

Sequential Dehydrogenation of Unsaturated Cyclic C₅ and C₆ Hydrocarbons on Pt(111)

William L. Manner, Gregory S. Girolami,* and Ralph G. Nuzzo*

*School of Chemical Sciences and the Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801**Received: July 15, 1998; In Final Form: September 25, 1998*

The structures and reactivities of various cyclic C₅ and C₆ hydrocarbons (cyclopentene, cyclopentadiene, cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene) adsorbed on Pt(111) have been examined by means of reflection–absorption infrared (RAIR) spectroscopy. At temperatures below 200 K, these molecules bind intact to the Pt(111) surface by means of strong interactions with C=C double bonds. Steric interactions between the surface and certain CH₂ groups on the ring systems figure prominently in determining the conformation adopted in the bound states of several of the molecular adsorbates (e.g., cyclopentene and cyclohexene). These bonding habits are identified both by observing significant electronic interactions that weaken certain C–H bonds (so-called mode softening) and also by developing analogies with trends seen with similar ring systems and complexes. At higher temperatures above 200 K, the C₅ species are dehydrogenated in high yield to a planar, surface-bound pentahaptocyclopentadienyl species (η^5 -C₅H₅) while the C₆ cyclic hydrocarbons react to give benzene; these surface-bound products, which are stable to temperatures >400 K, have been identified in earlier studies as well. The present work adds to the understanding of the nature and energetics of the sequential C–H bond activation processes involved in their formation. In addition, several intermediates lying along the reaction pathways to the respective planar intermediates have been identified and spectroscopically characterized for the first time. Most notably, we observe that 1,3-cyclohexadiene loses one hydrogen between 200 and 250 K to give a stable η^5 -cyclohexadienyl intermediate. An efficient partial dehydrogenation of cyclopentene at 250 K to give the corresponding diene is also observed. Our data also demonstrate the importance of heretofore unappreciated hyperconjugation effects in the vibrational spectroscopy of the C–H stretching modes of metal-surface-bound π systems. The insights developed in this study regarding such electronic interactions are used to develop an understanding of the binding sites and conformational states adopted by the various adsorbates and intermediates formed during their decomposition.

Introduction

The reactions of cyclic hydrocarbons on Pt(111) surfaces have been extensively investigated owing to their importance in petroleum reforming processes.¹ The dehydrogenation of cyclic alkanes and alkenes to aromatic hydrocarbons is particularly significant, since such processes increase the octane number of fuel mixtures and make it unnecessary to add octane enhancers such as methyl(*tert*-butyl)ether.

In this work, we explore the reactivity of a series of prototypical cycloalkenes on Pt(111)—namely, a series of unsaturated adsorbates possessing either C₅ or C₆ ring structures. Several excellent earlier studies (which are described below) have established that these adsorbates are initially transformed on Pt(111) by remarkably facile C–H bond scission reactions.^{2–10} The nature of the energetics of these processes remain incompletely understood however. This study presents the results of an investigation of these reactions using reflection–absorption infrared spectroscopy (RAIRS). Our results focus primarily on the vibrational spectroscopy of the C–H stretching region since the modestly intense modes found here report sensitively on both the structures and conformations of metal-bound hydrocarbon adsorbates and ligands more generally. These results complement those of earlier studies based on temperature-

programmed reaction spectroscopy (TPRS) and high-resolution electron energy loss spectroscopy (HREELS).

In earlier work it was shown that cyclopentene undergoes C–H bond activation on Pt(111) at 300 K to yield a planar, surface-bound adduct with a structure reminiscent of the pentahaptocyclopentadienyl anion (η^5 -C₅H₅).^{2,3} In contrast, cyclopentadiene has been reported to disproportionate on Pt(111) at 90 K to give adsorbed η^5 -C₅H₅ and cyclopentene.⁴ The cyclopentene so produced was reported to undergo coverage-dependent dehydrogenation to produce additional quantities of η^5 -C₅H₅ product at ~300 K. The η^5 -C₅H₅ species is stable to ~500 K, at which temperature it decomposes to give H₂ and a carbonaceous overlayer on the platinum surface.

The thermolytic chemistries exhibited by cyclic C₆ adsorbates are similar in many respects to those seen in the C₅ system. Previous studies suggest that cyclohexene binds to a Pt(111) surface in a η^2 (di- σ) fashion and that it converts to another di- σ form by 200 K.⁵ Between 200 and 240 K, this second form converts to a π -cyclohexenyl species, C₆H₉.^{5,6,11} At about 340 K, the cyclohexenyl species further dehydrogenates to surface-bound benzene (although a small amount disproportionates and desorbs as cyclohexene). Intermediates have not been identified during the conversion of either 1,4- or 1,3-cyclohexadiene to benzene on Pt(111), even though some degree of C–H bond activation commences at temperatures as low as 200 K and the formation of the benzene product is not complete

* Authors to whom correspondence should be addressed.

until 260 K.^{8–10} In general terms, all the C₆ ring systems undergo such rate/structure sensitive C–H bond scissions near or below 300 K to give bound C₆H₆ in substantial yields. Some fraction of this product benzene can desorb from the Pt(111) surface at higher temperatures ($T \geq 450$ K); a complex coverage-dependent partitioning occurs between this process and the fragmentation of the bound arene ring system.

Vibrational spectroscopy can provide key insights into the C–H bond activation processes that are involved in the thermolytic decomposition of these prototypical adsorbates. For example, the vibrational spectrum of a submonolayer coverage of cyclopentene on Pt(111) exhibits a low-frequency C–H stretching band near 2700 cm^{–1}.² This low-frequency band, which is commonly referred to as a “softened mode”, is indicative of C–H···M interactions between the near-surface (“proximal”) C–H bonds and the platinum atoms. Softened C–H vibrational modes have been observed for a variety of other alkanes adsorbed on numerous different transition metal surfaces.^{12–25} The low frequencies of these features suggest that the proximal C–H bonds are weakened by direct interactions with the surface. It has been proposed that the activation energy for cleavage of a C–H bond should decrease as the C–H stretching frequency decreases,²⁵ but more recent studies indicate that such a straightforward correlation may not hold generally.²⁶

This paper describes the use of reflection–absorption infrared spectroscopy (RAIRS) to follow the temperature-dependent chemistry of unsaturated C₅ and C₆ cycloalkenes on Pt(111). The spectra provide new information about the conformations adopted by these cycloalkenes and about the nature and energetics of the mechanisms by which they dehydrogenate. One important spectroscopic conclusion of this study is that low-frequency C–H stretching bands are not always assignable to proximal (i.e., near-surface) C–H groups; we show that some low-frequency C–H bands arise instead from nonsurface-contacting C–H groups whose stretching frequencies are perturbed by a previously unrecognized hyperconjugative interaction with adjacent surface-bound C=C double bonds.

Experimental Section

Studies were carried out in an ultrahigh-vacuum chamber with a base pressure of less than 4×10^{-10} Torr. The Pt(111) crystal, purchased from Cornell Laboratories, was oriented to within 0.5° and polished to a fine mirror finish by standard metallographic techniques. Typically, the Pt(111) crystal was cleaned by heating it at 950 K in the presence of 1×10^{-6} Torr of O₂ for 3 min and then annealing it in a vacuum at 1000 K for 2 min. If this protocol did not clean the surface sufficiently, the crystal was sputtered with Ar⁺ ions (1 keV) 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. Heating was performed by mounting the crystal on a Varian-style button heater (Spectra Mat). The crystal temperature was controlled over the range 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 using a Digilab FTS 60A spectrometer equipped with a narrow-band, liquid-nitrogen cooled, MCT detector. Reflection optics ($\sim f/12$) were aligned at near-grazing angles of incidence with respect to the crystal surface ($\sim 84^\circ$).²⁷ All RAIR spectra consist of 1024

scans taken at 4 cm^{–1} resolution over a total collection time of ~ 6 min (20 kHz modulation) and are presented as absorbance plots ($-\log R/R_0$).

All compounds used in this study were purchased from Aldrich and were $\geq 97\%$ pure with the exception of dicyclopentadiene. Dicyclopentadiene was $\geq 95\%$ pure and was converted to cyclopentadiene by thermal cracking in a glass apparatus fitted with a Vigreux column. The cyclopentadiene was used immediately after being prepared. Before being introduced into the chamber, all samples were degassed by subjecting them to several freeze/pump/thaw cycles. 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}). The ion gauge in this chamber is uncalibrated for hydrocarbons, and we therefore have used a qualitative measure of saturation to define an upper bound for these exposures based on the appearance of bands due to the weakly adsorbed multilayer.²⁸

Results

Reflection–Absorption Infrared Spectroscopy. Reflection–absorption infrared spectroscopy (RAIRS) is a powerful technique that is capable of providing information about the molecular structures, organizations, and orientations of surface-bound adsorbates.^{29,30} Since RAIRS is a local probe, it cannot, in general, yield the sort of direct structural characterizations as is possible for a system possessing long-ranged translational order using a diffraction-based method. It is a complimentary method, though, in that it is applicable to the characterization of complex polyatomic adsorbates and heterogeneous mixtures of reaction intermediates such as are of interest in this work. Structural characterizations by RAIRS are often built on insights gained from models. The molecular structure of an adsorbed species, or reaction intermediate for example, can often be determined by comparing its RAIR spectrum with that of a suitable model phase of known structure. Organometallic complexes provide one very important class of such model materials. For metal surfaces, information about the organization and orientation of an adsorbate can be obtained by virtue of the so-called surface-dipole selection rule: to be observable, a vibration must have a nonzero projection of its transition dipole moment onto the surface normal.^{31–34} In more quantitative terms, the RAIR intensity of a mode will be proportional to $\cos^2\theta$ where θ is the angle formed between the transition moment vector and the surface normal.³⁵ This approach has found wide application in the characterization of self-assembling organic thin-films on a variety of metal surfaces.³⁶ In the present study, we exploit these aspects of RAIRS spectroscopy to gain information about the structures and thermolytic chemistry of C₅ and C₆ cycloalkenes on Pt(111). Of particular interest in the present context is the use of RAIRS as a local probe to follow the progression of C–H bond scission reactions which convert these prototypical ring-systems into a series of more extensively dehydrogenated products.

