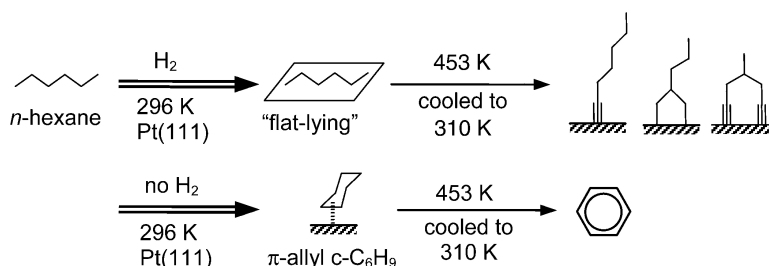Article

Adsorption and Reactions of C Hydrocarbons at High Pressures on Pt(111) Single-Crystal Surfaces Studied by Sum Frequency Generation Vibrational Spectroscopy: Mechanisms of Isomerization and Dehydrocyclization of *n*-Hexane

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Adsorption and Reactions of C$_6$ Hydrocarbons at High Pressures on Pt(111) Single-Crystal Surfaces Studied by Sum Frequency Generation Vibrational Spectroscopy: Mechanisms of Isomerization and Dehydrocyclization of *n*-Hexane

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Abstract: The adsorption geometries and surface reactions of various C$_6$ hydrocarbons (*n*-hexane, 2-methylpentane, 3-methylpentane, and 1-hexene) adsorbed on Pt(111) were investigated using sum frequency generation (SFG) surface vibrational spectroscopy. The adsorptions and reactions were carried out in 1.5 Torr of C$_6$ hydrocarbons in the absence and presence of excess hydrogen (15 Torr) and in the temperature range 296−453 K. At 296 K and in the presence of excess hydrogen, *n*-hexane and 3-methylpentane adsorbed molecularly on Pt(111) mostly in "flat-lying" geometries. Upon heating the sample up to 453 K, the molecules underwent dehydrogenation to form new surface species in "standing-up" geometries, such as hexylidyne and metallacyclic species. However, 2-methylpentane and 1-hexene were dehydrogenated to metallacyclobutane and hexylidyne, respectively, at 296 K in the presence of excess hydrogen. The dehydrogenated species remained unreacted on the surface upon heating the sample up to 453 K. The absence of excess hydrogen enhanced dehydrogenation of *n*-hexane and 3-methylpentane to form π-allyl c-C$_6$H$_9$ and metallacyclohexane, respectively, at 296 K. Upon heating to 453 K, the π-allyl c-C$_6$H$_9$ species underwent irreversible dehydrogenation, while hexylidyne and metallacyclic species remained unreacted. On the basis of these results, the mechanisms for catalytic isomerization and dehydrocyclization of *n*-hexane, which are the important "reforming" reactions to produce high-octane fuels over platinum, were discussed.

1. Introduction

The adsorption and catalytic surface reactions of alkanes on metal surfaces have been intensively studied because of fundamental interest and technological importance. Alkanes on metal surfaces are model systems for understanding two-dimensional ordering[1−3] and dynamic processes[4−8] of large organic molecules on surfaces that are associated with applications for adhesion, lubrication, and molecular electronics.[9−11] From the viewpoint of heterogeneous catalysis, catalytic surface reactions of alkanes with 6−10 carbons (C$_6$−C$_{10}$) on platinum-based catalysts are of importance in naphtha reforming processes that produce high-octane fuels.[12]

Most mechanistic studies of the alkane catalytic reactions on metal surfaces were carried out at high pressures by monitoring the reaction products in the gas phase.[13] This approach, however, has difficulty unraveling details of the reaction mechanisms. This is due to the lack of knowledge of the elementary steps comprising the overall catalytic reaction and reactive surface intermediates involved in a particular elementary step. As an alternative approach, various surface analytical techniques have been employed to probe surface species upon adsorption of alkane molecules on metal surfaces.[13−17] Among them are low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), high-resolution electron energy loss spectroscopy (HREELS), and reflection−absorption infrared spectroscopy (RAIRS).[13−17] These surface analytical techniques require low-pressure ($<10^{-6}$ Torr) environments to operate. At low pressure, only strongly bound species can exist on a surface, while weakly

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bound ones, which may be key reaction intermediates under ambient conditions, desorb quickly. Therefore, the surface species that are present at low pressure may not be directly related to those present at high pressures[18] and in the presence of excess hydrogen, which are the conditions in most naphtha reforming processes.[12]

Sum frequency generation (SFG) vibrational spectroscopy, a nonlinear optical technique, has recently been adopted to monitor surface species during catalytic reactions on metal surfaces under ambient conditions.[18−23] In SFG experiments, a visible beam and a tunable infrared beam are spatially and temporally overlapped on a surface. As the infrared beam is scanned over the frequency range of interest, vibrational spectra of molecules present on the surface are obtained via a second-order nonlinear optical process.[24−26] Due to the unique symmetry selection rule of the second-order nonlinear optical process, this technique can be more surface-sensitive than infrared and Raman spectroscopies, while electron spectroscopies cannot be employed at high reactant pressures necessary to monitor catalytic reactions.

In this study, we utilized SFG spectroscopy to investigate the adsorption geometries and surface reactions of C₆-alkane and C₆-alkene hydrocarbons on Pt(111) under ambient conditions. The C₆ hydrocarbon compounds of interest in this 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 large enough to undergo the full spectrum of skeletal rearrangement reactions involved in the hydrocarbon reforming processes including dehydrogenation, isomerization, cyclization, and dehydrocyclization.[27,28] 2- and 3-methylpentane are the main products from isomerizations of *n*-hexane. 1-Hexene is also produced during the *n*-hexane catalytic reactions on Pt(111). A Pt(111) single-crystal surface has been chosen in this study because it has the unique capability of carrying out all skeletal rearrangement reactions, while undesirable C−C bond scission is less significant on Pt(111) than on lower Miller index Pt surfaces or on other transition metal surfaces.[29] The adsorption and reaction studies of C₆-alkanes on metal surfaces have been hampered by their low dissociative sticking probability.[16,17,29] As a result, little is known about the surface species and their adsorption geometries upon C₆-alkane adsorption on Pt(111) at temperatures higher than cryogenic temperature.

It will be shown that the surface species and their adsorption geometries change dramatically with temperature and the presence of excess hydrogen. At 296 K and in the presence of excess hydrogen, *n*-hexane and 3-methylpentane are inactive on Pt(111) at 296 K, while 2-methylpentane and 1-hexene are readily dehydrogenated to form metallacyclobutane and hexylidyne, respectively. Upon heating to 453 K, *n*-hexane and

3-methylpentane are partly dehydrogenated to hexylidyne or metallacyclic species. At 296 K and in the absence of excess hydrogen, *n*-hexane and 3-methylpentane are readily dehydrogenated to form π-allyl c-C_6H_9 and metallacyclohexane, respectively. Upon heating to 453 K, the π-allyl c-C_6H_9 species underwent irreversible dehydrogenation, while hexylidyne and metallacyclic species remained unreacted.

On the basis of the SFG results, we discuss the mechanisms of the *n*-hexane catalytic reactions to form isomers and benzene on Pt(111). Our SFG results provide spectroscopic evidence that π-allyl c-C_6H_9 is a reactive surface intermediate during dehydrocyclization of *n*-hexane on Pt(111). In addition, our SFG results suggest that benzene formation from *n*-hexane on Pt-(111) does not proceed via a five-member cyclic intermediate as does isomerization, but rather proceeds through a direct 1−6 ring closure.

2. Experimental Section and Theory

All experiments were carried out on a Pt(111) single-crystal surface in a high-pressure/ultrahigh-vacuum (HP/UHV) system. The HP/UHV system is composed of a UHV chamber with a base pressure of 4×10^{-10} Torr and a high-pressure (HP) cell. The HP cell, where high-pressure catalysis studies were carried out, was connected to the UHV chamber through a gate valve. Two CaF_2 windows on the HP cell allowed input and output of both infrared and visible beams for SFG experiments. The Pt(111) crystal was cleaned by sputtering with Ar^+ ions (1 keV), heating at 900 K in the presence of 5×10^{-7} Torr O_2 for 2 min, and then annealing at 1200 K in UHV for 2 min. After a few cycles of cleaning, the Pt(111) crystal was transferred to the HP cell for SFG measurements. The Pt(111) surface was routinely checked by Auger electron spectroscopy (AES) for cleanliness.

