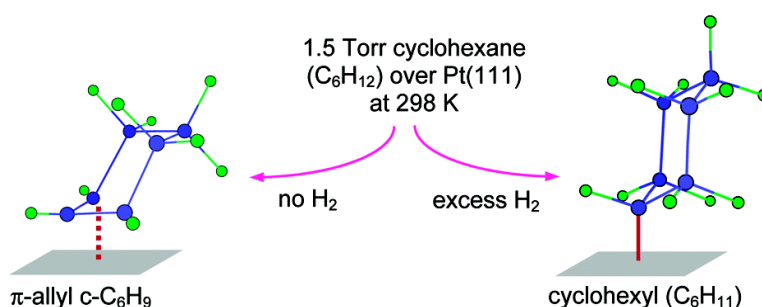Article

Evidence for Cyclohexyl as a Reactive Surface Intermediate during High-Pressure Cyclohexane Catalytic Reactions on Pt(111) by Sum Frequency Generation Vibrational Spectroscopy

Minchul Yang, and Gabor A. Somorjai

1.5 Torr cyclohexane (C$_6$H$_{12}$) over Pt(111) at 298 K

no H$_2$ excess H$_2$

π-allyl c-C$_6$H$_9$ cyclohexyl (C$_6$H$_{11}$)

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Evidence for Cyclohexyl as a Reactive Surface Intermediate during High-Pressure Cyclohexane Catalytic Reactions on Pt(111) by Sum Frequency Generation Vibrational Spectroscopy

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Abstract: Sum frequency generation (SFG) surface vibrational spectroscopy has been used to identify reactive surface intermediates in situ during catalytic dehydrogenation reactions of high-pressure cyclohexane (C_6H_{12}) on the Pt(111) crystal surface in the presence and absence of high-pressure hydrogen. These experiments provide the first spectroscopic evidence of cyclohexyl (C_6H_{11}) as a reactive surface intermediate during the cyclohexane catalytic conversion to benzene at high pressure in the presence of excess hydrogen. In addition, it was proposed from temperature-dependent SFG experiments that dehydrogenation of cyclohexyl is a rate-limiting step in the cyclohexane catalytic conversion to benzene.

1. Introduction

The adsorption and dehydrogenation of cyclohexane (C_6H_{12}) on the Pt(111) crystal surface has been studied extensively as a model system for cyclic hydrocarbon conversion, which is important in naphtha reforming processes.[1] Despite the large amount of research on the adsorption and reactions of cyclohexane on Pt(111), little is known regarding the identification of the surface intermediates and their surface chemistry in cyclohexane catalytic reactions, which are usually carried out at ambient pressures. This was mainly due to the lack of experimental techniques that can isolate and characterize surface intermediates during catalytic reactions at ambient pressures.

Various surface analytical techniques have been employed to identify thermally stable chemical species on the surface upon adsorption of cyclohexane on Pt(111) at low pressures ($<10^{-6}$ Torr) and at cryogenic temperatures. Among them are low-energy electron diffraction (LEED),[2,3] thermal desorption spectroscopy (TDS),[4−6] bismuth postdosing thermal desorption spectroscopy (BPTDS),[7] laser-induced thermal desorption (LITD),[4,8−10] high-resolution electron energy loss spectroscopy (HREELS),[7,11,12] and reflection−absorption infrared spectroscopy (RAIRS).[13] Briefly, cyclohexane adsorbs molecularly on Pt(111) at 100 K in a chair configuration (C_{3v}) with its molecular plane parallel to the metal surface.[14] At about 200 K, cyclohexane is dehydrogenated to form π-allyl c-C_6H_9. The C_6H_9 intermediate remains as a dominant surface species up to 280 K.[4,7] Above 280 K, π-allyl c-C_6H_9 converts to benzene.[4,7] Adsorbed benzene desorbs or decomposes at higher temperature.[7] The surface species that are present at low pressures/temperatures, however, may not represent all of those present at high pressures/temperatures and in the presence of excess hydrogen, which are the conditions in most chemical and petrochemical catalytic processes.

