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Kaitlin M. Bratlie, *University of California - Berkeley* Gabor A. Somorjai, *University of California - Berkeley*



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A Sum Frequency Generation Vibrational Spectroscopic Study of the Adsorption and Reactions of C₆ Hydrocarbons at High Pressures on Pt(100)

Kaitlin M. Bratlie and Gabor A. Somorjai*

Department of Chemistry, University of California, Berkeley, California 94720, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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Sum frequency generation (SFG) vibrational spectroscopy was used to investigate the adsorption geometries and surface reactions of various C₆ hydrocarbons (*n*-hexane, 2-methylpentane, 3-methylpentane, and 1-hexene) on Pt(100). At 300 K and in the presence of excess hydrogen, *n*-hexane, 3-methylpentane, and 2-methylpentane adsorb molecularly on Pt(100) mostly in "flat-lying" conformations. Upon heating the metal surface to 450 K, the molecules underwent dehydrogenation to form new surface species in "standing-up" conformations, such as hexylidyne and metallacyclic species. 1-Hexene, however, dehydrogenated to form metallocycle Pt₃ C-(CH₂)₅-Pt at 300 K in the presence of excess hydrogen and remained unreacted on the surface upon heating the metal surface to 450 K. Dehydrogenation was enhanced in the absence of excess hydrogen in the cases of *n*-hexane, 2-methylpentane, and 3-methylpentane to form metallocycle Pt₃=C-(CH₂)₅-Pt; 2-methyl-1-pentene and 4-methyl-1-pentene; and metallacyclohexane, respectively, at 300 K. These surface species remained unreacted after increasing the surface temperature to 450 K. The mechanisms for catalytic isomerization and dehydrocyclization of *n*-hexane were discussed on the basis of these results.

1. Introduction

The surface chemistry of alkanes on platinum surfaces is a central issue in understanding reforming reactions that produce high-octane gasoline.^{1–3} Identifying reactive surface intermediates is key for understanding the mechanisms of isomerization and dehydrocyclization of *n*-hexane to benzene. Furthermore, understanding how surface reaction intermediates are affected by metal surface structure can extend our knowledge of chemical bonding on single crystals to industrial catalysts.

Various surface analytical techniques have been employed to probe surface species upon adsorption of alkane molecules on metal surfaces at low pressures ($<10^{-6}$ Torr).^{4–8} Among these are low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), high-resolution electron energy loss spectroscopy (HREELS), and reflection absorption infrared spectroscopy (RAIRS).^{4–8} However, at low pressures, only strongly bound adsorbates will exist on the surface, while weakly bound species desorb quickly. These weakly bound species may be key intermediates in high-pressure reactions.

High-pressure studies of C₆ alkane hydrocarbons on Pt(111) have been investigated using sum frequency generation (SFG) vibrational spectroscopy.⁹ These studies found that *n*-hexane and 3-methylpentane are inactive on Pt(111) at 296 K in the presence of excess hydrogen. 2-Methylpentane and 1-hexene, however, readily dehydrogenate to form metallacyclobutane and hexylidyne. Heating the metal surface to 453 K partially dehydrogenated *n*-hexane and 3-methylpentane to hexylidyne and metallacyclohexane. In the absence of excess hydrogen, *n*-hexane and 3-methylpentane to form π -allyl c-C₆H₉ and metallacyclohexane at 296 K. Heating the metal surface to 453 K caused π -allyl c-C₆H₉ to undergo irreversible dehydrogenation to benzene, whereas the hexylidyne and

* To whom correspondence should be addressed. Tel: 510-642-4053. Fax: 510-643-9668. E-mail: somorjai@socrates.berkeley.edu. metallacyclic species remained unreacted. Since previous studies have been limited to Pt(111) single crystals, conducting these experiments on the Pt(100) single crystal will further our knowledge of this reaction, in particular how structure affects the reaction pathway.

In this study, sum frequency generation (SFG) vibrational spectroscopy is used to investigate adsorption geometries and surface reactions of C₆ alkane and alkene hydrocarbons on Pt-(100) under 1.5 Torr of hydrocarbon in the absence and presence of excess hydrogen at high temperatures (300–450 K). The C_6 hydrocarbons of interest in the study are *n*-hexane (C_6H_{14}), 2-methylpentane (C_6H_{14}), 3-methylpentane (C_6H_{14}), and 1-hexene (C_6H_{12}). *n*-Hexane is the simplest alkane molecule to undergo the full spectrum of skeletal rearrangement reactions involved in reforming: isomerization, dehydrogenation, cyclization, and dehydrocyclization.^{10,11} Under the electric dipole approximation, media with centrosymmetry and isotropic gases do not appear in the SFG spectrum. Since bulk platinum has a center of inversion, its contribution to the SFG signal is negligible. The symmetry at the surface of the platinum crystal is broken, giving rise to a surface specific signal. SFG is a more sensitive tool to study interfaces than infrared absorption and Raman spectroscopies since the SFG signal arises solely from the adsorbates. Electron spectroscopies typically cannot be employed under ambient pressure conditions necessary to perform catalytic reactions.