For SFG experiments, a mode-locked 20 ps, 20 Hz Nd:YAG laser with a 25 mJ/pulse energy output at 1064 nm was used to generate a tunable infrared (1300−3200 cm⁻¹) beam and a visible beam at 532 nm. The visible (200 μJ/pulse) and the infrared (100 μJ/pulse) beams were spatially and temporally overlapped on the Pt(111) surface with incident angles of 55° and 60°, respectively, with respect to surface normal. Both the infrared and the visible beams were p-polarized. As the infrared beam is scanned over the frequency range of interest, the sum frequency output from the Pt(111) crystal was collected by a photomultiplier and a gated integrator.

The theory of SFG for surface studies has been described in detail previously.[24,26,30] Briefly, SFG is a second-order nonlinear optical process in which an infrared laser beam at ω_{IR} is combined with a visible laser beam at ω_{VIS} to generate a sum frequency output at $\omega_{SF} = \omega_{IR} + \omega_{VIS}$. This process is only allowed in a medium without centrosymmetry under the electric dipole approximation. Platinum bulk is centrosymmetric, and its contribution to SFG is usually negligible. Isotropic gases in the HP cell do not generate SFG. Only the metal surface and adsorbates on the surface can generate SFG under the electric dipole approximation. The SFG signal, I_{SF}, is related to the incidence visible (I_{VIS}) and infrared (I_{IR}) beam intensities, and second-order susceptibility of the media ($\chi^{(2)}$) as

$$I_{SF} \propto |\chi^{(2)}|^2 I_{VIS} I_{IR} \qquad (1)$$

The second-order susceptibility $\chi^{(2)}$ is given by

$$\chi^{(2)} = \chi_{NR} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \qquad (2)$$

where χ_{NR} is the nonresonance contribution, and A_q, ω_q, and Γ_q denote

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the vibrational mode strength, the resonant frequency, and the line width of the qth vibrational mode, respectively. The nonresonance contribution, χ_{NR}, originates from the metal surface and is usually independent of the frequency of the infrared laser beam. In contrast, the second term is significantly enhanced when the frequency of the infrared laser beam is in resonance with a vibrational mode of the adsorbates. The vibrational mode strength A_q is given by[31]

$$A_{q,ijk} = \frac{2\pi}{h} N \langle \sum_{lmn} F_{q,ijk} (\hat{i}\cdot\hat{l})(\hat{j}\cdot\hat{m})(\hat{k}\cdot\hat{n}) R_{q,lm} \mu_{q,n} \rangle \quad (3)$$

where N is the number density of adsorbates, $F_{q,ijk}$ is the Fresnel factor, and $R_{q,lm}$ and $\mu_{q,n}$ are the Raman and the IR transition cross sections for the qth vibrational mode. i,j,k refers to the laboratory coordinates, and l,m,n refers to the molecular coordinates. The brackets indicate the spatial average of the molecular orientations. Because the Fresnel factor is complex, A_q can be expressed as $A_q = |A_q|e^{i\phi_q}$, where ϕ_q is the phase factor. χ_{NR} is also complex, given as $\chi_{NR} = |\chi_{NR}|e^{i\varphi}$. Finally, the SFG signal is written as

$$I_{SF} \propto ||\chi_{NR}|e^{i\varphi} + \sum_q \frac{|A_q|e^{i\phi_q}}{\omega_{IR} - \omega_q + i\Gamma_q}|^2 I_{VIS} I_{IR} \quad (4)$$

To analyze our SFG spectra, the SFG signal was first normalized to the intensity (I_{IR}) of the incident infrared beam on the surface. This is necessary because the gas molecules in the HP cell absorb some portion of the incident infrared beam. Detailed descriptions on the HP/UHV system and SFG measurement can be found elsewhere.[32,33]
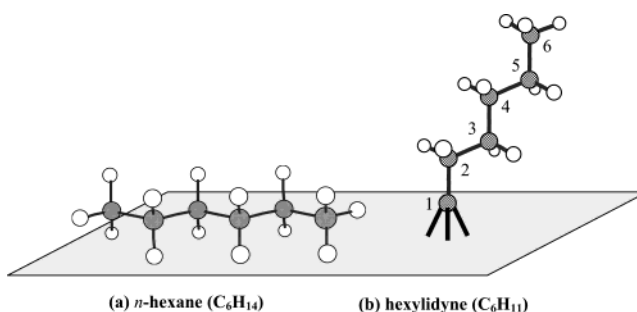
All alkane and alkene hydrocarbons used in this study were purchased from Aldrich ($\geq$99%). All samples were purified by several freeze−pump−thaw cycles before introduction to the HP cell. The reactant pressure was 1.5 Torr of C_6-hydrocarbon or 1.5 Torr of C_6-hydrocarbon and 15 Torr of hydrogen. In the latter case, hydrogen was always introduced first, followed by C_6-hydrocarbon. C_2−C_7 hydrocarbon impurities in the reactants were routinely checked using gas chromatography (GC). The hydrocarbon impurities were below 0.4%, and most of the impurities were light alkanes below C_5. The light alkanes are no more reactive than the reactants on Pt(111) and thus can be ignored in the SFG analysis.

3. Results and Analysis

3.1. Previous Studies of C_6-Alkane and C_6-Alkene Hydrocarbons Adsorbed on Pt(111) Under Low-Pressure (<10^{-6} Torr) Conditions. For our SFG spectral analysis, it is important to review the studies of C_6-alkane and C_6-alkene hydrocarbons adsorbed on Pt(111) under low-pressure (<10^{-6} Torr) conditions.

When *n*-hexane (C_6H_{14}) adsorbs on Pt(111) at 100 K, it binds molecularly to the surface, aligning its C−C bonds parallel to the surface in the trans−trans−trans (TTT) conformation (see Scheme 1a).[34−36] The atomic structure of the Pt(111) surface was not drawn in Schemes 1−7 because the adsorption sites of the proposed surface species are not known. The IR spectrum of the TTT-type *n*-hexane on the surface is characterized by two major bands at 2904 and 2929 cm^{-1} in the C−H stretching region.[35,36] The two bands are assigned to asymmetric stretches

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Scheme 1

(a) *n*-hexane (C_6H_{14})   **(b) hexylidyne (C_6H_{11})**

of CH_2 and CH_3 groups, respectively. These two bands are red-shifted by 20−30 cm^{-1} from those for *n*-hexane in the condensed phase.[37,38] These red shifts are due to the adsorbate−surface interaction and are commonly found in a system of a "flat-lying" alkane monolayer on a metal surface.[35,36] As the temperature increases, the *n*-hexane monolayer on Pt(111) desorbs molecularly at about 240 K with a desorption energy of 14.8 kcal/mol.[39] No indication of thermal decomposition of *n*-hexane on Pt(111) has been observed with increasing temperature.[39]

Contrary to *n*-hexane, 1-hexene (C_6H_{12}) on Pt(111) undergoes decomposition with increasing temperature. Ilharco et al.[40] reported that 1-hexene adsorbs molecularly on Pt(111) at 100 K with the molecular plane parallel to the surface. At 250 K, it converts into the hexylidyne (C_6H_{11}) species. RAIRS results showed that two types of hexylidyne conformers coexist on Pt-(111) at 250 K: trans−trans−trans (TTT) and gauche−trans−trans (GTT) conformers. Hexylidyne in the TTT conformation, as illustrated in Scheme 1b, aligns its molecular plane perpendicular to the surface, giving rise to a strong IR band for symmetric CH_3 stretch at 2877 cm^{-1}. The GTT conformer, which can be obtained by 90° rotation along C_2−C_3 bond, is characterized by a strong IR band for asymmetric CH_3 stretch at 2960 cm^{-1}.[40] Above 270 K, hexylidyne starts decomposition to form two types of metallacyclic species: One is a partially dehydrogenated form, [$Pt_3{\equiv}C{-}(CH_2)_5{-}Pt$], and the other is a completely dehydrogenated form, [$Pt_3{\equiv}C{-}(CH_2)_4{-}C{\equiv}Pt$]. No indication of fragmentation by C−C bond scission was observed below 500 K.[40] It should be noted that no studies, to our knowledge, on the adsorption of 2-methylpentane and 3-methylpentane on Pt(111) have been reported.