Unless otherwise noted, the RAIR spectra were collected for submonolayer coverages of the specified hydrocarbon. These monolayers were prepared by dosing from the background at 100 K, annealing the surface to the stated temperature, and then cooling the surface to 100 K before collecting the spectrum. We will focus our discussion on the bands that appear in the C–H stretching region because these bands are the most intense in the spectra and therefore of most use in assigning structures.

Cyclopentene on Pt(111). Temperature-dependent RAIR spectra of submonolayer coverages ($\theta_i \cong 0.8\theta_{\text{sat}}$) of cyclopent-

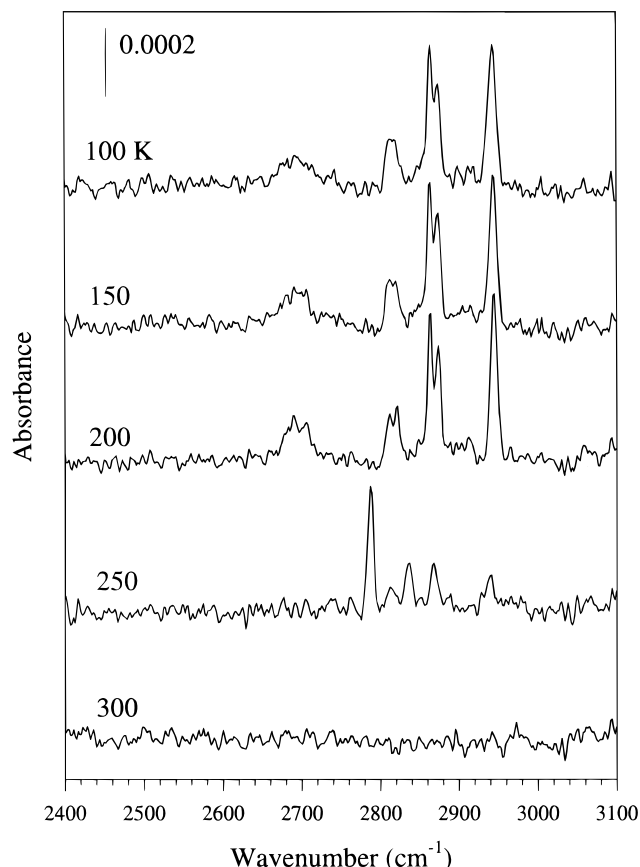


Figure 1. Reflection-absorption infrared spectra for a submonolayer of cyclopentene ($\theta_i \cong 0.8\theta_{\text{sat}}$) adsorbed on Pt(111) taken after annealing at the following temperatures: 100, 150, 200, 250, and 300 K.

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

assignments	100 K	150 K	200 K	250 K	300 K
$\text{CH}_2 \nu(\text{C}-\text{H}_{\text{distal}})^a$	2945	2944	2944	2940	
$\text{CH}_2 \nu_{\text{anti}}(\text{C}-\text{H})^{a,b}$	2864, 2874	2864, 2874	2863, 2874	2867	
$\text{CH}_2 \nu_{\text{anti}}(\text{C}-\text{H})^c$				2834	
$\text{CH}_2 \nu_{\text{sym}}(\text{C}-\text{H})^{a,b}$	2815	2811, 2819	2812, 2821	2813	
$\text{CH}_2 \nu_{\text{sym}}(\text{C}-\text{H})^c$				2787	
C-H out-of-plane bend ^d					818

^a From adsorbed cyclopentene. ^b Split band is due to a Fermi resonance between the antisymmetric stretch and the overtone of the methylene scissors bend. ^c From the adsorbed cyclopentadiene intermediate. ^d From the η^5 -cyclopentadienyl (Cp) intermediate.

tene on Pt(111) are shown in Figure 1; the mode assignments are presented in Table 1. At 100 K, the C-H stretching region (2400–3100 cm^{-1}) features five bands above 2800 cm^{-1} and one low-frequency band at 2694 cm^{-1} . The two bands near 2815 cm^{-1} are more completely resolved after the sample is annealed at higher temperatures (150 or 200 K). Below 200 K, cyclopentene adsorbs on Pt(111) without undergoing C-H activation processes,^{2,3} and therefore these six bands must arise from the intact molecule.

Chemical evidence (such as the fact that cyclopentene adsorbs more tightly to Pt(111) than does the saturated hydrocarbon cyclopentane) strongly suggests that the C=C double bond in cyclopentene is bound to the surface. The RAIR spectrum of cyclopentene on Pt(111) is consistent with this suggestion. The frequencies of the vinylic C-H stretches should be above 3000 cm^{-1} if the C=C double bond is not interacting with the surface; for example, the RAIR spectra of Pt(111) surfaces dosed

with norbornadiene (which contains such a noninteracting C=C double bond) exhibit a strong band in this region.³⁷ In contrast, the RAIR spectrum of cyclopentene contains no observable features above 3000 cm^{-1} . Instead, the coordination of the C=C double bond to the surface should shift the frequencies of the vinylic C-H stretches to $\sim 2950 \text{ cm}^{-1}$. The intensities of these bands should be very small, however, and it is likely that these bands are obscured by the strong band at 2945 cm^{-1} , whose true assignment we will discuss shortly.

The low-frequency feature at 2694 cm^{-1} closely resembles the “softened” modes seen for many saturated hydrocarbons (and certain other organic molecules) on platinum surfaces.^{13,18,25} This vibrational mode was also noted by Avery, who showed that the high-resolution electron energy loss spectrum of cyclopentene on Pt(111) contained a feature at $\sim 2695 \text{ cm}^{-1}$.² Softened C-H stretching modes are indicative of the presence of C-H...M interactions with the metal surface. We therefore assign the 2694 cm^{-1} feature to the C-H stretch of a near-surface (“proximal”) C-H bond of one or more of the methylene units of the cyclopentene ring. Although the softened C-H modes seen for cyclohexane and other saturated cyclic hydrocarbons are usually quite broad (fwhm > 150 cm^{-1}),^{12,15,17,19–25,38,39} the softened mode for cyclopentene is relatively narrow (fwhm $\sim 50 \text{ cm}^{-1}$). This point will be addressed in the Discussion section.

The five bands seen in the low-temperature spectrum between 2800 and 2950 cm^{-1} are interpreted as follows. The band at 2945 cm^{-1} is tentatively assigned to the surface-remote (“distal”) C-H bond of the methylene unit(s) involved in the direct C-H...M interaction. This band strongly resembles a feature at 2947 cm^{-1} seen in the RAIR spectrum of norbornene adsorbed on Pt(111); this latter band was also assigned to the distal C-H bond of the methylene bridge unit involved in a direct C-H...M interaction with the surface.⁴⁰ (The similarities between the vibrational spectra of cyclopentene and norbornene on Pt(111) are not accidental and will be addressed in the Discussion section.) If this assignment is correct, the 2945 cm^{-1} band is a pure mode involving a single C-H oscillator: the distal and proximal C-H oscillators of a methylene unit interacting with a surface will have different frequencies and thus will not be strongly coupled.

The appearance of four other bands in the high-frequency region of the RAIR spectrum is, at first glance, somewhat perplexing because this number is greater than expected. The four bands, however, are arranged in pairs. If we ignore the small 10 cm^{-1} splitting, the composite band at 2811/2819 cm^{-1} can be assigned to the symmetric C-H stretch of a methylene group, and the composite band at 2864/2874 cm^{-1} to the corresponding antisymmetric stretch. The frequencies of these composite peaks are some 30 cm^{-1} lower than those expected for “normal” methylene groups,^{41,42} and this shift may be a consequence of a weak hyperconjugation effect (see below).

We believe that the small 10 cm^{-1} splittings are due to Fermi resonances. The pair of bands at 2811 and 2819 cm^{-1} and the pair at 2864 and 2874 cm^{-1} are probably both generated by a Fermi resonance between a methylene C-H stretch and the overtone of the CH_2 scissors band at $\sim 1420 \text{ cm}^{-1}$.^{42,43} The 1420 cm^{-1} scissors mode is apparent in the RAIR spectrum of cyclopentene on Pt(111) (data not shown) and is also seen in the IR spectrum of the free molecule.⁴²

The RAIR bands narrow slightly when the cyclopentene-dosed surface is warmed to 150 and 200 K. We believe the organization of the overlayer contains defects at 100 K which are annealed out at higher temperatures.