It has been speculated that the first C−H bond cleavage in a cyclohexane adsorbate on Pt(111), leading to the formation of a cyclohexyl intermediate (C_6H_{11}), is a key elementary step for the dehydrogenation process. Providing the evidence for the cyclohexyl on the surface has been a difficult task to perform under low pressure/temperature conditions.[4] The difficulty arises from the fact that cyclohexane, like other alkanes,[15] has low dissociative sticking probability on platinum surfaces, and once formed, the cyclohexyl readily converts to more stable species, such as π-allyl c-C_6H_9, on the surface.[4]

In this study, the sum frequency generation (SFG) technique has been utilized to obtain vibrational spectra of surface species in situ during the high-pressure cyclohexane catalytic reactions on Pt(111). SFG, a nonlinear optical surface vibrational spectroscopy, has recently been employed to monitor surface species during catalytic reactions under high-pressure con-

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ditions.[16-19] This technique, when applied to studies of flat surfaces, can be more sensitive than infrared and Raman spectroscopies, while electron spectroscopies cannot be employed at the high reactant pressures necessary to monitor catalytic reactions. The SFG process is only allowed in a medium without centrosymmetry under the electric dipole approximation.[20,21] Platinum bulk is centrosymmetric and its contribution to SFG is usually negligible. Isotropic gases in the reaction cell do not generate SFG. Only the metal surface and the adsorbates on the surface can generate SFG under the electric dipole approximation.

We report evidence for cyclohexyl (C_6H_{11}) as a reactive surface intermediate during cyclohexane catalytic reactions on Pt(111) at high pressure (1.5 Torr of cyclohexane and 15 Torr of H_2) and at high temperature (>300 K). In no case, to our knowledge, is there experimental evidence for a stable cyclohexyl intermediate under high-pressure (>10^{-6} Torr) and high-temperature (>300 K) conditions. At low pressures/temperatures, LITD studies of submonolayer cyclohexane on Pt(111) have observed cyclohexyl at 205 K as a product of the thermal dehydrogenation.[4-6] Xu and Koel[22] have reported that cyclohexyl can be generated by electron-induced dissociation of cyclohexane multilayers on Pt(111). Even at low pressures/temperatures, to our knowledge, no spectroscopic evidence for the cyclohexyl intermediate on Pt surfaces has been reported. In addition, we propose here that dehydrogenation of cyclohexyl is a rate-limiting step in the cyclohexane catalytic conversion to benzene in the presence of excess hydrogen.

2. Experimental Section

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 it at 1100 K in the presence of 5×10^{-7} Torr of O_2 for 2 min, and then annealing it at 1150 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 cleanness.

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}) 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 the surface normal. Both the infrared and 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 sum frequency output was then normalized by the intensity of the incident infrared beam on the surface. This is

necessary because gas molecules in the HP cell absorb some portion of the incident infrared beam, to which sum frequency output is linearly proportional. Detailed descriptions on the HP/UHV system and SFG measurement can be found elsewhere.[23]

Cyclohexane (C_6H_{12}, 99.5%, Aldrich) was purified by freeze–pump–thaw treatment before being introduced in the HP cell. The reactant pressure was 1.5 Torr of cyclohexane, or 1.5 Torr of cyclohexane and 15 Torr of hydrogen. In the latter case, hydrogen was always introduced first, followed by cyclohexane. Note that mixing the two gases before introduction produced the same results in our SFG experiments.

3. Results

For our SFG spectral analysis, it is important to review the studies of cyclohexane adsorbed on Pt(111) under low-pressure (<10^{-6} Torr) conditions.