C_6-Alkane and C_6-alkene hydrocarbons on Pt(111) are complicated systems in that there may exist more than one conformer and reaction pathway, depending on temperature and pressure. Thus, it is necessary to set the criteria for the assignment of our SFG bands and the identification of corresponding chemical species on the surface. First, when C_6-alkanes are physisorbed on Pt(111), they align on the surface such that the number of carbon chains bonding to the metal surface is maximized. This has proven to be the case for *n*-alkanes (C_NH_{2N+2}, $N > 4$) on Au and Pt surfaces.[3,34,39] The adsorption energy of the *n*-alkanes increases with an increasing number of carbon chains: for example, the binding energy per carbon chain

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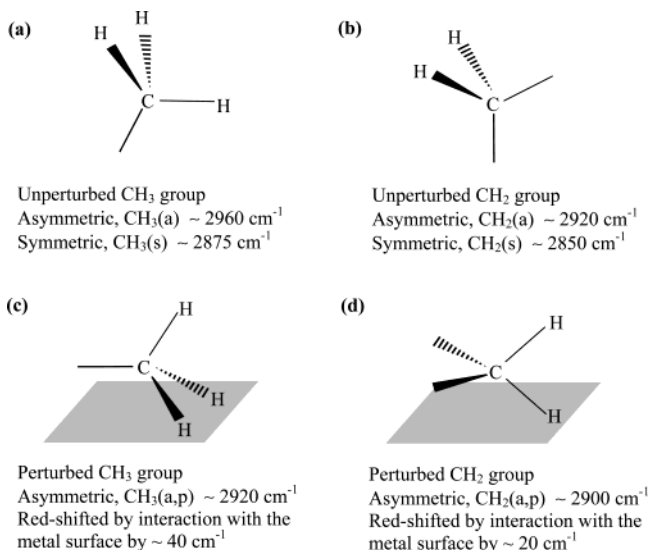
Figure 1. Schematic diagram of CH stretching modes.

for *n*-alkanes (6 < N < 10) on Pt(111) is about 2.1 kcal/mol.[39] Second, when C₆-alkanes and C₆-alkenes are dehydrogenated, they exist on the surface in largely two adsorption geometries: "flat-lying" and "standing-up" as in the case of hexylidyne in Scheme 1. The "standing-up" geometry can be more favorable than the "flat-lying" geometry when van der Waals interactions between adjacent carbon chains are dominant over carbon chain−metal interactions.

IR band positions for the CH stretching modes of interest are summarized in Figure 1. The IR spectrum for a "standing-up" adsorbate is featured by symmetric stretches of CH₃ and CH₂ groups. These symmetric stretches are denoted as CH₃(s) and CH₂(s), for further discussion. These bands appear at about 2875 and 2850 cm⁻¹, respectively, similar to those in the condensed phase. The IR spectrum for a "flat-lying" adsorbate on Pt(111) is featured by asymmetric stretches of CH₂ and CH₃ groups. These bands are red-shifted by 20−40 cm⁻¹ from those in the condensed phase because of their interactions with the metal surface. As a result, asymmetric CH₃ and CH₂ stretches, perturbed by the surface, appear at about 2920 and 2900 cm⁻¹, respectively. These two bands are denoted as CH₃(a,p) and CH₂-(a,p), respectively. Finally, unperturbed symmetric stretches of CH₃ and CH₂, denoted as CH₃(s) and CH₂(s), appear at about 2960 and 2920 cm⁻¹, respectively.

3.2. SFG Spectra of Surface Species on Pt(111) at 296 K in 1.5 Torr of C₆ Hydrocarbons and 15 Torr of Hydrogen. The SFG spectra of surface species on Pt(111) at 296 K in 1.5 Torr of C₆ hydrocarbons and 15 Torr of H₂ are shown in Figure 2. In order from the top in Figure 2 are *n*-hexane, 3-methyl-pentane, 2-methylpentane, and 1-hexene. To simplify the fitting of the SFG spectra, all resonance terms in eq 4 were assumed to be in phase; that is, the phase factor ϕ_q is independent of the vibrational mode. This assumption was previously used to analyze SFG spectra from *n*-alkanethiol monolayers on gold surfaces.[31] Equation 4 can then be rewritten as

$$I_{SF} \propto \left|\, |\chi_{NR}|e^{i\theta} + \sum_q \frac{|A_q|}{\omega_{IR} - \omega_q + i\Gamma_q} \,\right|^2 I_{VIS}I_{IR} \qquad (5)$$

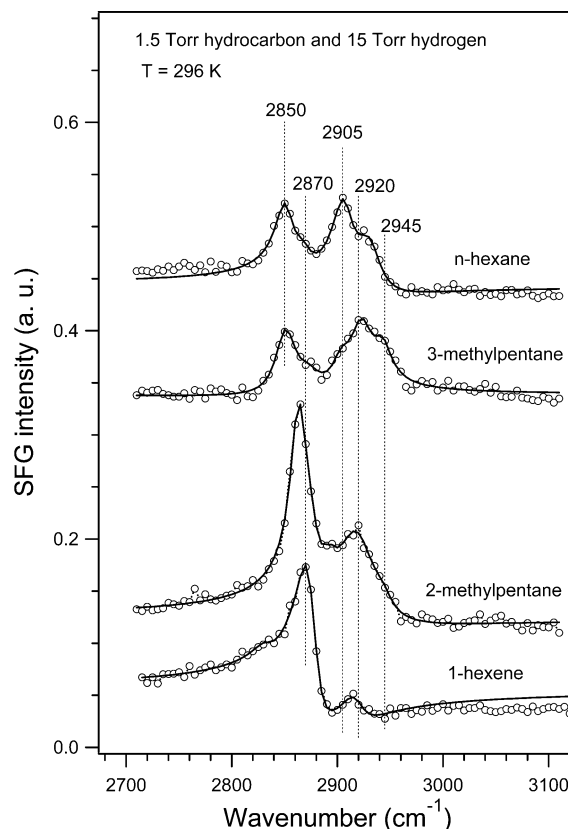where θ is the phase difference between the nonresonance and

Figure 2. SFG spectra of surface species on Pt(111) at 296 K in 1.5 Torr of C₆ hydrocarbons and 15 Torr of H₂. In order from the top are *n*-hexane, 3-methylpentane, 2-methylpentane, and 1-hexene, respectively. The solid lines correspond to fits using eq 5.

resonance components. The solid lines in Figure 2 correspond to fits using eq 5 where the fitting parameters are $|\chi_{NR}|$, θ, $|A_q|$, ω_q, and Γ_q. The parameters $|A_q|$, ω_q, and Γ_q determined from the fits are summarized in Table 1.

The relative magnitudes of $|A_q|$ between the vibrational modes are useful to evaluate molecular orientations of surface species because the Raman and the IR transition cross sections in eq 3 are sensitive to the molecular orientations.[41,42] In particular, SFG from adsorbates on a metal surface should obey the IR surface selection rule that only the IR transition dipole vector component perpendicular to the metal surface is accountable for the IR transition cross section, $\mu_{q,n}$. In addition, the nonresonant SFG signal from a Pt surface is much smaller than that from other metal surfaces such as Au and Ag. These may be the reasons why in some cases the IR and SFG spectra from a Pt surface adsorbed with hydrocarbons are similar in terms of the relative intensities between the vibrational modes. Among the cases are di-σ cyclohexene, 1,3-cyclohexadiene, and π-allyl C₆H₉ on Pt(111).[23,43−45]

In our SFG analysis, $|A_q|$ will be used to gain some insight on the molecular orientations but only for qualitative purpose. The limitation arises from the fact that the fitting was performed