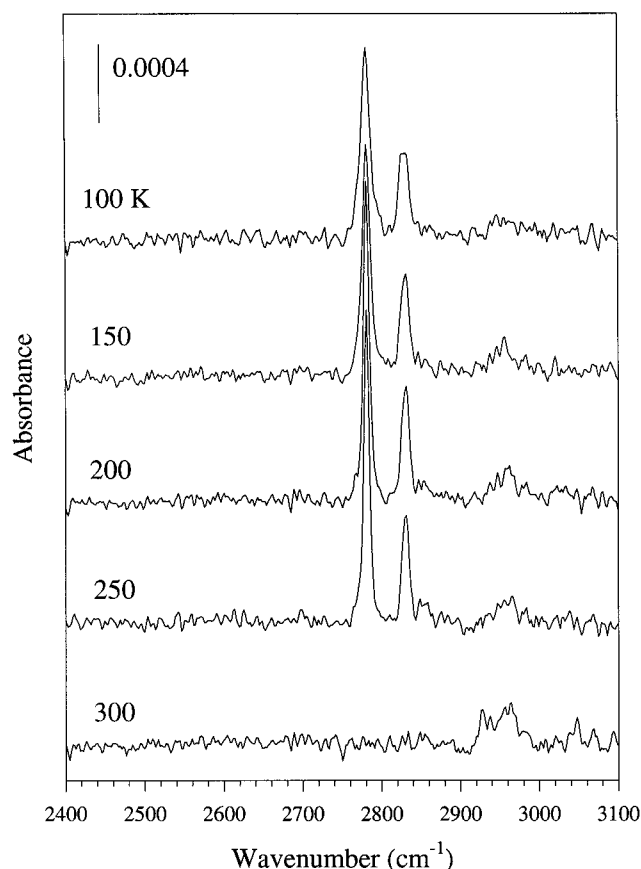


Figure 2. Reflection-absorption infrared spectra for a submonolayer of cyclopentadiene ($\theta_i \cong 0.8\theta_{\text{sat}}$) adsorbed on Pt(111) taken after annealing at the following temperatures: 100, 150, 200, 250, and 300 K.

At 250 K, the RAIR spectrum changes significantly. The softened mode disappears, while the modes above 2800 cm^{-1} drop in intensity by at least a factor of 4. New bands appear at 2787 and 2834 cm^{-1} which arise from a cyclopentene thermolysis product. As will be shown below, these new bands are precisely those seen for the Pt(111)-bound cyclopentadiene (C_5H_6) molecule. The finding that cyclopentene commences dehydrogenation at $\sim 250\text{ K}$ is consistent with previous temperature-programmed reaction studies.^{2,3} In these studies, however, the intermediate formation of cyclopentadiene evidenced in the present data was not observed. Instead, it was concluded that either the cyclopentene desorbs (primarily at higher coverages) or directly forms a planar C_5H_5 species as will be discussed below.

After the cyclopentene-dosed surface is heated further (300 K), the C–H stretching region of the RAIR spectrum becomes featureless at our signal-to-noise ratio, but a new band at 818 cm^{-1} grows in (see below). Other studies suggest that a cyclopentadienyl species (C_5H_5) is present on the surface at this temperature.^{2,3} Quantitative interpretation of these data collected by thermal desorption spectroscopy revealed that three hydrogen atoms were cleaved from adsorbed cyclopentene by 300 K, producing a stoichiometry of C_5H_5 . The C–H bonds of C_5H_5 should lie nearly parallel to the surface, and thus it is not surprising that the intensity of the C–H stretching bands are exceptionally weak in the RAIR spectrum. The 818 cm^{-1} band can be assigned to an out-of-plane C–H bend of the C_5H_5 unit, as will be discussed below.

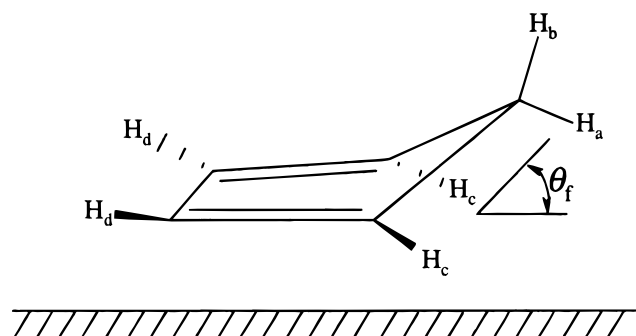
The cyclopentadienyl species is stable to $\sim 480\text{ K}$, at which point it starts to dehydrogenate. Between 750 and 800 K only a carbonaceous overlayer remains on the surface.^{2,3}

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

assignments	100 K	150 K	200 K	250 K	300 K
CH $\nu(\text{C-H})$ (vinyl) ^a	2952	2957	2959	2964	
CH ₂ $\nu_{\text{anti}}(\text{C-H})^a$	2830	2832	2832	2832	
CH ₂ $\nu_{\text{sym}}(\text{C-H})^a$	2781	2782	2782	2782	
C–H out-of-plane bend ^b					816

^a From adsorbed cyclopentadiene. ^b From the η^5 -cyclopentadienyl (Cp) intermediate.

SCHEME 1



Cyclopentadiene on Pt(111). The temperature-dependent RAIR spectra of a submonolayer of cyclopentadiene on Pt(111) are shown in Figure 2, and the mode assignments are given in Table 2. Between 100 and 250 K, the spectra are dominated by two bands at ~ 2782 and 2832 cm^{-1} ; these bands are the same as those seen when cyclopentene is heated to 250 K (see above). The identity of the 250 K cyclopentene thermolysis product as cyclopentadiene is therefore established.

Importantly, the RAIR spectra are *not* consistent with a previous suggestion⁴ that cyclopentadiene disproportionates above 90 K to a mixture of C_3H_5 and cyclopentene. No bands assignable to cyclopentene are seen. If such a disproportionation takes place at all, it must involve only a small fraction ($<10\%$) of the molecules on the surface.

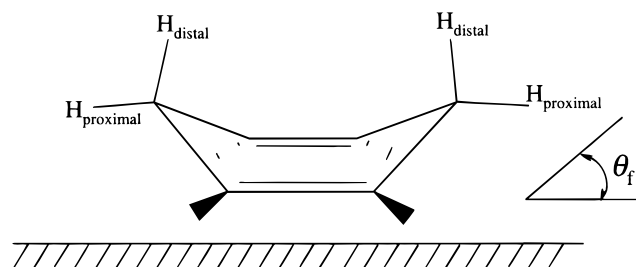
The absence of strong RAIR bands at frequencies above 3000 cm^{-1} again is consistent with the expectation that both C=C bonds of cyclopentadiene are bound to the surface. Although free cyclopentadiene is thought to be planar,⁴⁴ it is likely that some rehybridization of the olefinic carbons is induced by the surface interactions and that this in turn causes the methylene unit to be displaced away from the surface (i.e., out of the plane of the other four carbons; Scheme 1). Similar structural changes occur when cyclopentadiene coordinates to a single metal atom in a complex.^{45,46}

Rehybridization should also cause the vinyl C–H bonds to point slightly toward or away from the surface, and it is possible that the very weak feature(s) at $\sim 2950\text{ cm}^{-1}$ are the C–H stretches of the surface-bound vinyl groups.

The two strong bands at ~ 2782 and 2832 cm^{-1} must be assigned to the methylene unit of cyclopentadiene, but there are several different ways to assign them. The first possibility is that the methylene unit is unperturbed by interactions with the surface, and thus the two strong RAIR bands are due to the symmetric (2782 cm^{-1}) and antisymmetric (2832 cm^{-1}) linear combinations of the two C–H oscillators. This possibility does not, however, explain why the 2782 cm^{-1} band has such a low frequency.

A second possibility is that the frequency of the *proximal* C–H oscillator (C–H_a in Scheme 1) is lowered by C–H...M interactions with the surface. If the interaction were strong

SCHEME 2



enough, the two methylene C–H oscillators would be decoupled from one another, and the two strong RAIR bands would thus arise from the proximal C–H_a (2782 cm⁻¹) and distal C–H_b (2832 cm⁻¹) stretches. This possibility can be excluded immediately, however, because the line width of the band at 2782 cm⁻¹ is much too narrow to be attributed to a C–H stretching mode softened by a M···C–H interaction (in this case, the fwhm is ~12 cm⁻¹).

A third possibility is that the frequency of the *distal* C–H oscillator (C–H_b in Scheme 2) is lowered by electronic interactions with the adjacent π -system. In this case, the resulting large frequency difference would again uncouple the two oscillators. The two strong RAIR bands in this model, would be assigned to the distal C–H_b (2782 cm⁻¹) and proximal C–H_a (2832 cm⁻¹) stretches. This is the reverse of the assignment given in possibility (2).