Cyclohexane (C_6H_{12}) adsorbs molecularly on Pt(111) at 100 K in a chair configuration (C_{3v}) in which the molecular plane is parallel to the surface and three axial CH bonds are directly over three surface metal atoms.[14] Electronic interactions between the three axial hydrogen atoms and the three metal atoms cause a softening and broadening of the axial C–H bond stretching vibration frequency. As a result, the RAIR spectrum of cyclohexane on Pt(111) at a saturation coverage showed a very broad C–H stretching band in the range of 2400–2820 cm^{-1} along with two additional bands at 2903 and 2843 cm^{-1}.[13] At about 200 K, cyclohexane converts to a C_6H_9 intermediate. LITD studies[4,24] have suggested that C_6H_{11} and C_6H_{10} exist in sequence as metastable species at about 200 K before their conversion to a thermally stable C_6H_9 intermediate. The C_6H_9 intermediate exists as a dominant surface species on Pt(111) in the temperature range of 200–280 K.[4,7] It is believed that the C_6H_9 intermediate has an allylic structure on C_1, C_2, and C_3 positions with C_s symmetry (see Figure 1a), or π-allyl c-C_6H_9. The π-allyl c-C_6H_9 is characterized by two RAIRS bands at 2846 and 2930 cm^{-1}.[25] Above 280 K, π-allyl c-C_6H_9 converts to adsorbed benzene.[4,7] Benzene on the surface desorbs or decomposes at higher temperature.[7]

In this study, we first obtain SFG spectra during high-pressure cyclohexane catalytic reactions in the absence of high-pressure H_2 at 310 K. It will be shown that in this circumstance the major surface species is π-allyl c-C_6H_9. This can be predicted from the studies done at low pressures/temperatures, as described above. Then the SFG result in the absence of high-pressure H_2 will be used to analyze SFG spectra in the presence of high-pressure H_2.

3.1. SFG Spectrum Obtained upon Cyclohexane Adsorption at 1.5 Torr and at 310 K on Pt(111) in the Absence and Presence of 15 Torr of H_2. The SFG spectrum of surface species on Pt(111) at 310 K under 1.5 Torr of cyclohexane in the absence of high-pressure H_2 is shown in Figure 2a. The C–H stretching region features three bands at 2845, 2925, and 3000 cm^{-1}. The dominant bands at 2845 and 2925 cm^{-1} are typical of symmetric and antisymmetric C–H stretches of a methylene group, respectively. The weak band at 3000 cm^{-1} can be assigned to the aromatic C–H stretch from adsorbed

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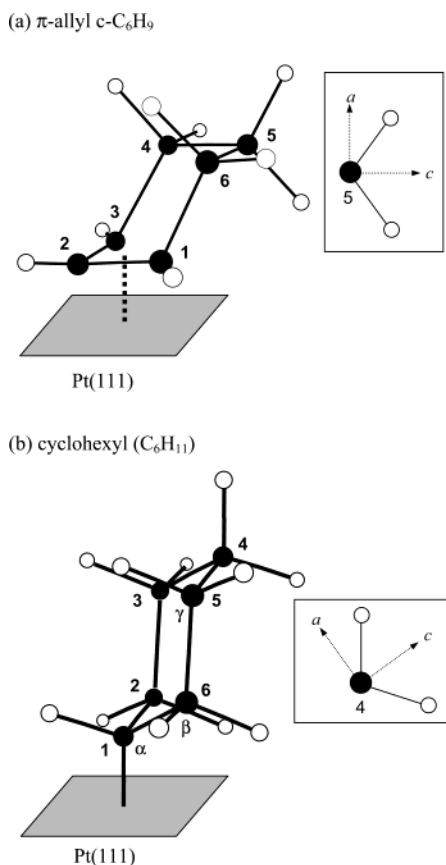(25) Manner, W. L.; Girolami, G. S.; Nuzzo, R. G. *J. Phys. Chem. B* **1998**, *102*, 10295.

