure); the symmetry of the bonding of the third π -bond must be much lower. For the planar conformer to be preferred on the surface, however, the enhancement in the binding energy must be sufficient to overcome the energetic cost of adopting the planar structure. In fact, the barrier to inversion through the planar form of CHT is known to be less than 6 kcal/mol.⁷⁶ It is, therefore, easy to rationalize that the planar form is adopted in order to facilitate this strong type of bonding to the surface.

Reactivity Patterns of Cyclic C₇ Hydrocarbons on Pt(111).

The TPR data monitoring the desorption of dihydrogen ($m/e = 2$) allow us to estimate the stoichiometries of the species formed via the sequential dehydrogenation of the cyclic C₇ hydrocarbons. This analysis follows the quantitative methods reported recently by Frei and Campbell.⁸ By integrating the intensity of each TPD feature and comparing this value with the total intensity measured for the entire spectrum, we can estimate (albeit approximately) the fraction of hydrogen that is lost at each temperature. These fractions can be used to deduce stoichiometries for the thermolysis products provided that no hydrogen is lost in other ways (for example as desorbing hydrocarbons). It is also helpful if the TPD features are well-resolved. Fortunately, the thermal behaviors of most of the cyclic C₇ hydrocarbons largely meet these criteria.

SCHEME 2. Reactivity Scheme for Cyclic C₇ Hydrocarbons on Pt(111)^a


^a The C₇H₇ product decomposes to carbon and hydrogen at $T > 425$ K.

The reaction patterns seen for all of the molecules we have studied are summarized in Scheme 2.

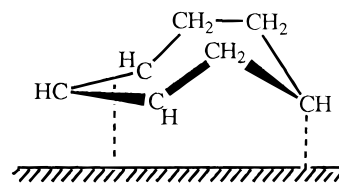
For CHA, the integration of the $m/e = 2$ profile was carried out from 275 to 825 K; this range excludes the low-temperature feature that results from the EI-induced cracking of the CHA that desorbs from the monolayer. The TPD intensity goes nearly to zero at ~ 400 K, and integration shows that $50 \pm 2\%$ of the 14 hydrogen atoms of CHA are lost below this temperature. Thus, the species present at 400 K has the approximate stoichiometry C₇H₇.

1,3-CHD and CHT behave similarly: the TPR intensity goes nearly to zero at ~ 390 K. For 1,3-CHD, 30% of the 10 hydrogen atoms are lost below this temperature; for CHT, 14% of the 8 hydrogen atoms desorb below 390 K. After the latter number is corrected for the presence of 1,3-CHD in CHT (an impurity which constitutes $\sim 15\%$ of the sample used), the integrations show that both 1,3-CHD and CHT generate species of approximate stoichiometry C₇H₇ at ~ 390 K.

These results suggest that CHA, 1,3-CHD, and CHT form (at least to a significant degree) the same product on Pt(111) upon flash annealing a surface-bound layer to 400 K. This conclusion is supported by the RAIRS results, which indicate that all three hydrocarbons undergo C–H bond activation by 400 K and yield a product in which all of the C–H bonds are essentially parallel to the plane of the surface.⁸⁵

The low-temperature desorption peak seen at 318 K in the $m/e = 2$ trace for 1,3-CHD corresponds to the loss of two hydrogens; this result suggests that the first step in the dehydrogenation of 1,3-CHD results in the formation of CHT. This result is strongly supported by the RAIRS studies.

For the more highly saturated hydrocarbons CHA and CHE, the TPR traces reveal that the dehydrogenation pathways have some unexpected aspects. First, although CHA converts to the C₇H₇ product upon heating, this conversion does not take place via CHE. This is a surprising conclusion. Normally, one would assume that the first products generated upon dehydrogenation of an alkane on a metal surface would be an alkyl (by the loss of one H atom) and an alkene (by the loss of two H atoms), the former converting to the latter by means of a β -hydrogen abstraction process. That this assumption is incorrect is clearly shown by the different TPR traces seen when CHA- and CHE-dosed surfaces are heated. There are several possible explanations of this behavior, but we favor the following: cycloheptane first loses one hydrogen atom to form a cycloheptyl group, but the next step is α -hydrogen abstraction to form a cycloheptyl-

SCHEME 3. Proposed Conformation of the C₇H₁₀ Intermediate Formed from CHE


idene unit. This hypothesis, if true, implies that α -hydrogen abstraction is faster than β -hydrogen abstraction for alkyl groups on Pt(111) surfaces (at least for the sterically and conformationally encumbered alkyls of concern here).