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Table 1. Fitting Results to Eq 5 and Assignments for the SFG Spectra of *n*-Hexane, 3-Methylpentane, 2-Methylpentane, and 1-Hexene at 296 K on Pt(111) at High Pressure (1.5 Torr) with 15 Torr of H_2

modes		*n*-hexane	3-methylpentane	2-methylpentane	1-hexene
$CH_2(s)$	ω_q	2851 ± 0.8	2850 ± 0.9		2833 ± 2.8
	$\lvert A_q \rvert$	0.40 ± 0.07	0.47 ± 0.06		0.077 ± 0.03
	Γ_q	10.3 ± 1.2	11.5 ± 1.5		10.8 ± 5.4
$CH_3(s)$	ω_q	2868 ± 0.1	2872 ± 4.7	2865 ± 2.5	2870 ± 0.4
	$\lvert A_q \rvert$	0.13 ± 0.07	0.07 ± 0.03	1.18 ± 0.96	1.06 ± 0.03
	Γ_q	10.0 ± 4.0	10.2 ± 2.3	9.1 ± 2.9	11.3 ± 0.42
$CH_2(a,p)$	ω_q	2907 ± 0.5	2903 ± 3.6	2893 ± 2.6	
	$\lvert A_q \rvert$	0.54 ± 0.07	0.15 ± 0.17	0.10 ± 0.10	
	Γ_q	11.8 ± 1.1	9.9 ± 6.5	7.9 ± 6.1	
$CH_3(a,p)$	ω_q	2931 ± 1.0	2922 ± 1.7		
	$\lvert A_q \rvert$	0.44 ± 0.08	0.51 ± 0.12		
	Γ_q	14.0 ± 1.8	13.0 ± 5.7		
$CH_3(FR)$	ω_q			2920 ± 2.0^a	2917 ± 1.4
	$\lvert A_q \rvert$			1.28 ± 0.25	0.22 ± 0.06
	Γ_q			22.5 ± 3.1	13.0 ± 3.4
$CH_3(a)$	ω_q		2942 ± 2.3	2944 ± 4.1	
	$\lvert A_q \rvert$		0.19 ± 0.15	0.08 ± 0.09	
	Γ_q		9.5 ± 4.5	10.0 ± 9.7	

a This SFG band includes a contribution from the symmetric stretch of a CH_2 group on carbons bonded to the surface (α- and γ-positions). See text for details.

under the assumption of identical ϕ_q's and $\lvert A_q \rvert$ contains the Fresnel factors that depend on the vibrational modes. Despite the fact that the Fresnel factors were not separable in our analysis, we believe that the relative magnitudes of $\lvert A_q \rvert$ between the vibrational modes still reflect the molecular orientations, mainly due to the IR surface selection rule. As shown in Figure 2 and Table 1, the relative magnitudes of $\lvert A_q \rvert$ between the vibrational modes vary (dramatically in some cases) with different molecules. This is due to different molecular orientations from corresponding surface species rather than different Fresnel factors that are similar for those C_6 hydrocarbons.

Hexane. There are three major bands at 2851, 2907, and 2931 cm^{-1} with a weak band at 2868 cm^{-1} (Table 1). The three major bands are assigned to unperturbed symmetric CH_2 ($CH_2(s)$), perturbed asymmetric CH_2 ($CH_2(a,p)$), and perturbed asymmetric CH_3 ($CH_3(a,p)$) stretching modes, respectively. The weak band at 2868 cm^{-1} is assigned to the unperturbed symmetric CH_3 ($CH_3(s)$) stretching mode. The strong $CH_3(a,p)$ peak indicates that the CH_3 groups align with their 3-fold rotational symmetry axis parallel to the surface, interacting with the metal surface. In addition, the strong $CH_2(a,p)$ peak indicates that the 2-fold rotational symmetry axis of the CH_2 groups is also parallel to the surface, interacting with the surface. These features are consistent with characteristics of the "flat-lying" *n*-hexane in the TTT conformation.[34-36]

The band at 2851 cm^{-1}, assigned to $CH_2(s)$, is not SFG active for the "flat-lying" *n*-hexane in the TTT conformation. The observation of this band in the SFG spectrum implies that there exist different conformers of *n*-hexane on the surface at 296 K. Temperature-dependent conformational changes of *n*-alkanes on metal surfaces have been studied by experiments[6,8,39] and computer calculations.[5,7,46,47] Molecular dynamics (MD) calculations[7] on the equilibrium and dynamics of *n*-alkanes on Pt(111) suggest that *n*-hexane exists in the TTT conformation for greater than 99% of the time at surface temperatures below 200 K. Molecular motions of the *n*-hexane adsorbates below 200 K

are described mainly by two-dimensional translation and rigid-body rotation parallel to the surface. Above 200 K, torsional motions around C−C bonds are thermally activated, giving rise to an increase in the fraction of conformational isomers in the gauche states. Spectroscopic and theoretical studies on *n*-hexane conformers in the liquid and gas phases reported that the enthalpy difference between the TTT and next stable conformers (TTG, TGT, TGG, and GTG) lies in the range of 0.4−2.0 kcal/mol,[48,49] which can be overcome at room temperature.

Near the *n*-hexane desorption temperature (240 K) from Pt-(111), there should be more segmental motions of CH_2 and CH_3 groups perpendicular to the surface, allowing various types of conformers. MD calculations[5] combined with TPD results[50] on desorption of *n*-alkanes from Au(111) proposed that the fraction of the TTT-type *n*-hexane (C_6H_{14}) at the desorption temperature (215 K) is 88%, but the fraction of the TTT-type *n*-decane ($C_{10}H_{22}$) at the desorption temperature (305 K) is 44%. Therefore, we predict that, upon *n*-hexane adsorption on Pt-(111) at 296 K, some fraction of conformers coexist with the TTT-type *n*-hexane adsorbates. This explains the observation of the $CH_2(s)$ band (2851 cm^{-1}) for *n*-hexane in Figure 2: This band originates from various conformers in the gauche states rather than from the TTT-type conformer.

3-Methylpentane. The SFG spectrum in the case of 3-methylpentane is similar to that in the case of *n*-hexane. The two major bands at 2850 and 2922 cm^{-1} are assigned to $CH_2(s)$ and $CH_3(a,p)$, respectively. The three weak bands at 2872, 2903, 2942 cm^{-1} are assigned to $CH_3(s)$, $CH_2(a,p)$, and $CH_3(a)$, respectively. The strong $CH_3(a,p)$ peak as compared with the $CH_3(s)$ peak indicates that CH_3 groups mainly align with their 3-fold rotational symmetry axis parallel to the surface, interacting with the metal surface. One difference from *n*-hexane is that the band at 2903 cm^{-1}, corresponding to $CH_2(a,p)$, is weaker

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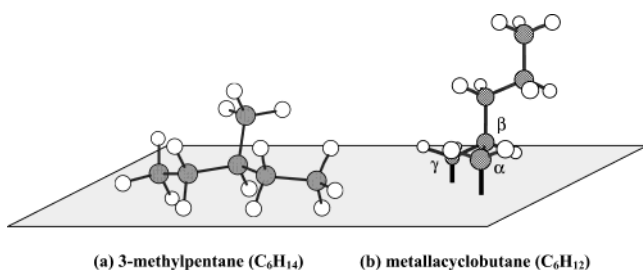(48) Mirkin, N. G.; Krimm, S. *J. Phys. Chem.* **1993**, *97*, 13887.
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Scheme 2

(a) 3-methylpentane (C₆H₁₄)   (b) metallacyclobutane (C₆H₁₂)

than that for *n*-hexane. Another difference is the appearance of a new band at 2942 cm^{-1}, which is assigned to CH$_3$(a).

To determine the adsorption geometry of 3-methylpentane on Pt(111) at 296 K, we apply the first criterion proposed in section 3.1: physisorbed C$_6$-alkanes align on Pt(111) such that the number of carbon chains bonding to the metal surface is maximized. The proposed adsorption geometry of 3-methylpentane at 296 K is illustrated in Scheme 2a, where two CH$_2$ groups and two terminal CH$_3$ groups are in contact with the metal surface while a central CH$_3$ group tilts away from the surface. This adsorption geometry can explain, qualitatively, our observations that |A_q[CH$_3$(a,p)]| for 3-methylpentane is similar to that for *n*-hexane while |A_q[CH$_2$(a,p)]| for 3-methylpentane is smaller than that for *n*-hexane. The reason is as follows. The vibrational mode strength, |A_q|, is proportional to the number density of adsorbates.[24,26,30] Assuming the same surface coverage on Pt(111) for *n*-hexane and 3-methylpentane, |A_q| should scale linearly with the number of the CH groups responsible for the *q*th mode in an adsorbate. Based on the proposed adsorption geometries, both *n*-hexane (Scheme 1a) and 3-methylpentane (Scheme 2a) have two terminal CH$_3$ groups interacting with Pt(111), resulting in similar magnitude in |A_q[CH$_3$(a,p)]| (0.44 and 0.51, respectively). In contrast, 3-methylpentane with two perturbed CH$_2$ groups on Pt(111) has a smaller |A_q[CH$_2$(a,p)]| (0.15) than *n*-hexane (0.54) with four perturbed CH$_2$ groups. The observed CH$_2$(s) band at 2851 cm^{-1} originates from various conformers in the gauche states, as in the case of *n*-hexane.