(a) π-allyl c-C$_6$H$_9$

(b) cyclohexyl (C$_6$H$_{11}$)

Figure 1. Schematic diagram of (a) π-allyl c-C$_6$H$_9$ and (b) cyclohexyl (C$_6$H$_{11}$) intermediates: solid and open circles represent carbon and hydrogen atoms, respectively. Insets in panels a and b represent directions of transition dipole vectors of the CH$_2$ group at C$_5$ in π-allyl c-C$_6$H$_9$ and at C$_4$ in cyclohexyl, respectively. The transition dipole vectors of the antisymmetric and symmetric stretches are along the *a*-axis and *c*-axis, respectively.
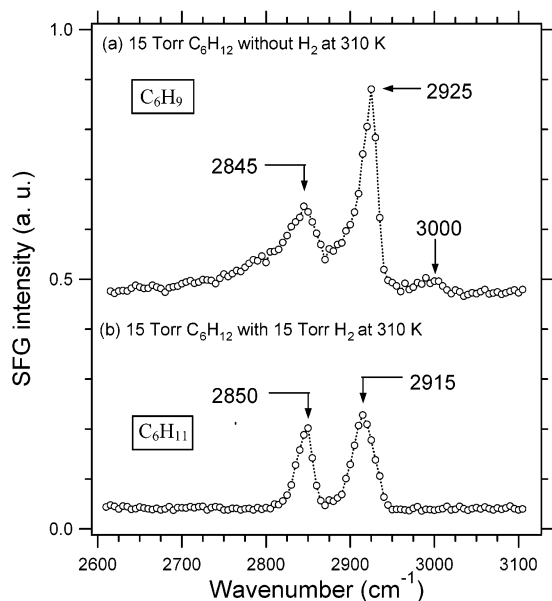

Figure 2. SFG spectra of surface species on Pt(111) at 310 K under 1.5 Torr cyclohexene (a) in the absence and (b) in the presence of 15 Torr of H$_2$. Dotted lines are drawn for visual aid.

benzene and/or phenyl.[26] The two bands at 2845 and 2925 cm^{-1}, in terms of their positions, broadness, and relative peak heights,

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are consistent with characteristics of π-allyl c-C$_6$H$_9$, according to the RAIRS and SFG results[25,27,28] for cyclohexene adsorption on Pt(111). It should be noted that the SFG spectrum at 310 K is different from RAIR and SFG spectra of molecularly adsorbed cyclohexadienes (C$_6$H$_8$), a dehydrogenated species from C$_6$H$_9$. RAIR[25] (SFG[27]) spectra of molecularly adsorbed 1,4-cyclohexadiene (C$_6$H$_8$) on Pt(111) show a single band at 2763 (2770) cm^{-1}. RAIR[25] (SFG[27]) spectra of molecularly adsorbed 1,3-cyclohexadiene (C$_6$H$_8$) show multiple bands at 2816, 2825 (2830), 2859 (2875), and 2881 (2900) cm^{-1}. The observation of π-allyl c-C$_6$H$_9$ as a major species at 310 K is also consistent with the results at low pressures, as described above, by considering that the conversion temperature of π-allyl c-C$_6$H$_9$ to benzene shifts to higher temperature at higher coverages due to a site-blocking effect.[27−29]

Figure 2b shows a SFG spectrum taken at 310 K under 1.5 Torr of cyclohexane and 15 Torr of H$_2$ on Pt(111). The symmetric and antisymmetric C−H stretching bands of a methylene group appear at 2850 and 2915 cm^{-1}, respectively. The features of the two bands in Figure 2b are noticeably different from those in Figure 2a. It is clear that the surface species accountable for the SFG spectra in Figure 2b is not π-allyl c-C$_6$H$_9$. It is also clear that the surface species in Figure 2b is neither cyclohexadiene (C$_6$H$_8$) nor benzene (C$_6$H$_6$).