Here it will be shown that the surface species and their adsorption geometries change radically with temperature and the presence of excess hydrogen. At 300 K and in the presence of excess hydrogen, *n*-hexane, 3-methylpentane, and 2-methylpentane are inactive on Pt(100) while 1-hexene readily dehydrogenates to form metallocycle $Pt_3 \equiv C-(CH_2)_5$ -Pt. Upon heating, both *n*-hexane and 2-methylpentane dehydrogenate to form hexylidyne while 3-methylpentane forms metallacyclohexane. At 300 K in the absence of excess hydrogen, all of the



Figure 1. SFG spectra of surface species on Pt(100) at 300K in 1.5 Torr of C₆ hydrocarbon and 15 Torr of H₂. In order from the top are *n*-hexane, 3-methylpentane, 2-methylpentane, and 1-hexene, respectively. Markers represent experimental data and solid lines represent the curve fits using eq 1.

hydrocarbons readily dehydrogenate. *n*-Hexane, 1-hexene, and 3-methylpentane form metallacyclic species on Pt(100): both *n*-hexane and 1-hexene form metallocycle $Pt_3 \equiv C-(CH_2)_5$ -Pt while 3-methylpentane forms metallacyclohexane. 2-Methylpentane is suggested to form 2-methyl-1-pentene and 4-methyl-1-pentene in the absence of excess hydrogen.

On the basis of our SFG results, we discuss the mechanisms of *n*-hexane catalytic reactions to form isomers and benzene on Pt(100) and we compare these mechanisms to those proposed for Pt(111). Our SFG results provide spectroscopic evidence that metallocycle Pt₃= $C-(CH_2)_5-Pt$ is a reactive surface intermediate during dehydrocyclization of *n*-hexane on Pt(100), giving credence to previous studies⁹ that suggest benzene formation does not occur through a five-member cyclic intermediate, as does isomerization, but through direct 1,6-ring closure.

2. Experimental

All experiments were carried out in a high-pressure/ultrahighvacuum (HP/UHV) system on a prepared Pt(100) single-crystal surface. The HP/UHV system consists of a UHV chamber operating at a base pressure of 2×10^{-9} Torr and a highpressure (HP) cell isolated from the UHV chamber by a gate valve. The UHV chamber is equipped with an Auger electron spectrometer (AES), quadrupole mass spectrometer (QMS) and Ar⁺ ion sputter gun. Two CaF₂ conflat windows on the HP cell allow transmission of infrared (IR), visible (VIS), and sum frequency radiation for SFG experiments. The reactant and product gases are constantly mixed via a recirculation pump.





SCHEME 2: 3-Methylpentane (C₆H₁₄) Adsorbed on Pt(100)



3-methylpentane (C₆H₁₄)

The Pt(100) crystal was cleaned by sputtering with Ar⁺ ions (1 keV) for 20 min, heating to 1123 K in the presence of 5 × 10^{-7} Torr O₂ for 2 min, and then annealing at 1123 K for 2 min. AES and LEED were used to verify the cleanliness of the Pt(100) surface after several cleaning cycles. The Pt(100) sample was then transferred into the HP cell for SFG reaction studies. 1-Hexene (≥99.8%, Fluka), n-hexane (≥99.7%, Fluka), 2-methylpentane (≥97%, Fluka), and 3-methylpentane (≥99%, Fluka) were purified by several freeze–pump–thaw cycles before introduction into the HP cell. Prior to the experiment, the hydrocarbons were checked for impurities by means of gas chromatography. Such impurities were below 0.5% and consisted of mostly light alkanes below C₆.