These three possibilities can be distinguished by an analysis of the relative intensities of the two methylene C–H stretching bands. In this analysis, we assume that the diene portion of the molecule is parallel with the surface. For possibility (1), if we assume that the oscillator strengths of the symmetric and antisymmetric modes are approximately equal,⁴⁷ we can estimate the dihedral “fold” angle (θ_f) of the cyclopentadiene ring from the $\cos^2\theta$ formula that relates the RAIR intensity of a mode to the angle θ formed between its transition direction and the surface normal.³⁵ The ratio I_{2782}/I_{2832} is ~2.5:1, and we calculate that the dihedral “fold” angle of the cyclopentadiene ring would have to be ~58°. This angle is significantly larger than those of ~37° seen for η^4 -cyclopentadiene ligands on discrete organometallic complexes.^{45,48} The required dihedral angle for this assignment appears to be unrealistically large (and does not explain the frequency shifts, as noted above).

Possibility (2) also gives an unrealistic dihedral angle for the cyclopentadienyl ring. If we assume that the proximal and distal oscillators act independently and have equal oscillator strengths, the dihedral angle would have to be approximately -17° to give the observed intensity ratio. In other words, the methylene group would have to be folded down *toward* the surface, and unacceptably short contacts with the surface would result.

For possibility (3), a dihedral angle of ~17° would be sufficient to produce the relative intensities of the two bands in the RAIR spectrum, again assuming that the proximal and distal C–H oscillators act independently and that their oscillator strengths are approximately equal. We believe that this is the most likely assignment for the two features present in the low-temperature spectra of cyclopentadiene.

A similar phenomenon has been noted previously in organometallic complexes that contain η^4 -cyclopentadiene and η^5 -cyclohexadienyl ligands. Such complexes exhibit a low-frequency IR band between 2730 and 2830 cm⁻¹,^{49–53} and isotopic labeling studies clearly demonstrate that the band is associated with the distal (i.e., metal-remote) C–H bond.^{54–56} In these organometallic molecules, the lowering of the distal

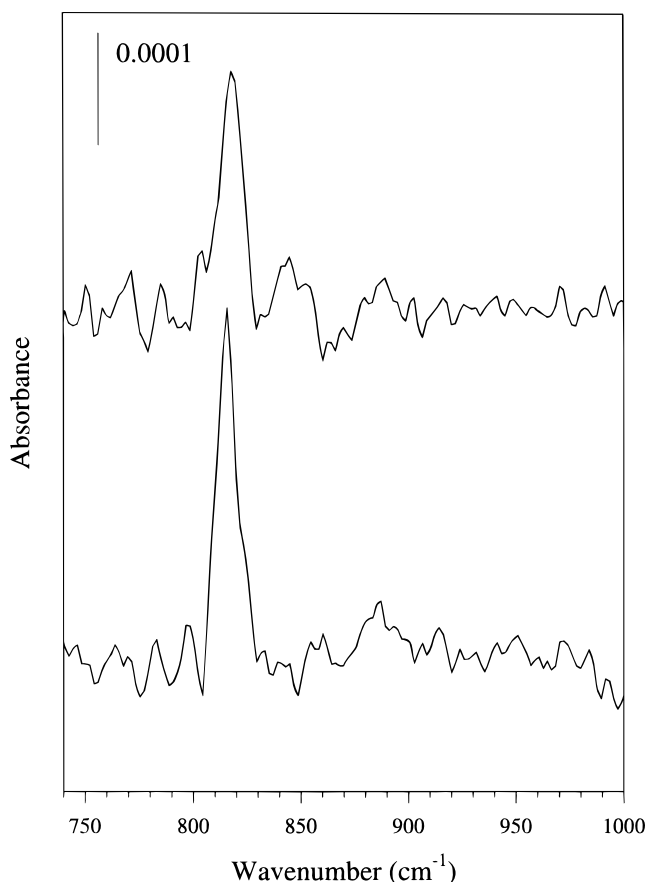


Figure 3. Reflection-absorption infrared spectra for monolayers of cyclopentene and cyclopentadiene dosed and acquired at 300 K.

C–H stretching frequency has been attributed to hyperconjugative drain of electron density from the distal C–H bonds through overlap with the adjacent π -orbitals.^{56,57}

We thus conclude that hyperconjugative effects on the distal C–H bond are most likely responsible for the low-frequency band seen at 2782 cm⁻¹ for cyclopentadiene on Pt(111); the “proximal” C–H bond is evidently not close enough to the surface to affect its stretching frequency significantly. The hyperconjugation effects are stronger in cyclopentadiene than in cyclopentene because the methylene group is adjacent to two C=C double bonds in the former molecule, but (at most) only one in the latter. Hyperconjugation constitutes a heretofore unappreciated mode-softening mechanism, one which gives rise to large perturbations of the vibrational spectra of surface-bound adsorbates but which does not involve direct C–H···M interactions. Hyperconjugative effects and direct C–H···M interactions both lead to the appearance of low-frequency C–H stretching bands, but the two effects can be distinguished by the line width of the resulting softened mode: ~10 cm⁻¹ for the former and over 50 cm⁻¹ for the latter.

Formation of the Cyclopentadienyl (C₅H₅) Ring System on Pt(111). When the cyclopentadiene-dosed surface is heated to 300 K, the RAIR spectrum changes significantly and only weak bands at ~2964 cm⁻¹ (broad) and ~817 cm⁻¹ are seen (Figure 3). The latter band is also seen when cyclopentene is heated to 300 K, and thus we conclude that both cyclopentene and cyclopentadiene are dehydrogenated at this temperature to form the same species. This conclusion agrees with previous HREELS studies in which Avery assigned a band at ~840 cm⁻¹ to the C–H out-of-plane bend of a surface-bound pentahapto-cyclopentadienyl species (η^5 -C₅H₅).^{2,4} The low intensity of the

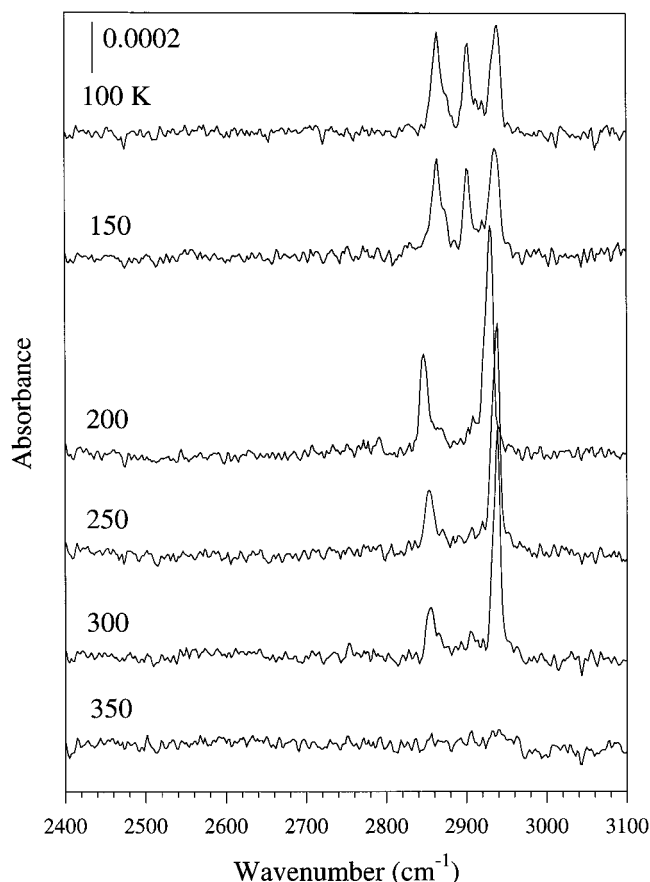


Figure 4. Reflection-absorption infrared spectra for a submonolayer of cyclohexene ($\theta_i \approx 0.8\theta_{\text{sat}}$) adsorbed on Pt(111) taken after annealing at the following temperatures: 100, 150, 200, 250, 300, and 350 K.

$\sim 2964 \text{ cm}^{-1}$ band shows that the C–H bonds are essentially parallel to the surface, as expected for an $\eta^5\text{-C}_5\text{H}_5$ species.

Our results are also consistent with the thermal reactivities of cyclopentene and cyclopentadiene explored by temperature-programmed desorption spectroscopy.^{2–4} Quantitative interpretation of the temperature-dependent hydrogen desorption from Pt(111) dosed with cyclopentene or cyclopentadiene revealed that the cyclopentadienyl fragment (C_5H_5) formed in modest-to-high yields at temperatures close to 300 K. Coverage-dependent data of Avery et al. also revealed that, at saturation coverages, cyclopentene was sterically displaced from the surface by the formation of the planar cyclopentadienyl fragment.^{2,4} This evolution was not observed at submonolayer coverages.