2-Methylpentane. The SFG spectrum in the case of 2-methylpentane is different from those in the cases of *n*-hexane and 3-methylpentane. The strong band at 2865 cm^{-1} is assigned to the unperturbed symmetric CH$_3$ stretch (CH$_3$(s)). The predominant CH$_3$(s) peak over the CH$_3$(a) and CH$_2$(a,p) peaks indicates that the 3-fold rotational symmetry axis for the CH$_3$ groups is nearly perpendicular to the metal surface. In addition, the very weak CH$_2$(a,p) peak indicates that the CH$_2$ groups are not in contact with the metal surface, as opposed to *n*-hexane and 3-methylpentane. These features represent the characteristics of "standing-up" geometry where the molecular plane is perpendicular to the metal surface. We propose that 2-methylpentane exists as a metallacyclobutane on Pt(111) at 296 K, in which two carbon atoms in α- and γ-positions bind with the surface through σ-bonding, as illustrated in Scheme 2b. The formation of metallacyclic species on Pt(111) through γ-hydride elimination has been reported from thermal decomposition of adsorbed neopentyl species [(CH$_3$)$_3$CH$_2$−] at 235 K.[51]

The peak centered at 2920 cm^{-1} has a much broader line width ($\Gamma_q = 23$ cm^{-1}) than other bands, implying that it is comprised of more than one CH stretching mode. One possible

contribution is the symmetric stretch of a CH$_2$ group on carbons bonded to the surface (α- and γ-positions). This stretching mode has been observed in the RAIRS and SFG spectra of σ-bonded hydrocarbons (C$_2$−C$_6$) on Pt(111) at 2900−2920 cm^{-1}.[18,40,52] Another possible contribution is the Fermi resonance (CH$_3$(FR)) of the CH$_3$ stretching mode by interaction with an overtone of a CH$_3$ bending mode.[31,53,54]

1-Hexene. Similar to the case of 2-methylpentane, the SFG spectrum in the case of 1-hexene is featured by a strong band at 2870 cm^{-1}, which is assigned to CH$_3$(s). We propose that the major surface species responsible for the SFG spectrum is a hexylidyne (C$_6$H$_{11}$) intermediate, as illustrated in Scheme 1b. The two weak bands at 2833 and 2917 cm^{-1} are most likely CH$_2$(s) and CH$_3$(FR), respectively. The values are about 10 cm^{-1} lower than those in the literature, for which a reason is not known at this point. As another possibility, the band at 2917 cm^{-1} may be CH$_2$(s) originating from GTT conformers. As described in the previous section, hexylidyne was previously observed upon 1-hexene adsorption on Pt(111) under UHV conditions.[40] Absence of the CH$_3$(a) band in our SFG spectrum indicates that the TTT conformer is dominant over the GTT conformer. The reason is likely that 1-hexene adsorption on Pt-(111) at high pressure (1.5 Torr) results in the formation of a self-assembled monolayer of densely packed hexylidyne on the surface in the TTT conformation, due to substantial intermolecular interactions.

3.3. Temperature-Dependent SFG Spectra of Surface Species in 1.5 Torr of the C$_6$ Hydrocarbons and 15 Torr of Hydrogen. The temperature-dependent SFG spectra of surface species on Pt(111) in 1.5 Torr of the C$_6$ hydrocarbons and 15 Torr of hydrogen are shown in Figures 3−6. The sample was initially kept at 296 K and then heated sequentially for each SFG measurement. After it was heated to 453 K, the sample was cooled to 310 K to examine the surface chemistry during a heating/cooling cycle.

The SFG spectrum for *n*-hexane at 296 K in Figure 3 is featured by the three major bands at 2851 (CH$_2$(s)), 2907 (CH$_2$-(a,p)), and 2931 cm^{-1} (CH$_3$(a,p)), as described in the previous section. The appearance of these bands along with negligible bands for CH$_3$(s) and CH$_3$(a) is indicative of the "flat-lying" adsorption geometry. Upon heating the surface, the bands broaden and their intensities decrease, becoming featureless at 453 K. A new band above 3000 cm^{-1} at 373 K arises probably from vinyl or aromatic CH stretch.[15,40] After the heating/cooling treatment, two new bands appear: a strong band at 2870 cm^{-1} (CH$_3$(s)) and a weak band at 2950 cm^{-1} (CH$_3$(a)).

The SFG band broadening with increasing temperature is a result of an increase in the disordering of *n*-hexane adsorbates on the surface. When the translational/rotational motions of the adsorbates are thermally activated, there exist multiple adsorption sites and intermolecular interactions, giving rise to inhomogeneous broadening of the SFG bands. A decrease in the peak intensity is due to a decrease in the surface coverage of the adsorbates by activated thermal desorption with increasing temperature. Another possible origin for the intensity decrease is the disordering of the adsorbates because SFG is a coherent process.[26]

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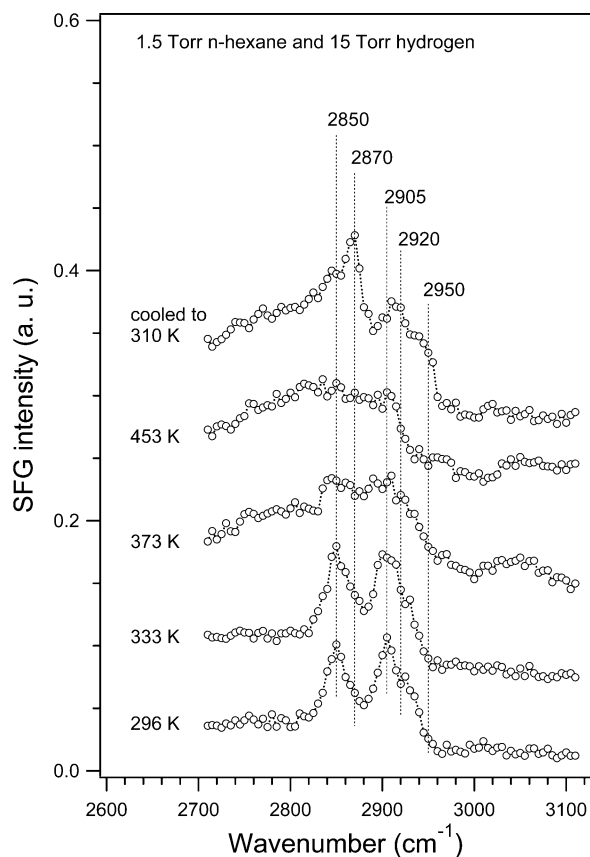
Figure 3. Temperature-dependent SFG spectrum of surface species on Pt-(111) in 1.5 Torr of *n*-hexane and 15 Torr of H₂ in the temperature range 296−453 K. The metal surface was initially kept at 296 K and then heated sequentially for each SFG measurement. The SFG spectrum on the top was obtained after the surface was cooled to 310 K. Dotted lines were drawn for visual aides.

Figure 4. Temperature-dependent SFG spectrum of surface species on Pt-(111) in 1.5 Torr of 3-methylpentane and 15 Torr of H₂ in the range 296−453 K. The SFG spectrum on the top was obtained after the surface was cooled to 310 K.

The appearance of the new bands, CH₃(s) and CH₃(a), after the heating/cooling treatment indicates that a new surface species was formed through an irreversible pathway, that is, a dehydrogenation process. Because the CH₃(s) peak is much stronger than the CH₃(a) peak, the new species is likely in a "standing-up" geometry. One possible species is hexylidyne (C_6H_{11}) in the TTT conformation (Scheme 1b). Its conformers such as GTT may coexist, making contribution to CH₃(a) (2950 cm⁻¹).[40] Alkylidyne on Pt(111) is formed by subsequent α-hydride elimination from adsorbed alkyl or alkene groups. Studies at low pressures reported that the alkylidyne formation on Pt(111) occurs at 200−300 K for C_2−C_6 alkyl and alkene molecules.[18,40,51,55] Another possible species in a "standing-up" geometry is metallacyclobutane or metallacyclohexane, as illustrated in Schemes 2b and 3a, respectively. These metallacyclic species are believed to be surface intermediates when *n*-hexane is isomerized to 2- or 3-methylpentane and vice versa.[56]