To identify the chemical species responsible for the SFG spectrum in Figure 2b, it is necessary to examine vibrational spectra of all possible surface species: cyclohexane (C$_6$H$_{12}$), cyclohexyl (C$_6$H$_{11}$), and cyclohexene (C$_6$H$_{10}$). The vibrational spectrum of cyclohexane adsorbed on Pt(111) is characterized by a very broad C−H stretching band in the range of 2400−2820 cm^{-1}, resulting from electronic interactions of three axial CH bonds with three surface metal atoms.[14] We found that when a SFG spectrum was taken in the range of 2400−2800 cm^{-1}, it showed no peak at all. Therefore we exclude the possibility of the existence of molecularly adsorbed cyclohexane on Pt(111) at 310 K under 1.5 Torr of cyclohexane and 15 Torr of H$_2$. Syomin and Koel[30] have reported that cyclohexyl can be generated by electron-induced dissociation of cyclohexane on Au(111) at 90 K and its infrared spectrum features two dominant bands at 2852 and 2923 cm^{-1} as well as the lack of the soft C−H stretch mode.

The absence of molecularly adsorbed cyclohexane is also expected by thermodynamic consideration to estimate the relative surface coverage of cyclohexane and cyclohexyl on Pt-(111). According to semiempirical thermodynamic calculations by Koel et al.,[31] cyclohexyl on Pt(111) is more stable than cyclohexane on Pt(111) by 7 kcal/mol. Assuming these two surface species are at equilibrium at 298 K, surface coverage of cyclohexane is estimated to be an order of 5 smaller than that of cyclohexyl.

Cyclohexene adsorption on Pt(111) below 200 K leads to the formation of a di-σ-type cyclohexene (C$_6$H$_{10}$).[25,32,33] The

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RAIR[25] (SFG[27]) spectra of a di-σ-type cyclohexene on Pt(111) are characterized by three bands at 2938 (2958), 2902 (2918), and 2864 (2875) cm^{-1}. The relative intensities of the three bands are comparable. The RAIR bands at 2938 and 2864 cm^{-1} are assigned to asymmetric and symmetric stretches of unperturbed methylene group, respectively, and the band at 2902 cm^{-1} to C−H stretch interacting with the metal surface. Thus the characteristics of the bands for a di-σ-type cyclohexene cannot account for the SFG spectrum in Figure 2b.

In conclusion, the surface species responsible for the SFG spectra in Figure 2b is neither cyclohexane (C_6H_{12}), cyclohexene (C_6H_{10}), cyclohexenyl (C_6H_9), cyclohexadiene (C_6H_8), nor benzene (C_6H_6). Consequently, cyclohexyl (C_6H_{11}) is the only possible species responsible for the SFG spectra in Figure 2b.

The difference in the relative band intensities and broadness of the symmetric and asymmetric stretches between π-allyl c-C_6H_9 and cyclohexyl (C_6H_{11}) can be understood by considering the difference in their adsorption geometry on Pt(111). The relative SFG intensity of the symmetric and antisymmetric C−H stretch is sensitive to the geometrical orientations of CH_2 groups.[34−37] The surface selection rule of SFG and RAIRS for adsorbates on a metal surface allows one to observe only C−H stretches with nonzero transition dipole vectors along the normal direction to the surface. Proposed adsorption geometries of π-allyl c-C_6H_9 and cyclohexyl on Pt(111) are illustrated in Figure 1. For the π-allyl c-C_6H_9 intermediate in Figure 1a, CH_2 groups at C_4, C_5, and C_6 positions can contribute to the SFG bands shown in Figure 2a. Particularly, the transition dipole vector (along the *a*-axis in the inset of Figure 1a) of the antisymmetric stretch of the CH_2 group at C_5 is nearly perpendicular to the metal surface, resulting in the strong SFG signal of the antisymmetric CH_2 stretch at 2925 cm^{-1}. By contrast, the transition dipole vector (along the *c*-axis) of the symmetric stretch is nearly parallel to the metal surface, resulting in no SFG signal for the stretching mode. Consequently, the SFG band at 2845 cm^{-1} is attributed to the symmetric C−H stretches at C_4 and C_6. The low-frequency tail in the band at 2845 cm^{-1} is probably due to inhomogeneous interactions between the symmetric C−H stretches and the metal surface.