The driving force for the formation of C_5H_5 must be related to the aromatic nature of this species. The great stability of the cyclopentadienyl anion is, of course, one reason for its widespread use in organometallic chemistry.^{58,59}

Cyclohexene on Pt(111). Temperature-dependent RAIR spectra of cyclohexene on Pt(111) are shown in Figure 4, and mode assignments are summarized in Table 3. The bands seen generally agree with those noted in a previous HREELS study;⁵ for example, the absence of bands above 3000 cm^{-1} again is consistent with the expectation that cyclohexene binds to the surface by means of its C=C bond. Unlike the HREEL spectrum, however, the RAIR spectrum reveals much more structure because of the higher resolution of this technique. At 100 and 150 K, three well-separated RAIR bands are seen in the C–H stretching frequency region at 2864, 2902, and 2938 cm^{-1} . If cyclohexene binds to the surface by means of its C=C bond, then all of these bands must arise from the methylene

TABLE 3: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of Cyclohexene on Pt(111)

assignments	100 K	150 K	200 K	250 K	300 K	350 K
$\text{CH}_2 \nu(\text{C-H}_{\text{distal}})^a$	2938	2936				
$\text{CH}_2 \nu(\text{C-H}_{\text{distal}})^b$			2930	2938	2939	
$\text{CH}_2 \nu_{\text{anti}}(\text{C-H})^a$	2902	2902				
$\text{CH}_2 \nu_{\text{sym}}(\text{C-H})^a$	2864	2864				
$\text{CH}_2 \nu_{\text{sym}}(\text{C-H})^b$			2846	2853	2855	
C–H out-of-plane bend ^c						831

^a From adsorbed cyclohexene. ^b From the cyclohexenyl (C_6H_9) intermediate. Alternative assignments possible (see text) ^c From adsorbed benzene.

groups.⁶⁰ The intensities and frequency differences rule out the possibility that the number of bands is increased by Fermi effects.

The two bands at 2864 and 2902 cm^{-1} are best assigned to symmetric and antisymmetric methylene C–H stretches, respectively. The frequencies of these two bands are typical of unperturbed methylene groups (i.e., unaffected by hyperconjugation effects or C–H \cdots M interactions). The third band at 2938 cm^{-1} matches the frequency of the 2945 cm^{-1} band noted above for cyclopentene. In a like fashion, we assign this band to the distal C–H oscillator(s) of methylene group(s) that are experiencing direct C–H \cdots M interactions with the platinum surface. A corresponding softened mode due to the proximal C–H oscillator should also be observed. In the Discussion section, we reveal how the structure of the C–H \cdots M binding interaction in this system leads to an exceptionally broad softened mode that is difficult to distinguish from the baseline. A similar situation has been noted for a closely related structural analogue, bicyclo[2.2.2]octene.⁴⁰

When the cyclohexene-dosed surface is heated to 200 K, the three bands at 2864, 2902, and 2938 cm^{-1} disappear, and two new bands at 2846 and 2930 cm^{-1} grow in. Upon heating further (250 and 300 K), the latter bands become more intense and the higher-frequency band sharpens. As judged from previous studies of cyclohexene on Pt(111),^{5,6,11} it is likely that the new bands are due to a cyclohexene dehydrogenation product. Interestingly, the RAIR bands of the dehydrogenation product do not match those of either 1,4- or 1,3-cyclohexadiene on Pt(111) (see below); thus, dehydrogenation does not occur by loss of two hydrogen atoms. Instead, Henn et al. have suggested that thermolysis of cyclohexene on Pt(111) results in the loss of one allylic hydrogen atom and formation of a cyclohexenyl, C_6H_9 , intermediate;^{5,6,11} i.e., only *one* C–H bond of cyclohexene is cleaved at $\sim 200 \text{ K}$. The RAIRS data strongly support this interpretation. We note that other unsaturated hydrocarbons adsorbed on Pt(111) are known to react by cleavage of an allylic C–H bond.^{1,10,17}

Our RAIRS data are consistent with (but by themselves are not proof of) a cyclohexenyl structure for the thermolysis product generated from cyclohexene at 200–300 K. The C–H stretches of the three surface-bound C–H units probably lie near 2950 cm^{-1} but should be weak (owing to the RAIRS selection rule). There are at least two possible assignments for the bands appearing at 2846 and 2930 cm^{-1} . One is that they arise from the symmetric and antisymmetric stretching motions, respectively, of the methylene units of the $\eta^3\text{-C}_6\text{H}_9$ species. The separation between these two bands (84 cm^{-1}) is significantly larger than the $\sim 45 \text{ cm}^{-1}$ separation seen for cyclopentene and cyclohexene, however, and this difference leaves us somewhat uncertain as to the validity of this assignment. Alternatively, it is possible that the 2930 cm^{-1} band is a distal C–H stretch

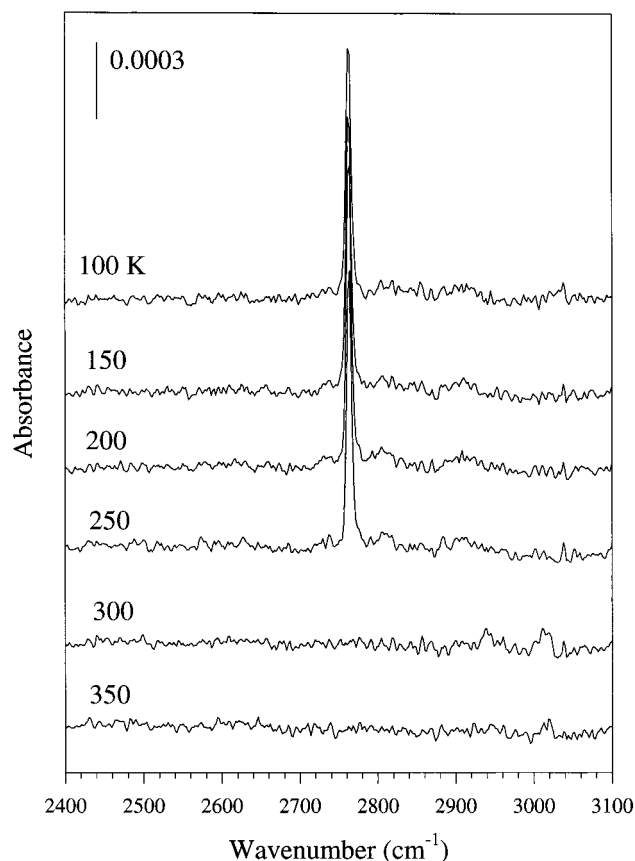


Figure 5. Reflection-absorption infrared spectra for a submonolayer of 1,4-cyclohexadiene ($\theta_i \cong 0.8\theta_{\text{sat}}$) adsorbed on Pt(111) taken after annealing at the following temperatures: 100, 150, 200, 250, 300, and 350 K.

TABLE 4: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of 1,4-Cyclohexadiene on Pt(111)

assignments	100 K	150 K	200 K	250 K	300 K	350 K
$\text{CH}_2 \nu(\text{C}-\text{H}_{\text{distal}})^a$	2763	2763	2763	2763		
C-H out-of-plane bend ^b					828	829

^a From adsorbed 1,4-cyclohexadiene. ^b From adsorbed benzene.

of a methylene unit whose proximal hydrogen atom is engaged in a $\text{C}-\text{H}\cdots\text{M}$ interaction (compare with $\sim 2940 \text{ cm}^{-1}$ for cyclopentene and cyclohexene). The 2846 cm^{-1} feature would then arise from an unperturbed methylene (although in this case, we would expect a greater multiplicity of bands to be seen).

When the surface is heated above 300 K, the intensities of RAIR features due to the cyclohexenyl fragment diminish, and by 350 K they disappear entirely. In agreement with other studies,^{5,6,8,9,11} this result suggests that benzene has now formed on the surface (see below).

1,4-Cyclohexadiene on Pt(111). Between 100 and 250 K, a submonolayer of 1,4-cyclohexadiene on Pt(111) gives a remarkably simple RAIR spectrum: in the C-H stretching region, only a single sharp band at 2763 cm^{-1} is present (Figure 5, Table 4). A previous study indicated that 1,4-cyclohexadiene adsorbs intact at 100 K, and at $\sim 250 \text{ K}$ dehydrogenation commences (forming benzene).¹⁰ We conclude, therefore, that this single vibrational feature is a signature for 1,4-cyclohexadiene. Once again, no bands appear at frequencies above 3000 cm^{-1} , and we conclude that 1,4-cyclohexadiene binds to the surface by means of both C=C bonds. Although calculations suggest that free 1,4-cyclohexadiene is a planar molecule,⁶¹ rehybridization

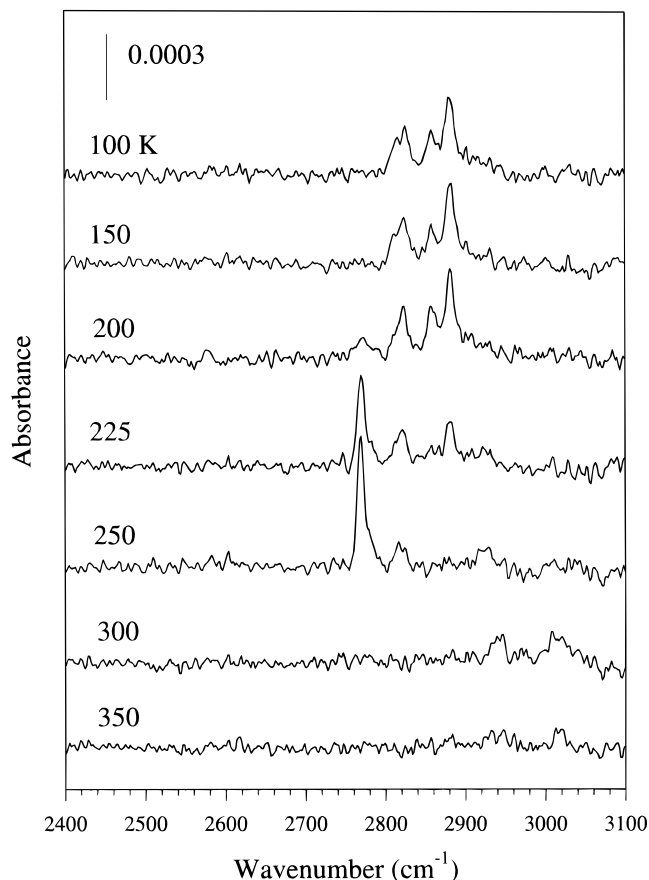


Figure 6. Reflection-absorption infrared spectra for a submonolayer of 1,3-cyclohexadiene ($\theta_i \cong 0.8\theta_{\text{sat}}$) adsorbed on Pt(111) taken after annealing to the following temperatures: 100, 150, 200, 225, 250, 300, and 350 K.

of the olefinic carbons will undoubtedly cause the molecule to adopt a boatlike conformation on the surface, as shown below (Scheme 2).