A Nd:YAG laser (1064 nm fundamental having a 20 ps pulse width operating at a 20 Hz repetition rate) was used to create a tunable IR (1800–4000 cm⁻¹, 5 cm⁻¹ resolution) and a second-harmonic VIS (532 nm) beam. The VIS (200 μ J) and the IR (200 μ J) beams were spatially and temporally overlapped on the Pt(100) surface with incident angles of 55° and 60°, with respect to the surface normal. All spectra were taken using a ppp polarization combination (SFG, VIS, and IR beams were all p-polarized). The generated SFG beam was sent through a monochromator and the signal intensity was detected with a photomultiplier tube and a gated integrator as the IR beam was scanned over the range of interest. Spectra were curve fit using a previously reported procedure^{12,13} to a form of the equation

$$I_{\rm SFG} \propto |\chi_{\rm NR}^{(2)} e^{i\phi_{\rm NR}} + \sum_{q} \frac{A_q}{\omega_{\rm IR} - \omega_q + i\Gamma_q} e^{i\gamma_q}|^2 \qquad (1)$$

where $\chi_{NR}^{(2)}$ is the nonresonant nonlinear susceptibility, $e^{i\phi_{NR}}$ is the phase associated with the nonresonant background, A_q is the strength of the qth vibrational mode, ω_{IR} is the frequency of the incident infrared laser beam, ω_q is the frequency of the *q*th vibrational mode, Γ_q is the natural line width of the qth vibrational transition, and $e^{i\gamma_q}$ is the phase associated with the *q*th vibrational transition. Detailed descriptions on the HP/UHV system and SFG measurement can be found elsewhere.^{14–19}

3. Results

3.1. SFG Spectra of Surface Species on Pt(100) at 300 K in 1.5 Torr of C₆ Hydrocarbons and 15 Torr of Hydrogen. The SFG spectra of surface species on Pt(100) at 300 K in 1.5 SCHEME 3: (a) 2-Methylpentane (C_6H_{14}) Adsorbed on Pt(100) and (b) Metallacyclobutane (C_6H_{12}) Adsorbed on Pt(111)



(a) 2-methylpentane (C₆H₁₄)

(b) metallacyclobutane (C6H12)

SCHEME 4: Metallocycle $Pt_3 \equiv C - (CH_2)_5 - Pt$ Adsorbed on Pt(100)



metallocycle Pt3=C-(CH2)5-Pt

Torr of C_6 hydrocarbons and 15 Torr of H_2 are shown in Figure 1. In order from the top in Figure 1 are *n*-hexane, 3-methylpentane, 2-methylpentane, and 1-hexene. The solid lines in Figure 1 correspond to fits using eq 1.

Hexane. There are two major bands at 2860 and 2915 cm⁻¹. The band at 2860 cm⁻¹ is assigned to a mixture of unperturbed symmetric CH₂ and CH₃ stretches (CH₂(s) and CH₃(s)). The CH₂(s) and CH₃(s) stretches are typically located at ~2850 and ~2870 cm⁻¹, making the assignment of the spectral feature located at 2860 cm⁻¹ to either a CH₂ or CH₃ group difficult. Furthermore, the peak width of the observed mode is ~60 cm⁻¹, implying that multiple resonances are responsible for the spectral feature of stretches: perturbed asymmetric CH₂ and CH₃ (CH₂(a, p) and CH₃(a, p)). Perturbed asymmetric CH₂ and CH₃ are generally centered at ~2900 and ~2920 cm⁻¹. Akin to the symmetric stretch discussed above, assignment of this mode to one functional group is not possible chiefly since the peak width is ~45 cm⁻¹.

Previous studies of *n*-hexane on $Pt(111)^9$ have been able to distinguish the peaks responsible for the CH2 and CH3 functional groups for both the symmetric and perturbed asymmetric cases. Based on the strong CH₃(a, p) peak, Yang and Somorjai⁹ determined that the CH₃ groups align with their 3-fold rotational symmetry axis parallel to the surface, thus interacting with the metal surface. The CH₂ groups were also predicted to align with their 2-fold rotational symmetry axis parallel to the surface based on the strong CH₂(a, p) peak. The asymmetric perturbed CH₂ and CH₃ groups are characteristic of the "flat-lying" n-hexane in the trans-trans (TTT) conformation (see Scheme 1).^{20,21} However, the presence of the symmetric CH₂ and CH₃ groups is not in line with this assessment. The metal surface selection rule (MSSR) forbids IR modes that are parallel to the metal surface. As seen in Scheme 1, the dipole moment for the symmetric CH₂ and CH₃ stretches for an *n*-hexane molecule adsorbed on a metal surface will not be allowed. On the basis of the observation of symmetric CH₂ and CH₃ stretches in the sum frequency spectrum, the adsorbate must exist in different conformations on the surface.