The SFG spectra in the case of 3-methylpentane show temperature dependences similar to those in the case of *n*-hexane, as seen in Figure 4. The absence of the CH₃(s) and CH₃(a) bands at 296 K is indicative of a "flat-lying" adsorption geometry. Upon heating the sample, the SFG bands broaden and their intensities decrease. After the heating/cooling treat-
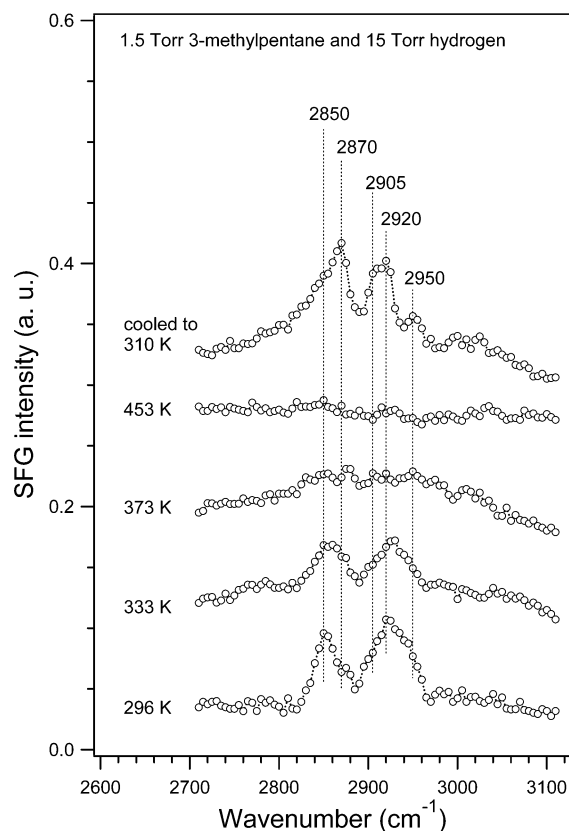
ment, a strong band appears at 2870 cm⁻¹, assigned to CH₃(s). A proposed surface intermediate responsible for the new band is a metallacyclohexane (Scheme 3a).

Contrary to the cases of *n*-hexane and 3-methylpentane, the heating/cooling treatment induces little change in the SFG spectra for 2-methylpentane and 1-hexene, as seen in Figures 5 and 6. These results indicate that metallacyclic species and hexylidyne are thermally stable species on Pt(111) in the temperature range 296−453 K. This is consistent with our findings that adsorbed *n*-hexane and 3-methylpentane partly converted into metallacyclic species or hexylidyne upon heating to 453 K. The proposed adsorption geometries and thermal chemistry of the C_6 hydrocarbons in the presence of excess hydrogen are summarized in Schemes 4−7. Note that the proposed molecular structures are the ones that best satisfy the criteria set in section 3.1.

3.4. SFG Spectra of Surface Species on Pt(111) at 296 K in 1.5 Torr of C_6 Hydrocarbons in the Absence of Excess Hydrogen. The SFG spectra of surface species on Pt(111) at 296 K in 1.5 Torr of C_6-alkane and C_6-alkene hydrocarbons in the absence of excess hydrogen are shown in Figure 7. The SFG spectrum for *n*-hexane features two bands at 2845 and 2920 cm⁻¹. The characteristics of the two SFG bands, in terms of peak positions, and relative broadness and intensities, match well those of a cyclohexenyl, π-allyl c-C_6H_9, intermediate. The π-allyl c-C_6H_9 intermediate (Scheme 3b) has been observed upon adsorption of cyclohexane or cyclohexene on Pt(111) at high pressure[23,57] and low pressure.[45,58,59] The two bands at 2845 and 2920 cm⁻¹ are assigned to CH₂ symmetric (CH₂(s)) and

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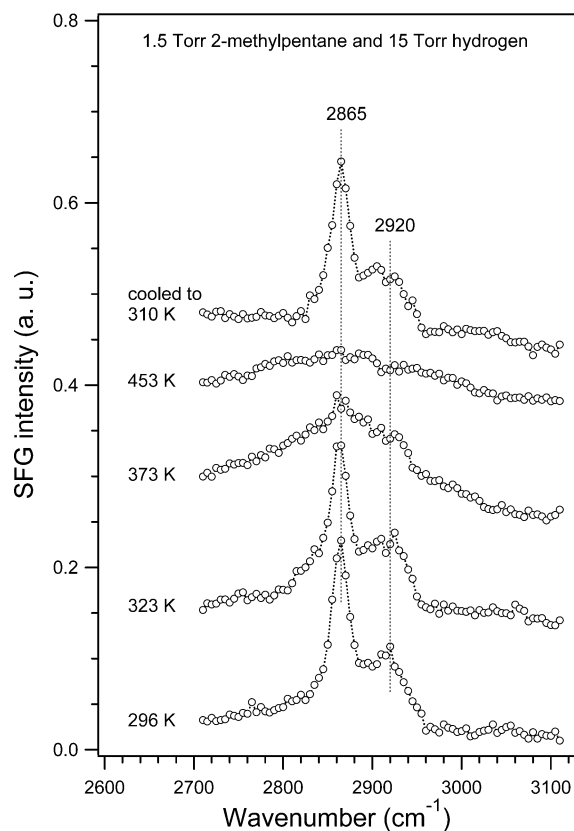(56) Davis, B. H. *Catal. Today* **1999**, *53*, 443.

Figure 5. Temperature-dependent SFG spectrum of surface species on Pt-(111) in 1.5 Torr of 2-methylpentane and 15 Torr of H_2 in the temperature range 296−453 K.

asymmetric $(CH_2(a))$ stretches, respectively. The proposed adsorption geometry[42,58,60,61] of π-allyl c-C_6H_9 is such that CH_2 groups at the C_4, C_5, and C_6 positions can contribute to the SFG signal. In particular, the CH_2 group at the C_4 position is responsible for the strong $CH_2(a)$ peak at 2920 cm^{-1} due to the IR surface selection rule. One may attempt to assign the band at 2920 cm^{-1} to the $CH_3(a,p)$ mode rather than the $CH_2(a)$ mode. It was impossible, however, to find any reasonable adsorption geometry that can be characterized by the $CH_2(s)$ and $CH_3(a,p)$ bands.

Special care was taken to determine the percentage of reactive impurities such as cyclohexane and cyclohexene that can form π-allyl c-C_6H_9 upon adsorption on Pt(111) at 296 K in the absence of hydrogen.[23,57] Cyclohexane and cyclohexene in the n-hexane reactant were found to be below the GC detection limit (10^{-5}%). A simple calculation can show that the surface coverages of these impurities are negligible even at the high limit. The underlying assumption in the calculation is that the relative surface coverages are proportional to $P \times \exp(-\Delta H_a/RT)$, where P is the partial pressure and ΔH_a is the adsorption enthalpy. Using the values of ΔH_a for cyclohexane (−14 kcal/mol),[62] cyclohexene (−17 kcal/mol),[62] and n-hexane (−14.8 kcal/mol)[39] in the literature, the relative surface coverages of

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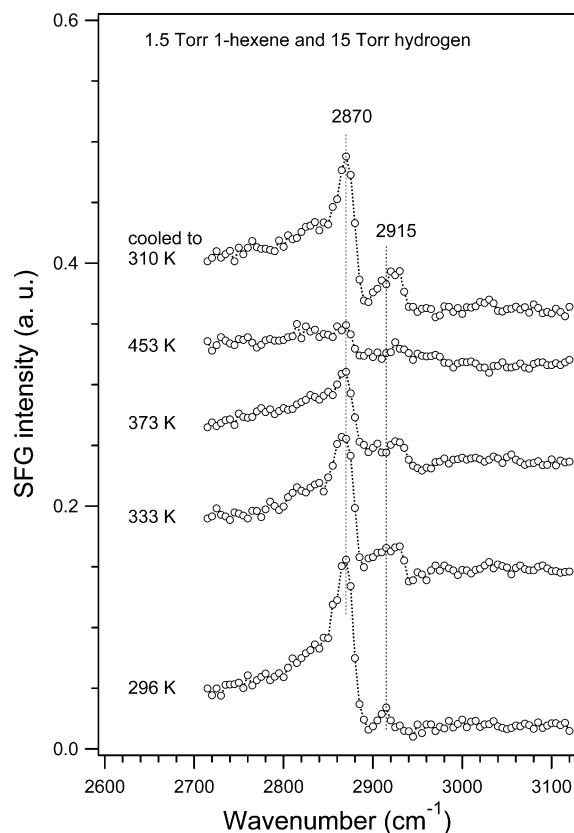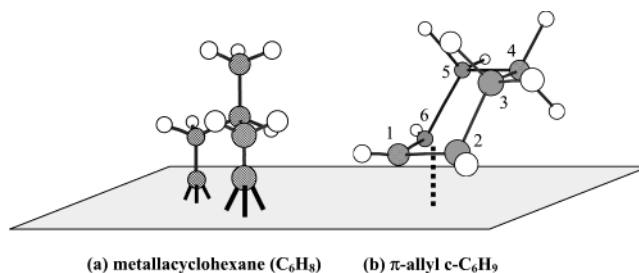(62) Koel, B. E.; Blank, D. A.; Carter, E. A. *J. Mol. Catal. A* **1998**, *131*, 39.