The band at 2763 cm^{-1} clearly must arise from the C-H motions of the methylene groups, but this frequency is exceptionally low for a C-H oscillator. Although one might be tempted to ascribe this band to proximal C-H oscillators that are perturbed by $\text{C}-\text{H}\cdots\text{M}$ interactions with the surface, this mode is far too sharp to be consistent with such an assignment. Instead, we propose that the 2763 cm^{-1} feature is best assigned to distal C-H oscillators that are perturbed by a hyperconjugative interaction with the metal-bound π -system. This interaction is similar to that described above for cyclopentadiene. The stretch due to the proximal C-H bonds of the methylene units is not observed, and we conclude that the transition moment for this mode must be nearly parallel to the surface.⁶² For this to be the case, the methylene groups would have to be displaced upward away from the surface by $\sim 50^\circ$ (θ_f in Scheme 2). Since the function $\cos^2\theta$ varies weakly near this limit, the latter analysis likely overestimates the value of θ_f .

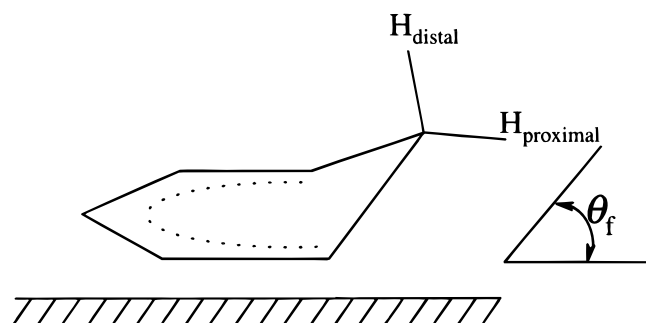
When the 1,4-cyclohexadiene-dosed surface is heated to 300 K, the 2763 cm^{-1} band disappears; very weak features are just discernible at 2930 and 3020 cm^{-1} (these band locations are consistent with the formation of benzene, see below).

1,3-Cyclohexadiene on Pt(111). At 100 K, the RAIR spectrum of a submonolayer of 1,3-cyclohexadiene adsorbed on Pt(111) exhibits four distinct bands in the C-H stretching region centered at 2816 , 2825 , 2859 , and 2881 cm^{-1} (Figure 6, Table 5; the low signal-to-noise ratios of these spectra should

TABLE 5: Frequencies (in wavenumbers) and Mode Assignments for RAIR Spectra of 1,3-Cyclohexadiene on Pt(111)

assignments	100 K	150 K	200 K	225 K	250 K	300 K	350 K
$\nu(\text{C-H})^a$	2816, 2825, 2859, 2881	2812, 2824, 2858, 2883	2822, 2858, 2882	2821, 2882	2819		
$\text{CH}_2 \nu(\text{C-H}_{\text{distal}})^b$			2771	2770	2769		
C-H out-of-plane bend ^c						825, 891	825, 890

^a Various C-H stretching modes from adsorbed 1,4-cyclohexadiene. ^b From the η^5 -cyclohexadienyl intermediate. ^c From adsorbed benzene.

SCHEME 3

be noted). The absence of strong bands above 3000 cm^{-1} is consistent with the view that both $\text{C}=\text{C}$ bonds are coordinated to the surface, a conclusion that was reached in earlier studies.¹⁰ The four C-H stretching bands in these spectra can again be divided into two pairs, one pair near 2820 cm^{-1} (symmetric methylene stretches) and the other near 2870 cm^{-1} (antisymmetric methylene stretches). The splitting within each pair may be caused by Fermi resonances, as suggested above for cyclopentene.

When the surface is heated to 200 K a new band at 2769 cm^{-1} begins to grow in, owing to the onset of a thermolysis process. By 250 K, the 1,3-cyclohexadiene adsorbate has been extensively converted to this thermolysis product. The general appearance of this latter spectrum resembles that of the isomer 1,4-cyclohexadiene on Pt(111) (see above), except that the frequency seen here is slightly different (2769 vs 2763 cm^{-1}). It seems unlikely, however, that 1,3-cyclohexadiene would isomerize to 1,4-cyclohexadiene because the conjugated 1,3 isomer should be more stable thermodynamically even on a surface.^{63–65}

Other studies have shown that the allylic C-H bonds of 1,3-cyclohexadiene become labile above 200 K,^{8,10} and accordingly we propose that the species responsible for the 2769 cm^{-1} band is a η^5 -cyclohexadienyl species (C_6H_7) that is formed by the activation of a single allylic C-H bond. A similar η^5 -cycloheptadienyl dehydrogenation product is thought to form when 1,3-cycloheptadiene is heated to 225–275 K on a Pt(111) surface.¹⁵ This C_7 intermediate is characterized by the presence of a single band at 2768 cm^{-1} whose frequency is essentially identical to that seen here for the η^5 -cyclohexadienyl intermediate.

We believe that the $\sim 2770\text{ cm}^{-1}$ band is best assigned to the distal C-H stretch of a methylene group, and that the frequency of this mode is significantly perturbed by hyperconjugation effects (see above). The absence of a feature due to the proximal C-H bond suggests that the transition direction for this mode must be nearly parallel to the surface (as was proposed above for 1,4-cyclohexadiene). This orientation would be produced if the methylene unit were displaced upward away from the surface by $\sim 50^\circ$ (θ_f in Scheme 3). For comparison, in discrete organometallic complexes containing the η^5 -cyclohexadienyl ligand, the methylene unit forms a dihedral angle $40\text{--}50^\circ$ with respect to the plane defined by the other five carbon atoms.^{55,66–68}

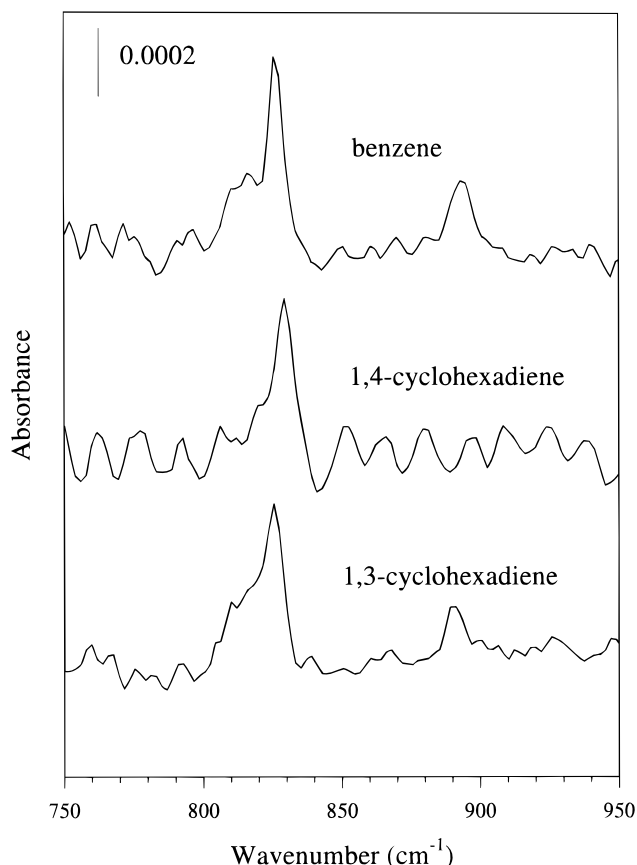


Figure 7. Reflection-absorption infrared spectra for monolayers of benzene and 1,3-cyclohexadiene dosed and acquired at 350 K. The RAIR spectrum for 1,4-cyclohexadiene was acquired by annealing a submonolayer ($\theta_f \approx 0.8\theta_{\text{sat}}$) dosed at 100 K at 350 K and cooling to 100 K after approximately 1 min (the baseline noise precluded observation of the weaker band in this spectrum).