Conformational changes of *n*-alkanes on Pt(111) have been studied by RAIRS,²² temperature programmed desorption (TPD),²³ laser-induced thermal desorption (LITD),²⁴ and molecular dynamics (MD).²⁵⁻²⁸ Theoretical calculations on the dynamics and equilibrium of *n*-alkanes on Pt(111) have stated that *n*-hexane adsorbs in the TTT conformation greater than 99% of the time at temperatures below 200 K.²⁶ The fraction of conformational isomers in gauche states increases above 200 K since torsional motions around the C-C bonds are thermally activated. Previous spectroscopic and theoretical studies on *n*-hexane conformers in the liquid and gas phases report the enthalpy change between the TTT conformer and the next stable conformers (TTG, TGT, TGG, and GTG) to be in the range of 0.4-2.0 kcal/ mol.^{29,30} At room temperature there will be sufficient energy to overcome this barrier and form conformational isomers of n-hexane. Based on the above information, the adsorbates present at 300 K are suggested to be conformational isomers of "flat-lying" n-hexane.

3-Methylpentane. The SFG spectrum of 3-methylpentane is strikingly similar to that of *n*-hexane: two major bands appear at 2860 and 2915 cm⁻¹. As is the case of *n*-hexane, the mode at 2860 cm⁻¹ is assigned to a mixture of CH₂(s) and CH₃(s) while the mode at 2915 cm⁻¹ is assigned to a mixture of CH₂-(a, p) and CH₃(a, p). The difference between the *n*-hexane and 3-methylpentane spectra can be observed when examining the relative intensities of the symmetric and perturbed asymmetric stretches. The asymmetric stretches in the *n*-hexane spectrum are less intense than the symmetric stretches as compared to the 3-methylpentane, which has comparable intensities for the symmetric and asymmetric stretches. This difference lends to the interpretation that two different adsorbates are being observed.

Previous work by Yang and Somorjai⁹ on the Pt(111) surface asseverated that physisorbed C₆ alkanes adsorb in a manner that will maximize the number of carbon chains bonding to the metal surface on Pt(111). Based on the presence of an unperturbed asymmetric CH₃ stretch, Yang and Somorjai⁹ proposed an adsorption geometry which is illustrated in Scheme 2. The proposed geometry involves the CH₂ and terminal CH₃ groups interacting with the metal surface while the central CH₃ group tilts away from the surface. The similarities between the spectra for Pt(111) and Pt(100) in the presence of 1.5 Torr 3-methylpentane and 15 Torr H₂ have led to the conclusion that similar surface species are present on both metal surfaces.

2-Methylpentane. The SFG spectrum of the surface species present in 1.5 Torr 2-methylpentane and 15 Torr H₂ is somewhat similar to *n*-hexane and 3-methylpentane. One noticeable difference from the 2-methylpentane spectrum and those of *n*-hexane and 3-methylpentane is that there appears to be a much weaker interaction between the nonresonant nonlinear susceptibility and the resonance at 2915 cm⁻¹. This may be explained



Figure 2. Temperature-dependent SFG spectra of surface species on Pt(100) under 1.5 Torr of *n*-hexane and 15 Torr of H₂ in the temperature range of 300-450K. The top SFG spectrum was taken after the metal surface was cooled from 450 to 300 K. Symmetric CH₂ and CH₃, perturbed asymmetric CH₂ and CH₃, and vinylic (-C=C-H) bands are identified. Markers represent experimental data and solid lines represent the curve fits using eq 1.

by a weaker interaction between the adsorbate and the metal surface and implies that the surface species present upon adsorption of 2-methylpentane is different from those present when n-hexane and 3-methylpentane adsorbed.

Two major peaks are present at 2870 and 2915 cm⁻¹. As in the *n*-hexane and 3-methylpentane cases, the feature at 2870 cm⁻¹ is assigned to a mixture of symmetric CH₂ and CH₃ stretches, while the feature at 2915 cm⁻¹ is assigned to perturbed asymmetric CH₂ and CH₃ stretches. To determine the adsorption geometry of 2-methylpentane, we apply criterion proposed by Yang and Somorjai:⁹ C₆ alkanes physisorb in such a way as to maximize the number of carbon chains bonding to the metal surface. This information coupled with the knowledge that the spectrum for 3-methylpentane is very similar to 2-methylpentane leads to the conclusion that 2-methylpentane adsorbs in a similar fashion as 3-methylpentane. As seen in Scheme 3a, the proposed adsorption geometry involves the two CH₂ and two of the terminal CH₃ groups interacting with the metal surface while the third terminal CH₃ group is tilted away from the surface.

This proposed adsorption geometry is quite different from the molecular geometry on Pt(111). A much stronger symmetric stretch is observed on Pt(111). On the basis of the strong symmetric stretch, the adsorbate is determined to be in a "standing-up" conformation on Pt(111) with two carbon atoms interacting with the surface to form a metallacyclobutane (see Scheme 3(b)).