For the cyclohexyl intermediate, the CH_2 group at C_4 makes a major contribution to the asymmetric SFG band at 2915 cm^{-1}, as shown in Figure 2b. The transition dipole vectors of the antisymmetric stretch at C_2, C_3, C_5, and C_6 are nearly parallel to the surface, and thus only the CH_2 group at C_4 can be SFG-active for the antisymmetric stretching mode. For the CH_2 group at C_4, since the transition dipole vectors of the asymmetric (along the *a*-axis in the inset in Figure 1b) and symmetric (along the *c*-axis) C−H stretches tilt approximately 36° and 54° from normal to the surface, both stretches may produce comparably strong SFG signals. The *c*-axis at C_2, C_3, C_5, and C_6 tilts from the surface only by ∼18°, giving rise to a weak symmetric SFG band. Moreover, if negligible interactions with the metal surface are assumed, these four CH_2 groups constitute an inversion symmetry, which allows no SFG signal. In conclusion, the comparable SFG intensities of the two bands for cyclohexyl,
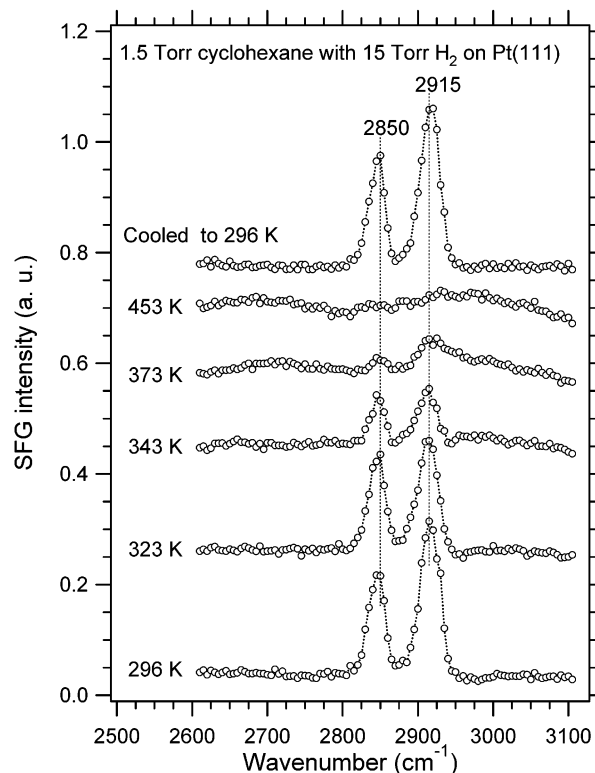
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Figure 3. Temperature-dependent SFG spectra of cyclohexyl surface species on Pt(111) under 1.5 Torr of cyclohexene and 15 Torr of H_2 in the range 296−453 K. The metal surface was initially kept at 296 K and then heated sequentially for each SFG measurement. The SFG spectrum at the top was taken after the metal surface was cooled to 296 K. Dotted lines are drawn for visual aid.

which are different from the case of π-allyl c-C_6H_9, can be understood mainly by considering the orientation of the CH_2 group at C_4 in Figure 1b. It is interesting to find that the symmetric C−H stretching band for cyclohexyl does not show the low-frequency tail, differing from the case for C_6H_9. This implies that the CH_2 group associated with the symmetric band for cyclohexyl is distant from the metal surface, which is consistent with the proposed adsorption geometry in Figure 1b, and thus is not affected by the adsorption environments.

3.2. Temperature-Dependent SFG Spectra Obtained upon Cyclohexane Adsorption at 1.5 Torr on Pt(111) in the Presence of H_2 at 15 Torr. The temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr of cyclohexane and 15 Torr of H_2 are shown in Figure 3. The metal surface was initially kept at 296 K and then heated sequentially for each SFG measurement. Two bands are shown at 2850 and 2915 cm^{-1}, which are assigned to symmetric and asymmetric C−H stretches of a methylene group from cyclohexyl (C_6H_{11}) intermediate. Since the band positions remain exactly the same in the temperature range of 296−453 K, we believe that the two bands come from the same chemical species, cyclohexyl (C_6H_{11}). The relative intensities of the two bands at 2850 and 2915 cm^{-1} are slightly changed with the temperature, probably due to the orientational changes of the cyclohexyl intermediate with temperature.