Figure 6. Temperature-dependent SFG spectrum of surface species on Pt-(111) in 1.5 Torr of 1-hexene and 15 Torr of H_2 in the temperature range 296−453 K.
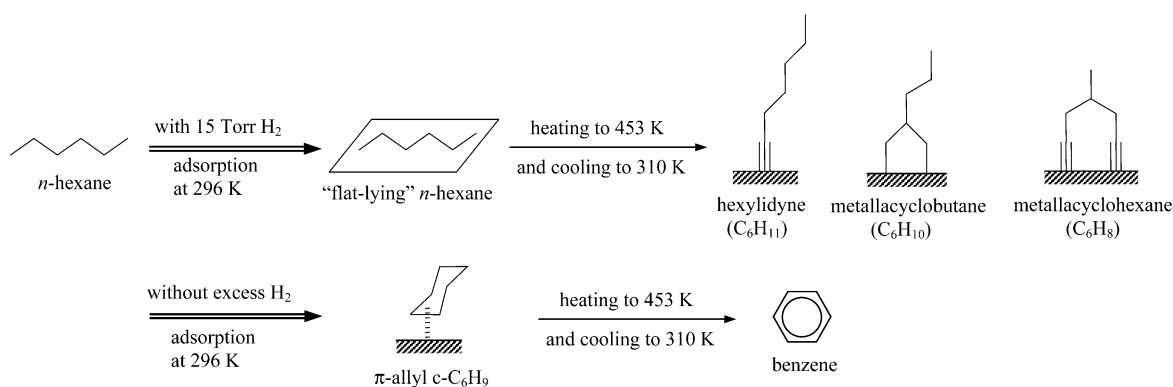
Scheme 3

(a) metallacyclohexane (C₆H₈)   (b) π-allyl c-C₆H₉

cyclohexane and cyclohexene to n-hexane at 296 K were calculated to be less than 10^{-6}.

The SFG spectrum for 3-methylpentane in Figure 7 is very similar to the SFG spectrum in Figure 4 that was obtained after the heating/cooling cycle in the presence of excess hydrogen. We propose that the strong band at 2870 cm^{-1} $(CH_3(s))$ originates from metallacyclohexane. In the cases of 2-methylpentane and 1-hexene, there is little difference between the SFG spectra in the presence and absence of excess hydrogen (Figures 2 and 7, respectively).
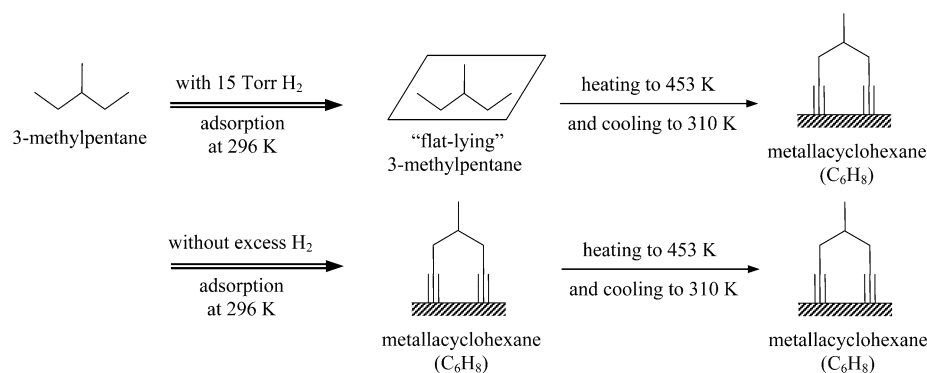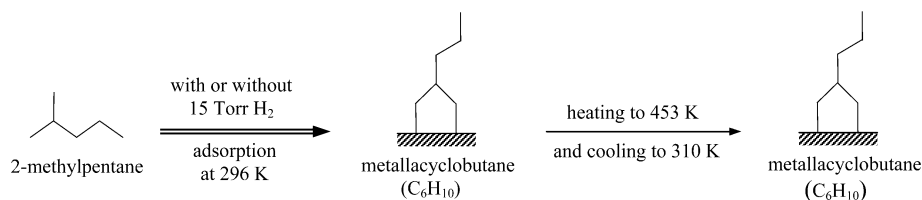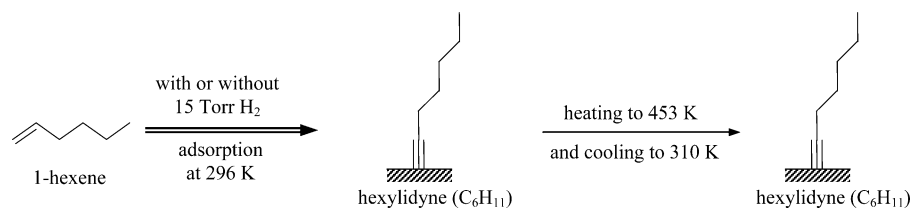
The temperature-dependent SFG measurements in 1.5 Torr of C_6 hydrocarbons in the absence of excess hydrogen were also performed using the same experimental scheme described in section 3.3. Similar to the case of the presence of excess hydrogen, the SFG bands decreased and became featureless with increasing temperature. The main difference is that for n-hexane the two SFG bands (2845 and 2920 cm^{-1}) at 296 K, assigned to π-allyl c-C_6H_9, disappeared after the heating/cooling treatment. This is due to irreversible dehydrogenation of the

Scheme 4

Scheme 5

Scheme 6

Scheme 7

intermediate to form benzene or phenyl groups.[23] For 2-methylpentane, 3-methylpentane, and 1-hexene, the major peaks at 296 K, representing "standing-up" geometries, reappeared after the heating/cooling treatment. The adsorption geometries and thermal chemistry of the C_6 hydrocarbons in the absence of excess hydrogen are summarized in Schemes 4−7. The temperature-dependent SFG spectra can be found in the Supporting Information.

4. Discussion

4.1. Adsorption Geometries and Surface Reactions of the C_6 Hydrocarbons on Pt(111). Our SFG measurements probed surface species and their reactions in 1.5 Torr of C_6 hydrocarbons on Pt(111) in the absence and presence of excess hydrogen. At 296 K and in the presence of excess hydrogen, *n*-hexane and 3-methylpentane absorb molecularly on Pt(111) in a mixture

of all-trans-state and gauche-state conformers. Upon heating to 453 K, some portion of *n*-hexane and 3-methylpentane in the "flat-lying" geometries were dehydrogenated to form surface species in the "standing-up" geometries: hexylidyne and metallacyclic species. However, at 296 K and in the presence of excess hydrogen, 2-methylpentane and 1-hexene formed metallacyclobutane (via α- and γ-carbon atoms) and hexylidyne, respectively. The dehydrogenated species remained unreacted during the heating/cooling treatment.