Figure 3. Temperature-dependent SFG spectra of surface species on Pt(100) under 1.5 Torr of 3-methylpentane and 15 Torr of H_2 in the temperature range of 300–450 K. The top SFG spectrum was taken after the metal surface was cooled from 450 to 300 K. Symmetric CH₂ and CH₃ and perturbed asymmetric CH₂ and CH₃ bands are identified. Markers represent experimental data and solid lines represent the curve fits using eq 1.

1-Hexene. The SFG spectrum in the case of 1-hexene is dissimilar to the cases of *n*-hexane, 3-methylpentane, and 2-methylpentane. Three strong bands are present in the SFG spectrum at 2860, 2915, and 2950 cm⁻¹. Previous RAIRS³¹ studies on 1-hexene adsorption under UHV conditions on Pt(111) have shown three peaks at 2880, 2911, and 2938 cm⁻¹, which have been assigned as CH₂(s), CH₂(s) (bound to surface), and CH₂-(a), respectively. On the basis of these assignments, Ilharco et al.³¹ have proposed that the adsorbate present on the surface is metallocycle Pt₃=C-(CH₂)₅-Pt, as illustrated in Scheme 4. The similarity between the RAIRS and SFG spectra leads us to conclude that the adsorbate present under 1.5 Torr of 1-hexene and 15 Torr of H₂ is metallocycle Pt₃=C-(CH₂)₅-Pt.

3.2. Temperature-Dependent SFG Spectra of Surface Species in 1.5 Torr of C₆ Hydrocarbons and 15 Torr of Hydrogen. The temperature-dependent SFG spectra of the surface species on Pt(100) under 1.5 Torr of C₆ hydrocarbon and 15 Torr of H₂ are shown in Figures 2–5. The crystal was initially held at 300 K and sequentially heated for each SFG measurement. After reaching 450 K, the crystal was cooled to 300 K to examine the reversibility of the reaction and the surface chemistry during the heating/cooling cycle.

As described in the previous section, *n*-hexane adsorbs in a "flat-lying" geometry at 300 K on Pt(100) with two major peaks at 2860 and 2915 cm⁻¹, which were assigned as $CH_2(s)/CH_3$ -(s) and $CH_2(a, p)/CH_3(a, p)$. Upon heating the surface, the bands



Figure 4. Temperature-dependent SFG spectra of surface species on Pt(100) under 1.5 Torr of 2-methylpentane and 15 Torr of H_2 in the temperature range of 300–450 K. The top SFG spectrum was taken after the metal surface was cooled from 450 to 300 K. Symmetric CH₂ and CH₃; perturbed asymmetric CH₂ and CH₃; and vinylic CH bands are identified. Markers represent experimental data and solid lines represent the curve fits using eq 1.

in the SFG spectra broaden. This is most likely the result of the thermal activation of the translational/rotational motions of the adsorbates giving rise to many adsorption structures, ultimately giving rise to inhomogeneous broadening of the observable SFG bands. At 375 K a new band at 3000 cm⁻¹ appears in the spectrum, most likely arising from a vinylic stretch.^{31,32} This vinylic stretch has been assigned to the partial dehydrogenation of *n*-hexane. Further heating the surface increases the relative intensity of the peak at 2860 cm⁻¹ and decreased the relative intensity of the peak at 2915 cm⁻¹. A shoulder is also observed at 2825 cm⁻¹. Previous studies on the Pt(111) surface⁹ have shown a similar SFG spectrum, which was ascribed to hexylidyne (see Scheme 5). RAIRS studies³¹ have shown that hexylidyne exists in the TTT and GTT conformations. We have assigned the peaks as follows: 2825 cm⁻¹ corresponds to CH₂(s) (GTT), 2860 cm⁻¹ corresponds to CH₃(s) (TTT), and 2915 cm⁻¹ corresponds to CH₂(a) (GTT/ TTT). Heating the crystal to 450 K and cooling to 300 K reveals a similar spectrum to the initial spectrum at 300 K, indicating that "flat-lying" n-hexane is present on the surface and that hexylidyne was formed through a reversible pathway.