Formation of Benzene from 1,4- and 1,3-Cyclohexadiene on Pt(111). When the 1,4- and 1,3-cyclohexadiene-dosed surfaces are heated to 300 K, dehydrogenation occurs, and the only features seen in the RAIR spectrum are weak C-H stretches at ~ 2930 and 3020 cm^{-1} and two C-H out-of-plane bending modes⁶⁹ at approximately 825 and 890 cm^{-1} (Figure 7). These bands are precisely those expected for surface-bound benzene.⁷⁰ This conclusion is again supported by other studies (e.g., temperature-programmed desorption spectroscopy) that show that benzene is generated from cyclohexadienes in this temperature range.^{9,10}

Discussion

Many structural factors have been reported to influence the bonding and reactivities of hydrocarbons on transition metal surfaces. Among these are the identity of the metal involved, its crystallographic orientation and step density, the presence of functional groups in the adsorbate (such as π -bonds), and even more subtle features such as the orientations adopted by the adsorbate on the surface and the geometrical matches occurring between its functional groups and specific sites on

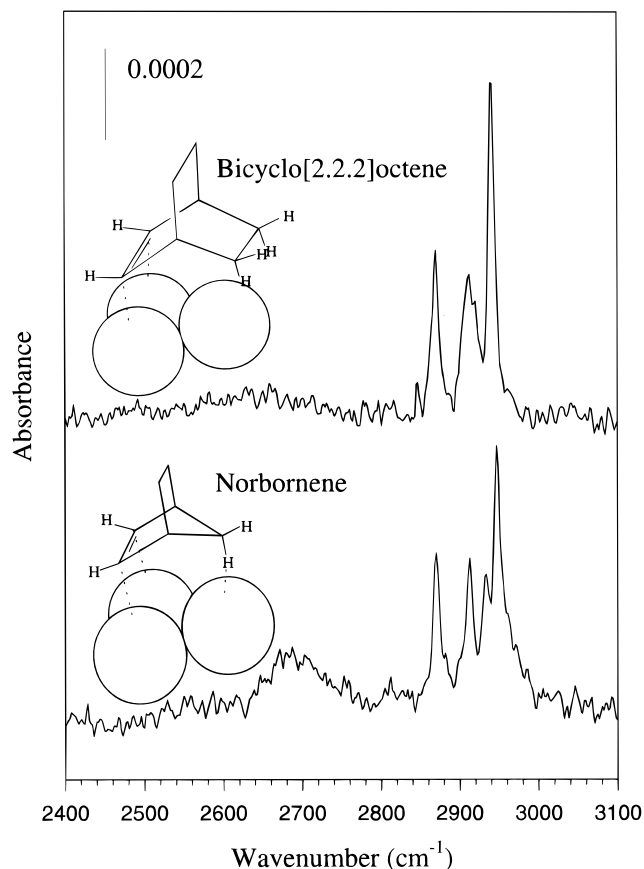


Figure 8. Reflection-absorption infrared spectra for a submonolayers of norbornene and bicyclo[2.2.2]octene adsorbed on Pt(111) taken at 132 K.

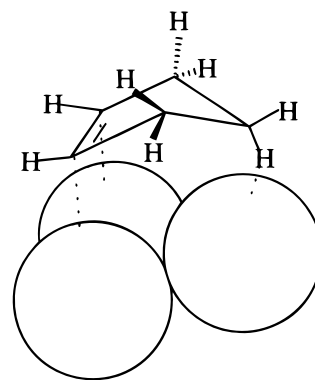
the surface. We discuss below how C_5 and C_6 cycloalkenes bond to Pt(111) and how the organizational details of these bonding modes may be related to the reactions seen at higher temperatures.

Bonding Similarities between the Monocyclic Alkenes Cyclopentene and Cyclohexene and the Bicyclic Alkenes Norbornene and Bicyclo[2.2.2]octene. The RAIR data presented above strongly suggest that the bonding of cyclopentene and cyclohexene to Pt(111) is very similar to that involved in the coordination of the bicyclic olefins norbornene and bicyclo[2.2.2]octene, respectively, to this surface.⁴⁰ To facilitate the present discussion, we present here the RAIR spectra obtained for monolayer coverages of norbornene and bicyclo[2.2.2]octene on Pt(111) along with the assigned low-temperature bonding configurations on Pt(111) (Figure 8).⁴⁰

When norbornene binds to Pt(111), two parts of the hydrocarbon framework contact the surface: the $C=C$ double bond and one hydrogen atom of the bridging methylene unit (the latter forming a $C-H\cdots M$ interaction). Norbornene thus binds to Pt(111) by presenting one of its five-membered rings (an "exo" face) toward the surface. This preferential bonding arises in part because the "exo" faces of norbornene are more accessible sterically than is the "endo" face.⁷¹⁻⁷³ RAIRS does not establish the structure of the site to which the double bond is bound. If we assume that the $C=C$ bond of norbornene bridges between two adjacent Pt atoms (as is generally thought to be the case for other olefins^{2,37,40,74-77}), then the proximal $C-H$ bond of the bridging methylene group points almost directly toward an atop site on the (111) surface.⁴⁰

Because norbornene and cyclopentene both bind to Pt(111) by means of a five-membered ring with one $C=C$ double bond,

SCHEME 4



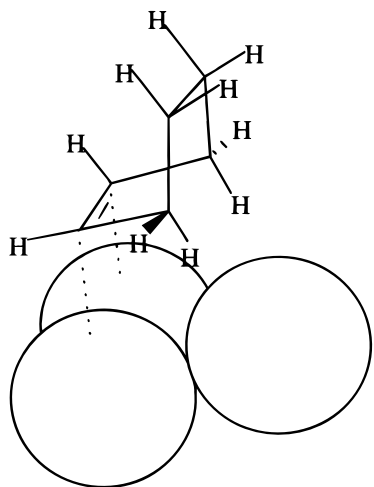
it is not surprising that the RAIR spectra of the two molecules are remarkably similar. The $C-H\cdots M$ interaction formed by norbornene produces a relatively intense, but narrow line width softened mode at $\sim 2680\text{ cm}^{-1}$ and, most intriguingly, cyclopentene on Pt(111) shows a nearly identical band (Figure 1). We also find that both norbornene and cyclopentene give a strong band at $\sim 2945\text{ cm}^{-1}$, which is assignable to the stretching mode of the distal $C-H$ of the Pt-contacting methylene group.

The constraints of the bicyclic framework of norbornene dictate that the five-membered ring presented to the surface is folded: the bridging methylene group is closer to the surface than are the two bridgehead carbon atoms. The similarities between the spectra of norbornene and cyclopentene on Pt(111) strongly suggest that this same bonding configuration is adopted by cyclopentene; i.e., the central methylene group is folded *down* toward the surface. This structure is shown in Scheme 4. This configuration should be favorable, because the steric interactions between the surface and the CH_2 groups adjacent to the $C=C$ bond are minimized. If the molecule were flipped so that the flap pointed up, the π -bonding interaction with the surface would be lessened by the steric repulsions due to the close proximity of the axial allylic $C-H$ bonds to the surface.

The $C=C$ bond is undoubtedly responsible for a large fraction of the absorption energies of the cycloalkenes on platinum. From the literature precedent,^{2,74,76} we assume that cyclopentene is bound with its $C=C$ bond over a bridging site. This preferential bonding mode pins the cyclopentene molecules to the surface in a specific fashion and establishes a pattern of registry for interactions occurring with other segments of the adsorbate. Because cyclopentene has relatively little conformational freedom, the location of the rest of the molecule with respect to the surface can be specified in detail; the proximal $C-H$ bond of the homoallylic methylene group is almost directly over an atop site. The geometries of the $C-H\cdots M$ interactions are thus identical for norbornene and cyclopentene.

The softened modes seen for cyclopentene and norbornene are unusually narrow. The line widths of $\sim 50\text{ cm}^{-1}$ are similar to those seen for the commensurately ordered phases of monolayers of *n*-alkanes on Pt(111).^{13,18} In contrast, the softened modes observed for saturated cyclic hydrocarbons adsorbed on Pt(111) are typically greater than 150 cm^{-1} .^{15,17,19,21} It is becoming increasingly clear from the now considerable body of data available that the line widths of softened modes are strongly influenced by both site heterogeneity and the nature of the surface site it probes.^{13,16,18,37,40} If the proximal $C-H$ bonds are interacting with a variety of surface sites, the softened mode will be a convolution of overlapping components with different frequencies, and will thus be broad. The narrow

SCHEME 5



softened mode seen for cyclopentene (and norbornene) is a consequence of two factors: the registry of every molecule with respect to the surface is the same (this in turn is a consequence of the specific binding mode involving interactions of the C=C bonds); and (2) the geometry of the molecule is such that a C-H bond is projected at a relatively steep angle down onto an atop site of a nearby platinum atom (this is a consequence of the conformationally rigid nature of the bicyclic molecule norbornene and the small size of the hydrocarbon ring in cyclopentene, for which only two conformations are possible).