The absence of excess hydrogen enhanced dehydrogenation of *n*-hexane and 3-methylpentane. In the absence of excess hydrogen, *n*-hexane and 3-methylpentane were dehydrogenated to form π-allyl c-C_6H_9 and metallacyclohexane, respectively, even at 296 K. Dehydrogenation of 2-methylpentane and 1-hexene in the absence of excess hydrogen produced metal-
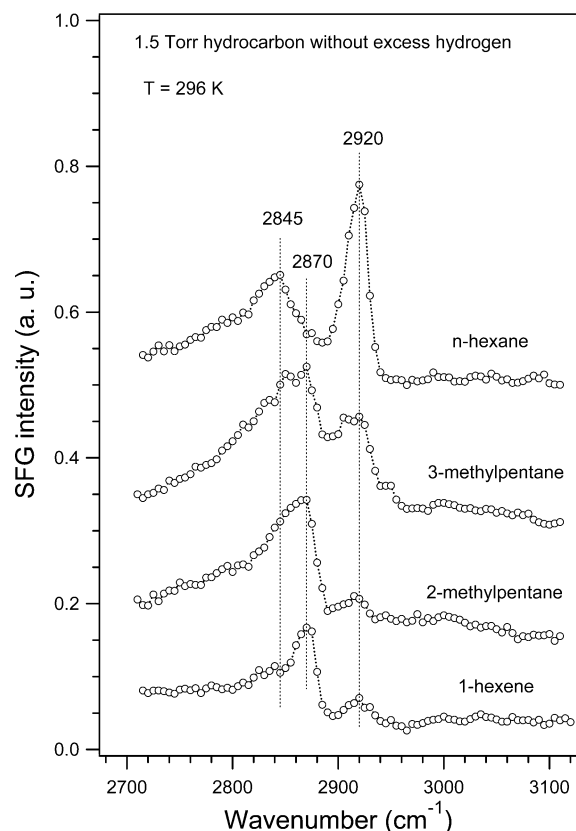
Figure 7. SFG spectra of surface species on Pt(111) at 296 K in 1.5 Torr of C₆ hydrocarbons in the absence of excess hydrogen. In order from the top are *n*-hexane, 3-methylpentane, 2-methylpentane, and 1-hexene, respectively.

lacyclobutane and hexylidyne, respectively, at 296 K. The dehydrogenated species remained unreacted during the heating/cooling treatment. However, π-allyl c-C₆H₉ disappeared after the heating/cooling treatment. This is due to irreversible dehydrogenation of the intermediate to form benzene or phenyl groups.[23]

Fragmentation of the C₆ hydrocarbons via C−C bond scission was not considered in our SFG analysis regarding the new surface species generated by the heating/cooling cycle in the presence of excess hydrogen. C−C bond scission is highly endothermic and usually occurs after the formation of highly dehydrogenated surface species, such as alkylidyne and met-allacyclic species, and at elevated temperatures.[17] Ilharco et al.[40] reported from RAIRS results for 1-hexene adsorption on Pt-(111) that there was no indication of the fragmentation via C−C bond scission below 500 K. Similar results have been reported for 1-pentene adsorption on Pt(111) by Avery et al.[63] Moreover, it is known that excess hydrogen suppresses the fragmentation of hydrocarbons on a Pt surface. The presence of atomic steps in large concentrations on higher Miller index platinum surfaces would unlock reaction channels involving C−C bond scission. The Pt(111) surface does not have these defect sites available in large concentrations.

4.2. Reaction Mechanisms of Isomerization and Dehydrocyclization of *n*-Hexane. Isomerization and dehydrocyclization of *n*-alkanes is one of the most important reactions in naphtha reforming processes because they produce the largest increase

in octane number. *n*-Hexane on Pt-based catalysts has been studied extensively as a model system to understand the reaction mechanisms.[12,13,28,56] Catalytic reactions of *n*-hexane on Pt-based catalysts in the presence of excess hydrogen include, in general, four classes of reactions: (a) dehydrocyclization to form benzene, (b) cyclization to form methylcyclopentane, (c) isomerization to form 2- and 3-methylpentane, and (d) hydrogenolysis to form smaller hydrocarbons.[28,56] Although enormous progress has been made in studies of the reaction kinetics, functionality of active sites, and structural sensitivity, a detailed understanding of elementary reaction steps and reactive surface intermediates in the reaction steps still remains to be explored.

Davis et al.[28] studied the catalytic reactions of *n*-hexane on Pt single-crystal surfaces at ambient pressure and above 570 K. They suggested from gas chromatography (GC) measurements that the dehydrocyclization occurs via direct 1,6-ring closure rather than ring enlargement of methylcyclopentane. Direct 1,6-ring closure can take place via two different pathways. One is the consecutive dehydrogenation of *n*-hexane to hexane−hexadiene−hexatriene followed by cyclization.[56,64] The other is the formation of cyclohexane followed by its consecutive dehydrogenation to cyclohexene−cyclohexadiene−benzene.[65] However, isomerization of *n*-hexane is believed to occur via formation of methylcyclopentane, followed by hydrogenolysis to form 2- and 3-methylpentane.[56]

One of the most interesting observations in this study is the formation of π-allyl c-C₆H₉ from *n*-hexane at 296 K in the absence of excess hydrogen. In the presence of excess hydrogen, *n*-hexane adsorbs molecularly on Pt(111) at 296 K. Upon heating, it converts into different surface species with "standing-up" geometry, most likely either hexylidyne via stepwise α-hydride elimination or metallacyclic species via hydrogenolysis of methylcyclopentane. Without excess hydrogen, dehydrocyclization of *n*-hexane to π-allyl c-C₆H₉ occurs predominantly even at 296 K. Neither metallacyclic species nor hexylidyne were detected during the heating/cooling cycle of π-allyl c-C₆H₉ in the range 290−450 K, and vice versa. This implies that dehydrocyclization of *n*-hexane to form π-allyl c-C₆H₉ proceeds via a different reaction pathway from dehydrogenation of *n*-hexane to form a hexylidyne or metallacyclic species. Our previous SFG studies[23] of high-pressure cyclohexene (C₆H₁₀) on Pt(111) showed that π-allyl c-C₆H₉ is a reactive intermediate in the cyclohexene conversion to benzene: π-allyl c-C₆H₉ converts into 1,3-cyclohexadiene (C₆H₈) followed by the benzene formation. All of these results lead us to conclude that π-allyl c-C₆H₉ is a reactive surface intermediate for dehydrocyclization of *n*-hexane to benzene. This conclusion supports the proposed mechanism of direct 1,6-ring closure[28] rather than ring enlargement of methylcyclopentane for dehydrocyclization of *n*-hexane. Furthermore, we propose that direct 1,6-ring closure takes place via formation of cyclohexane followed by the consecutive dehydrogenation rather than the consecutive dehydrogenation of *n*-hexane to hexane−hexadiene−hexatriene followed by cyclization.

Isomerization of *n*-hexane on Pt(111) to form 2- or 3-methylpentane at high pressures/temperatures is believed to occur via formation of a methylcyclopentane intermediate followed

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by its hydrogenolysis.[27,28,56] It has been speculated that this reaction pathway should include metallacyclic species as a reactive intermediate.[17,56] Our SFG results showed that metallacyclic species and hexylidyne from the C_6 hydrocarbons were formed either by heating to 450 K in the presence of excess hydrogen or at room temperature in the absence of excess hydrogen. This leads us to suggest that metallacyclic species and hexylidyne are reactive intermediates in the process of *n*-hexane isomerization through the methylcyclopentane formation. Note that this reaction pathway is distinctive from dehydrocyclization of *n*-hexane to benzene.

Finally, we discuss the hydrogen effect on the reaction pathways in the *n*-hexane reforming process. Davis et al.[28] reported from the GC measurements during the *n*-hexane reforming reactions on Pt(111) that the gas product ratio of benzene to methylcyclopentane increases with decreasing hydrogen pressure; that is, dehydrocyclization of *n*-hexane to benzene is favored over cyclization to methylcyclopentane in hydrogen-deficient environments. Our spectroscopic measurements of the surface species during the reactions show that dehydrocyclization of *n*-hexane is the dominant pathway in the absence of excess hydrogen over isomerization of *n*-hexane. This is consistent with the GC results by Davis et al.

5. Conclusions

This study demonstrated the capability of the SFG technique to probe reactive surface intermediates and elucidate reaction pathways in the hydrocarbon reforming processes. *n*-Hexane and 3-methylpentane were inactive on Pt(111) at 296 K in the presence of excess hydrogen. 2-Methylpentane and 1-hexene were readily dehydrogenated to form metallacyclobutane and hexylidyne even at 296 K, regardless of the presence of excess hydrogen. *n*-Hexane was dehydrogenated to form hexylidyne or metallacyclic species at high temperature in the presence of excess hydrogen. Hexylidyne and metallacyclic species were also main surface intermediates in the dehydrogenation of 2- and 3-methylpentane. These results suggest that hexylidyne and metallacyclic species are reactive surface intermediates in the isomerization process of *n*-hexane.

The absence of excess hydrogen opened a different reaction channel to *n*-hexane: dehydrocyclization to benzene. Our SFG results provided spectroscopic evidence that π-allyl c-C_6H_9 is a reactive surface intermediate in the dehydrocyclization of *n*-hexane. In addition, our SFG results supported that the benzene formation from *n*-hexane on Pt(111) does not proceed via a five-member cyclic intermediate as does isomerization, but rather proceeds through a direct 1−6 ring closure.

Supporting Information Available: Temperature-dependent SFG spectra of surface species on Pt(111) 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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