The SFG spectra in the case of 3-methylpentane are remarkably similar to that of *n*-hexane. Increasing the surface temperature to 375 K shows little change in the vibrational signature of the surface adsorbate, much like in the case of *n*-hexane. Upon heating to 425 K, the relative intensities of the symmetric



Figure 5. Temperature-dependent SFG spectra of surface species on Pt(100) under 1.5 Torr of 1-hexene and 15 Torr of H₂ in the temperature range of 300-450 K. The top SFG spectrum was taken after the metal surface was cooled from 450 to 300 K. Symmetric CH₂ and CH₃ and asymmetric CH₂ and CH₃ bands are identified. Markers represent experimental data and solid lines represent the curve fits using eq 1.

and asymmetric stretches change. This may be due to dehydrogenation of the adsorbed 3-methylpentane to metallacyclohexane since the CH₃ group is now aligned with the surface normal, thus increasing its relative intensity in the SFG spectrum as compared to the "flat-lying" 3-methylpentane whose methyl group is tilted toward the metal surface. Another alternative explanation for the spectra is that 3-methylpentane isomerizes to form n-hexane upon adsorption. This rearrangement is less likely since the relative intensities of the adsorbate observed during 3-methylpentane adsorption at 425 K are not consistent with the relative intensities observed during *n*-hexane adsorption at the same surface temperature. Furthermore, in the case of *n*-hexane, a vinylic stretch is observed at 3000 cm⁻¹ after heating the crystal to 375 K. No such stretch was observed in the case of 3-methylpentane, indicating that the adsorbate present under 1.5 Torr of 3-methylpentane and 15 Torr of H₂ is different that in the presence of 1.5 Torr of *n*-hexane and 15 Torr of H₂. Cooling the surface from 450 to 300 K reveals that the temperature dependent changes in the adsorption of 3-methylpentane are reversible.

The SFG spectra in the case of 2-methylpentane show temperature dependences different from those in the cases of *n*-hexane and 3-methylpentane, as seen in Figure 4. Increasing the surface temperature to 375 K results in the increase of the CH₂(a, p)/CH₃(a, p) peak and the appearance of a stretch at 3000 cm⁻¹. The stretch at 3000 cm⁻¹ has been attributed to a



Figure 6. SFG spectra of surface species on Pt(100) at 300K under 1.5 Torr of C_6 hydrocarbons in the absence of excess hydrogen. In order from the top are *n*-hexane, 3-methylpentane, 2-methylpentane, and 1-hexene. Markers represent experimental data and solid lines represent the curve fits using eq 1.

vinylic stretch.³² Further heating the crystal surface to 425 K results in the disappearance of the vinylic stretch along with the $CH_2(a, p)/CH_3(a, p)$. The vibrational spectrum observed at 425 K bears striking resemblance to the case of 1.5 Torr of *n*-hexane and 15 Torr of H₂ at 425 K. Therefore, the surface species present at 425 K is determined to be hexylidyne. Upon cooling the surface to 300 K, a spectrum similar to "flat-lying" *n*-hexane is observed. It should be noted that the peak positions of the cooled to 300 K spectrum are very similar to the initial spectrum at 300 K, however, the relative peak intensities are not similar. Based on the relative intensities of the CH₂(s)/CH₃-(s) and $CH_2(a, p)/CH_3(a, p)$, the adsorbate present after cooling to 300 K is assigned as "flat-lying" n-hexane. Identifying the adsorbate responsible for the vibrational signature at 375 K is difficult since there is a paucity of vibrational spectroscopic studies of 2-methylpentane. What can be said about the intermediate is that it is some intermediate in the rearrangement of 2-methylpentane to hexylidyne.

Contrary to the cases of *n*-hexane, 3-methylpentane, and 2-methylpentane, very little change is observed in the SFG spectra for 1-hexene during the heating/cooling treatment, as seen in Figure 5. These results indicate that metallocycle $Pt_3 \equiv C-(CH_2)_5$ -Pt is a thermally stable species on Pt(100) in the temperature range 300-450 K. The proposed adsorption geometries and thermal chemistry of the C₆ hydrocarbons in the presence of excess hydrogen are summarized in Schemes 7-10.

SCHEME 5: Hexylidyne (C_6H_{11}) in the (a) TTT and (b) GTT Conformations Adsorbed on Pt(100) and Pt(111)





SCHEME 6: Metallacyclohexane (C₆H₈) Adsorbed on Pt(100) and Pt(111)⁹



metallacyclohexane (C6H8)

3.3 SFG Spectra of Surface Species on Pt(100) at 300 K under 1.5 Torr of C₆ Hydrocarbons in the Absence of Excess Hydrogen. The SFG spectra of the surface species on Pt(100) at 300 K under 1.5 Torr of C₆ hydrocarbons in the absence of excess hydrogen are shown in Figure 6. The SFG spectrum for *n*-hexane features three bands at 2860, 2920, and 2955 cm⁻¹. The peak positions, relative intensities, and widths are very similar to the case of 1.5 Torr of 1-hexene and 15 Torr of H₂ (see Figure 5). We propose that the surface species present in this case is also metallocycle Pt₃=C-(CH₂)₅-Pt (see Scheme 4).