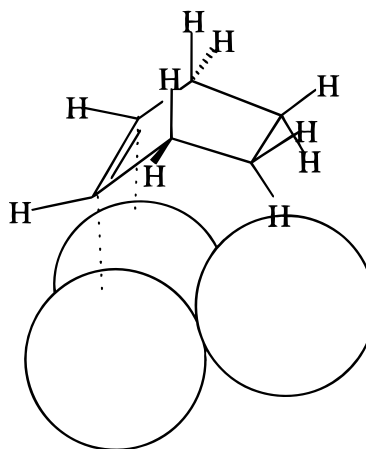
Just as the RAIR spectra of norbornene and cyclopentene are very similar, the RAIR spectrum of the bicyclic alkene bicyclo[2.2.2]octene on Pt(111) closely resembles that of cyclohexene on this same surface. For both molecules, the RAIR spectrum in the "normal" C-H stretching region consists of three sharp bands at ~ 2940 , 2905 , and 2860 cm^{-1} .⁷⁸ We infer that the bonding habits of cyclohexene and bicyclo[2.2.2]octene on Pt(111) are probably very similar. Bicyclo[2.2.2]octene binds to Pt(111) by means of its C=C double bond and one of the two CH_2CH_2 groups (Figure 8).⁴⁰ Thus, both molecules bind to the surface by means of a six-membered ring that contains one C=C bond.

There is another similarity between the RAIR spectra of bicyclo[2.2.2]octene and cyclohexene; neither spectrum contains a prominent softened C-H mode like those seen for norbornene and cyclopentene. For bicyclo[2.2.2]octene, the RAIR spectrum features a very broad softened mode (which is extremely difficult to distinguish from the baseline). We believe the lack of a prominent softened mode in these latter spectra is a consequence of the fact that the proximal methylene C-H bonds of bicyclo[2.2.2]octene project toward a different type of surface site than do the proximal methylene C-H bonds of norbornene (given similar assumptions as to the C=C bond binding site, then the C-H \cdots M interactions occur near a bridge site). From the similar lack of a sharp softened mode for cyclohexene, we conclude that a similar registry of the proximal methylene C-H bonds likely exists for this molecule as well.

The structure of bicyclo[2.2.2]octene provides a good model of the two possible conformations of bound cyclohexene. Previous reports concluded, quite intuitively, that cyclohexene adopted a bonding habit on Pt(111) with a positive value of θ_f , one similar to that shown below (Scheme 5).^{8,9}

Bonding in this fashion, however, would either cause the allylic C-H bonds to form unacceptably close contacts with the surface, or would weaken the bonding with the C=C double bond. The frequencies and multiplicities of the bands seen in

SCHEME 6



the C-H stretching region of the RAIR spectra are also hard to rationalize for this geometry.

The results in this study suggest that another bonding mode may in fact be adopted. As noted above, the flipping of this geometry by 180° (Scheme 6) greatly reduces steric interactions involving the axial allylic C-H bonds. Based on the lines of evidence developed above, we believe this structural habit is indeed the one prominent in the adsorbate bonding on the surface.

This latter structure, which contains C-H_{distal} bonds that are roughly parallel to the surface normal direction, also best explains the appearance of the $\sim 2940\text{ cm}^{-1}$ band in the RAIR spectrum (which is diagnostic of distal C-H bonds of methylene units whose proximal C-H bonds are in contact with the surface). This model also closely follows the structure proposed above for cyclopentene.

The bonding geometry of cyclohexene shown in Scheme 6 also rationalizes what has been the most perplexing aspect of the mode assignments reported previously for bicyclo[2.2.2]octene on Pt(111), namely the extremely large line width of the softened mode seen in the low-temperature RAIR spectra. It now seems clear, on the basis of a broader comparison with the spectra of norbornene, cyclopentene, and cyclohexene, that highly symmetric interactions at (what the literature would suggest are) atop sites lead to softened modes which are "uncharacteristically" narrow ($\sim 50\text{ cm}^{-1}$). The database available to us, though, remains limited in that we have not found conformationally rigid adsorbates which probe other sites (bridge, 3-fold hollow) as clearly as those here explore interactions occurring at atop sites.

The Reactivities of Cyclopentadiene and Cyclohexene on Pt(111)—Comparisons with Previous Studies. On the basis of HREELS data, it was suggested that cyclopentadiene disproportionates at 90 K to form the cyclopentadienyl anion and cyclopentene.⁴ The formation of the latter molecule was inferred from the presence of a low-frequency feature at $\sim 2780\text{ cm}^{-1}$ which was assigned to the softened mode of cyclopentene. The RAIR spectra we present here do not support this conclusion. The softened mode for cyclopentene has a very different frequency ($\sim 2695\text{ cm}^{-1}$), and evidently the low resolution of the HREEL spectra made it difficult to recognize the 85 cm^{-1} frequency difference. Instead, the anomalously low-frequency band (which occurs at 2782 cm^{-1} in our RAIR spectra) appears to be better assigned to a hyperconjugatively shifted distal C-H stretch of the methylene unit of cyclopentadiene itself. Our RAIR data also show that the line widths of the cyclopentene softened mode ($\sim 50\text{ cm}^{-1}$) and the cyclopentadiene distal C-H

stretch ($\sim 10\text{ cm}^{-1}$) are very different and thus underscore the different electronic effects which contribute to each.

Other groups have suggested that cyclohexene converts to a cyclohexenyl species (C_6H_9) on Pt(111) at temperatures near 200 K.^{5,6} Our RAIR spectra are consistent with this hypothesis. Henn et al., for example, have suggested that cyclohexene undergoes a configuration change between 95 and 200 K (both cyclohexene configurations, however, are bound to the surface in a di- σ fashion).⁵ This conversion was inhibited at high coverages, a suggestion consistent with our RAIRS results, which were obtained at high coverage.

A bismuth-postdosing TPD study of the cyclohexadienes (the 1,4 and 1,3 isomers) on Pt(111) showed that these adsorbates convert to benzene by 260 K; no intermediate was detected.¹⁰ Our spectra suggest that the conversion of 1,3-cyclohexadiene to benzene proceeds through a transient η^5 -cyclohexadienyl species, although the energetics of its formation and decomposition appear to be very similar and rate-structure sensitive. In contrast, the initial C-H bond scission in 1,4-cyclohexadiene appears to have a somewhat higher activation energy and thus does not give the cyclohexadienyl intermediate in detectable quantities.

Reaction Chemistries Related to Adsorption Geometries of the C_5 and C_6 Cyclic Hydrocarbons on Pt(111). Our RAIR studies confirm that all of the C_5 and C_6 hydrocarbons are readily dehydrogenated on Pt(111). We find, however, that the hydrocarbons may be divided into two classes, ones marked by differences in the temperature at which the initial C-H bond activation step occurs. For cyclopentene, cyclohexene, and 1,3-cyclohexadiene, this temperature is below 250 K (the reaction temperature for cyclohexene is probably less than 200 K). For cyclopentadiene and 1,4-cyclohexadiene, however, the C-H bonds are activated only above 250 K. The distinctions made here are clearly somewhat arbitrary in that the activation energy differences are at best a few kcal/mol. Even so, the reaction temperature for the initial C-H bond activation step can be correlated with the geometry adopted by the adsorbate on the surface. For the more rigid cyclopentadiene and 1,4-cyclohexadiene adsorbates, the methylene groups are projected away from the surface as depicted above (consequently, these C-H bonds should be more difficult to cleave). In contrast, for cyclohexene, cyclopentene, and 1,3-cyclohexadiene, the C-H bonds of some of the methylene groups lie in close proximity to the surface (and thus might therefore be more susceptible to cleavage). The energies differentiating these C-H bond activating chemistries are extremely modest and entirely consistent with the effects that conformational dynamics might have on the kinetics of such processes.

Hyperconjugative Effects on the Stretching Frequencies of Distal C-H Bonds of Allylic Methylene Units. The RAIR spectra of hydrocarbons adsorbed on metal surfaces often exhibit low-frequency C-H stretching vibrations between 2600 and 2800 cm^{-1} .^{13,15,16,18,19,21,25,37,40} In many cases, these bands reflect the presence of direct $\text{C-H}\cdots\text{M}$ interactions between certain C-H oscillators and the surface, interactions which greatly affect the normal modes of vibration.

The data in this paper demonstrate that another mechanism also can lower the frequency of C-H stretching vibrations of surface-bound hydrocarbons. This mechanism does not require direct metal contacts in the same sense as the above and affects C-H bonds that are pointing away from the surface. As has been seen in certain discrete molecular systems, methylene groups adjacent to a metal-bound π -system can be affected by hyperconjugation effects that drain electron density from the

distal C-H bond.^{50,56} This effective polarization of the electron density shifts the distal C-H stretching frequencies to low values ($2700\text{--}2800\text{ cm}^{-1}$). These hyperconjugatively shifted bands are distinctive because their line widths are much narrower ($\sim 10\text{--}15\text{ cm}^{-1}$) than the low-frequency bands which result from direct $\text{C-H}\cdots\text{M}$ interactions ($> 50\text{ cm}^{-1}$). This hyperconjugation effect is most pronounced when the methylene group is located directly adjacent to (i.e., between) two π -systems: this is true for the species cyclopentadiene, 1,4-cyclohexadiene, cyclohexadienyl, and cycloheptatriene,¹⁵ all of which show a narrow band between 2700 and 2800 cm^{-1} . Hyperconjugatively shifted bands are also seen for certain adsorbates, such as the cycloheptadienyl anion, in which the methylene groups are directly adjacent to only one π -system.¹⁵ The hyperconjugation interaction, though, should depend sensitively on the dihedral angle adopted between the C-H bond and the nodal plane of the metal-bound π -system. Factors that increase this dihedral angle should increase the extent of hyperconjugation and the consequent frequency shifts seen for the distal hydrogen atoms of allylic methylene groups.

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