The second unexpected result of the TPR studies is that, unlike the other C₇ hydrocarbons examined in this study, CHE does not convert cleanly to the C₇H₇ species. The first feature in the $m/e = 2$ TPR trace, which occurs at 290 K (Figure 2), corresponds to the loss of about 18% of the 12 hydrogen atoms of cycloheptene. Thus, two of the C–H bonds are cleaved at or below 290 K, even though there is very little change in the RAIRS spectrum at this temperature (Figure 6, 300 K). Interestingly, the RAIRS data indicate that the species formed in this temperature range is not 1,3-CHD. These results parallel those found in a recent study performed by Frei and Campbell on *cis*-cyclooctene.⁸ They concluded that an η^3, η^1 species of C₈H₁₂ stoichiometry is generated upon hydrogen abstraction from the α and γ methylenes of the cycloalkene. We make a similar suggestion: cycloheptene initially loses a hydrogen atom from an α and a γ methylene group to form an η^3, η^1 species of stoichiometry C₇H₁₀ (Scheme 3).

The second CHE dehydrogenation step is signaled by the appearance of a feature at ~ 420 K in the $m/e = 2$ TPR trace (Figure 2). At temperatures above 440 K, the TPR trace closely resembles those seen for the other C₇ hydrocarbons. We conclude from these observations that many of the η^3, η^1 -C₇H₁₀ molecules present at 290 K lose another three hydrogen atoms by 440 K to generate the same C₇H₇ product, but, because this process is taking place at a higher temperature than seen for the other cyclic C₇ hydrocarbons, the C₇H₇ product is decomposing as it forms.

We estimate that the activation energy for conversion to the C₇H₇ species is about 4 kcal/mol higher for CHE than for the other cyclic C₇ hydrocarbons (see below). The higher barrier for CHE must be a consequence of the details of the dehydrogenation pathway, which probably involve intermediates generated by activation of nonallylic methylene groups, as discussed above. In the η^3, η^1 -C₇H₁₀ intermediate (the structure of which is illustrated in Scheme 3), the molecule is pinned to the surface at two points. The conformational constraints imposed by the geometries of the Pt–C bonds and the cyclic nature of the molecule may make it difficult to bring the C–H bonds of the remaining methylene groups close enough to the surface to initiate C–H bond activation. In other words, activation of the remaining methylene C–H bonds can be accomplished only by overcoming a substantial barrier caused by conformational constraints.⁸⁶

In contrast, for the other cyclic C₇ alkenes, dehydrogenation evidently takes place by the sequential activation of allylic C–H bonds, in which each individual C–H activation step converts a homoallylic CH₂ group into an allylic CH₂ group that is poised to be activated in the next step. In this way, the dehydrogenation process never involves activation of nonallylic methylene groups or formation of intermediates in which further C–H bond activation is conformationally constrained.

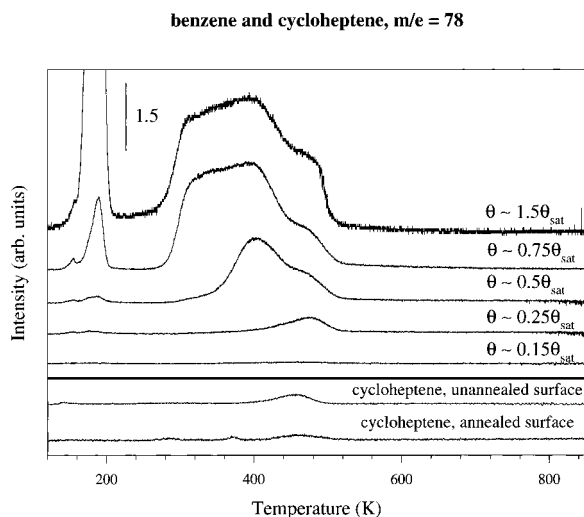


Figure 9. Temperature-programmed reaction spectra in the $m/e = 78$ channel for (lower panel) cycloheptene ($\theta \cong 2.0 \theta_{\text{sat}}$) on a well-annealed surface, cycloheptene ($\theta \cong 2.0 \theta_{\text{sat}}$) on an unannealed surface damaged by sputtering with 500 eV Ar⁺ ions, and (upper panel) increasing coverages of benzene on a well-annealed surface.

Assessment of the Benzene Yield from Cycloheptene by TPRS. The TPRS data suggest that some benzene forms during the thermolytic decomposition of all the cyclic C₇ molecules studied, with the possible exception of CHA. The largest quantity was obtained from the decomposition of CHE (the amount desorbing into the gas phase is, nevertheless, very small). Interestingly, this molecule must undergo the most extensive amount of C–H bond activation to form this aromatic product.