The SFG spectrum for 3-methylpentane features three bands at 2860, 2915, and 2955 cm⁻¹, which are assigned as CH₂(s)/ CH₃(s), CH₂(a), and CH₃(a), respectively. Previous studies on Pt(111)⁹ have observed similar features of similar intensities to the spectrum shown in Figure 6. Yang and Somorjai attributed the vibrational signature to metallacyclohexane (see Scheme 6). Metallacyclohexane is believed to be a surface intermediate in the isomerization of 3-methylpentane to *n*-hexane and vice versa.² Another possible interpretation is that the adsorbate present under 1.5 Torr of 3-methylpentane is metallocycle Pt₃ C $-(CH_2)_5$ -Pt based on the peak positions. However, we believe that metallacyclohexane is the more likely surface adsorbate based on the relative intensities of the observed modes in the case of 3-methylpentane.

The SFG spectrum in the case of 2-methylpenatane exhibits four peaks at 2860, 2905, 2955 and 3030 cm⁻¹ that are assigned as CH₂(s)/CH₃(s), CH₂(a, p), and vinylic -C=C-H stretches. The vinylic stretch indicates that 2-methylpentane has dehydrogenated on the surface. The identification of this intermediate is difficult since there is a dearth of spectroscopic studies examining the surface intermediates present during 2-methylpentane adsorption. However, two possible candidates for the surface species are 2-methyl-1-pentene and 4-methyl-2-pentene based on infrared spectroscopy.³³ Both of these molecules have modes present at 2870, 2925, 2960, and 3070 cm⁻¹. In the case of 1-hexene, there is very little difference between the SFG spectra in the presence and absence of excess hydrogen (Figures 1 and 6). Cooling the surface temperature from 450 to 300 K

SCHEME 7: Observed Surface Species under 1.5 Torr of *n*-Hexane in the Presence and Absence of Excess H_2 on (a) Pt(100) and (b) $Pt(111)^9$



SCHEME 8: Observed Surface Species under 1.5 Torr of 3-Methylpentane in the Presence and Absence of Excess H_2 on (a) Pt(100) and (b) $Pt(111)^9$



shows that all of the reactive surface intermediates observed in the absence of excess hydrogen are reversible, indicating that they are thermally stable intermediates (see Supporting Information).

4. Discussion

The most important reactions in naphtha reforming processes are isomerization and dehydrocyclization because they produce the largest increase in octane number. Catalytic reactions of n-hexane on platinum based catalysts have been used as a model system to elucidate the reaction mechanisms.^{1,2,4,34} Four classes of reactions occur during reforming of n-hexane on platinum based catalysts in the presence of excess hydrogen: (1) dehydrocyclization to form benzene, (2) cyclization to form methylcyclopentane, (3) isomerization to form 2- and 3- methylpentane, and (4) hydrogenolysis to form smaller hydro-

SCHEME 9: Observed Surface Species under 1.5 Torr of 2-Methylpentane in the Presence and Absence of Excess H_2 on (a) Pt(100) and (b) $Pt(111)^9$



SCHEME 10: Observed Surface Species under 1.5 Torr of 1-Hexene in the Presence and Absence of Excess H_2 on (a) Pt(100) and (b) $Pt(111)^9$



carbons.^{2,9,34} Extensive studies have investigated macroscopic information such as reaction kinetics through the functionality of active sites and surface structure.^{2,10} However, to have a detailed understanding of elementary reaction steps, the reactive surface intermediates must be identified. Yang and Somorjai⁹ have made considerable progress in this arena by using SFG to investigate adsorbates present on the Pt(111) surface during *n*-hexane isomerization and dehydrocyclization. To further understand the catalytic reactions of *n*-hexane on platinum based catalysts, a molecular level understanding of the adsorbates present during reaction on other surface structures is necessary.

n-Hexane adsorption on Pt(111) and Pt(100) yields quite similar adsorbates in the presence of excess hydrogen, as summarized in Scheme 7. Initially, *n*-hexane adsorbs in a "flatlying" conformation. Increasing the surface temperature dehydrogenates the "flat-lying" species to form hexylidyne. In the absence of hydrogen, different adsorbates exist on the platinum surfaces: metallocycle Pt₃=C-(CH₂)₅-Pt on Pt(100) and π -allyl c-C₆H₉ on Pt(111). Similar surface species are observed on Pt(100) and Pt(111) in the case of 3-methylpentane (see Scheme 8). In the presence of excess hydrogen, "flat-lying" 3-methylpentane is observed, which dehydrogenates to metallacyclohexane as the surface temperature is increased. Metallacyclohexane is also observed in the absence of hydrogen on both surfaces and is believed to be a surface intermediate when *n*-hexane isomerizes to 3-methylpentane and vice versa.² Furthermore, the rate of isomerization from *n*-hexane to 3-methylpentane has shown little dependence on surface structure,¹⁰ which supports this theory.

Metallacyclobutane is believed to be an intermediate in the isomerization of *n*-hexane to 2-methylpentane² and is only observed on the Pt(111) surface. In the case of 2-methylpentane on Pt(100), "flat-lying" 2-methylpentane forms hexylidyne without forming metallacyclobutane. This may indicate that the isomerization of metallacyclobutane occurs so rapidly on Pt-(100) that it cannot be observed in the SFG spectrum. Without hydrogen, 2-methylpentane undergoes another different reaction pathway, through a dehydrogenated species speculated to be 2-methyl-1-pentene or 4-methyl-1-pentene (see Scheme 9).

In the case of 1-hexene, the dehydrogenated products are observed on both Pt(111) and Pt(100) in the presence and absence of hydrogen: hexylidyne is formed on the Pt(111) surface, while metallocycle Pt₃≡C-(CH₂)₅-Pt is formed on Pt(100). Previous work³⁵ has suggested that the intermediate for dehydrocyclization of 1-hexene is a hexa- σ -bonded triene. This species is clearly not present on either surface since there is no vinylic mode observed. This may indicate that under the experimental conditions benzene is not produced. Alternatively, the observation of metallocycle $Pt_3 \equiv C - (CH_2)_5 - Pt$ may indicate that cyclization occurs prior to dehydrogenation in the formation of benzene. Yang and Somorjai⁹ found in the case of *n*-hexane, production of benzene occurs primarily through the formation of π -allyl c-C₆H₉ and proposed that direct 1,6-ring closure occurs via formation of cyclohexane followed by consecutive dehydrogenation rather than consecutive dehydrogenation of *n*-hexane followed by cyclization. We have expanded upon the 1,6-ring closure mechanism by purporting that metallocycle $Pt_3 \equiv C - (CH_2)_5 - Pt$ is the reactive intermediate in forming π -allyl c-C₆H₉, which in turn forms benzene. Furthermore, we suggest that the cyclization of metallocycle $Pt_3 \equiv C - (CH_2)_5 -$ Pt to form π -allyl c-C₆H₉ is the rate determining step in *n*-hexane dehydrocyclization to benzene. This assertion is based on studies by Davis et al.¹⁰ that investigated structure sensitivity of aromatization of *n*-hexane and found that the reaction is markedly maximized on Pt(111) surfaces. Combining the gasphase production data with the molecular level information provided by SFG leads us to the conclusion that the 1,6-ring closure is faster on Pt(111) leading to a larger production of benzene.

5. Conclusions

Through the use of SFG we were able to probe reactive surface intermediates and elucidate reaction pathways in hydrocarbon reforming processes. n-Hexane, 3-methylpentane, and 2-methylpentane were inactive on Pt(100) at 300 K in the presence of excess hydrogen. However, 1-hexene readily dehydrogenated to form metallocycle Pt₃≡C-(CH₂)₅-Pt, regardless of the presence of excess hydrogen. At high surface temperature, n-hexane and 2-methylpentane dehydrogenated to form hexylidyne in the presence of excess hydrogen. 3-Methylpentane also underwent dehydrogenation at elevated temperature to form metallacyclohexane. In the absence of excess hydrogen, dehydrogenation of each hydrocarbon was enhanced: *n*-hexane formed metallocycle $Pt_3 \equiv C - (CH_2)_5 - Pt$, 2-methylpentane formed 2-methyl-1-pentene and 4-methyl-1pentene, and 3-methylpentane formed metallacyclohexane. These results support previous claims⁹ that metallacyclohexane is a reactive surface intermediate in the isomerization of 3-methylpentane to *n*-hexane and vice versa. Additionally, metallocycle $Pt_3 \equiv C - (CH_2)_5$ -Pt is suggested to be a reactive surface intermediate in the direct 1,6-ring closure of *n*-hexane in the formation of benzene.

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Supporting Information Available: Temperature-dependent SFG spectra of the surface species on Pt(100) in 1.5 Torr of C_6 hydrocarbons in the absence of excess hydrogen. This material is available free of charge via the Internet at http://pubs.acs.org.

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