Figure 9 shows the $m/e = 78$ TPR spectra obtained from several related experiments. The two spectra in the bottom panel are for large coverages ($\theta \cong 2.0 \theta_{\text{sat}}$) of CHE: the lower spectrum was obtained on a crystal that was carefully cleaned and annealed according to the protocol described in the Experimental Section, whereas the upper spectrum was obtained on a cleaned but unannealed surface. An integration of the peak areas suggests that about twice as much benzene desorbs from the unannealed surface (TPR spectra measured at other m/e values confirm the assignment of this peak to benzene). The yield in either case, though, is very low (see below).

The spectra in the upper panel show TPRS traces obtained from a well-ordered substrate which had been dosed with various quantities of benzene. These latter spectra are similar to those described by several other groups and serve to illustrate the strong coverage dependence of the benzene desorption kinetics.^{7,25,87} It is seen here that extensive fragmentation of the benzene occurs at low coverages and that the amount that desorbs molecularly increases dramatically when $\theta \geq 1/4 \theta_{\text{sat}}$. We note that the data in Figure 9 also show a low-temperature peak at 180 K (a temperature coincident with that of the multilayer desorption peak) even at coverages far from θ_{sat} . This feature is evident in the data reported by others as well, and, as far as we are aware, has not been explained.^{7,87}

From a comparison of the spectra shown in Figure 9, we conclude that only a small fraction of the adsorbed CHE is converted to benzene. Determining a precise yield by TPRS is not possible, however, owing to the strong coverage dependencies that operate in this system. For the highest yield case (the unannealed surface), the amount of benzene desorbing into the gas phase is similar to that seen for an authentic benzene overlayer at a coverage $\theta \cong 0.25 \theta_{\text{sat}}$. We cannot conclude,

however, that this amount of benzene is generated upon the decomposition of a saturation overlayer of CHE. Instead, the reaction to form benzene is more likely to be a minor pathway that occurs primarily at defect sites on the Pt(111) surface. Support for this conclusion comes from the observation that there are no vibrational features evident in the RAIR spectra of adsorbed CHE that are characteristic of a benzene product at any temperature up to 400 K (where desorption commences).

The Nature of the C₇H₇ Species. Scheme 2 summarizes the reaction pathways followed by the various cyclic C₇ hydrocarbons on Pt(111). The data suggest that all of these molecules yield a planar η^7 -cycloheptatrienyl product in varying amounts at temperatures between 325 and 375 K. This product is formed by a series of sequential C–H bond activation steps, the barriers for which show significant rate-structure sensitivities. As judged from the RAIR spectra, the final conversion to the C₇H₇ species takes place at ~ 325 K for CHA, 1,3-CHT, and CHT, but at ~ 375 K for CHE. These temperatures were maintained for ~ 1 min during the annealing experiments, and from this time scale we can estimate the rates of formation of C₇H₇. The activation barriers for the formation of this planar species from the various cyclic C₇ hydrocarbons examined here are estimated to be ~ 22 kcal/mol for CHA, 1,3-CHD, and CHT, but ~ 26 kcal/mol for CHE.⁸⁸

The RAIR spectra explicitly confirm that the C₇H₇ species formed from the cyclic C₇ hydrocarbons is, indeed, a planar η^7 -cycloheptatrienyl unit. The intensities of the out-of-plane C–H bending modes for the C₇H₇ species are very similar to those of a monolayer of benzene dosed at the same temperature, but the frequencies are different: these modes appear at 825 and 894 cm^{−1} for benzene vs 790 and 847 cm^{−1} for the C₇H₇ species.⁸⁹

Organometallic complexes containing cycloheptatrienyl ligands constitute a well-known structural class.^{90–92} Depending on the exact nature of the complex, the cycloheptatrienyl ligand is usually assigned a formal charge of either +1 or −3; both of these correspond to aromatic (4n+2) electronic configurations.^{83,92,93} Such analogies probably do not hold as precisely in the current instance, although it is likely (owing to the high energy of the Fermi level of Pt(111)) that the surface-bound cycloheptatrienyl unit is an electron-rich species.

As judged from the TPR results, the planar C₇H₇ species begins to decompose at ~ 425 K (for a ramp rate of 2 K/s; this temperature corresponds to an activation energy of ~ 27 kcal/mol).⁸⁸ The thermolysis principally affords surface-bound carbon, although small amounts of benzene (corresponding to much less than a monolayer) also desorb at ~ 460 K. The data suggest that the desorption of benzene may occur at defects on the Pt(111) surface. Most interestingly, the benzene yield was largest when CHE was used as the adsorbate, a result notable in that the conversion of this adsorbate into the planar C₇H₇ species is particularly inefficient. These observations further suggest that the η^7 species is not an intermediate in the formation of benzene.

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Supporting Information Available: One figure and a discussion of the RAIR spectra of multilayers of CHA, CHE, CHD, and CHT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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