As the surface temperature increases, the SFG bands decay in intensity, becoming featureless at 453 K. We also observed that the SFG spectrum changes reversibly in the temperature range of 296−453 K. The SFG spectrum at the top in Figure 3

$C_6H_{12}(g)$ $C_6H_{10}(g) + 2H(a)$

$14 \updownarrow \sim 0$ $17 \updownarrow \sim 0$

$C_6H_{12}(a) \underset{17}{\overset{10}{\rightleftharpoons}} C_6H_{11}(a) + H(a) \underset{\sim 0}{\overset{12}{\rightleftharpoons}} C_6H_{10}(a) + 2H(a) \underset{41}{\overset{9}{\rightleftharpoons}} C_6H_9(a) + 3H(a)$
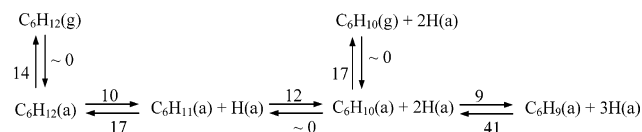
Figure 4. Activation energies (kilocalories per mole) for elementary reaction steps for dehydrogenation of cyclohexane to benzene on Pt(111), from ref 31: (g) and (a) represent gas phase and adsorbed species, respectively.

was obtained after the metal surface was cooled from 453 to 296 K. This spectrum is very similar to that at 296 K, obtained before the surface temperature was increased. It should be noted that there is no indication of existing dehydrogenated species from cyclohexyl (C_6H_{11}), such as C_6H_{10}, C_6H_9, C_6H_8, and benzene during a heating−cooling cycle. The decrease in the SFG intensity with increasing temperature is the result of the decrease in the surface coverage of cyclohexyl. At higher temperature, cyclohexyl (C_6H_{11}) can be more readily hydrogenated to form cyclohexane (C_6H_{12}), which eventually desorbs. In other words, increasing temperature increases the desorption rate of the cyclohexyl intermediate, via hydrogenation, resulting in the decrease of the SFG intensity. As an alternative possibility, the increase in the disordering of the cyclohexyl intermediate can cause the decrease in the SFG intensity because SFG is a coherent process.[20]

4. Discussion: Dehydrogenation of Cyclohexyl as a Rate-Limiting Step

Our SFG results showed in situ observation of surface species during the adsorption and reaction of 1.5 Torr of cyclohexane on Pt(111) with and without 15 Torr of H_2. In the absence of high-pressure H_2, a dominant surface species at 310 K is π-allyl c-C_6H_9 (Figure 1a). By contrast, in the presence of 15 Torr of H_2, a dominant surface species at 310 K is cyclohexyl (C_6H_{11}) (Figure 1b). In no case, to our knowledge, is there experimental evidence for a stable cyclohexyl intermediate at high pressures ($>10^{-6}$ Torr). Moreover, cyclohexyl (C_6H_{11}) is the only surface species observed in the temperature range of 296−453 K in the presence of 15 Torr of H_2 (Figure 3).

It is important to consider the elementary steps in the dehydrogenation processes of high-pressure cyclohexane to form benzene on Pt(111) in the presence of high-pressure hydrogen. Most of the cyclohexane conversion processes in industries are carried out in the presence of high-pressure hydrogen.[1] Figure 4 illustrates a stepwise reaction mechanism and activation energies for the dehydrogenation of cyclohexane to benzene on Pt(111), which was proposed by Koel et al.[31] from calculations based on experimental results. Our SFG results have demonstrated that the conversion of cyclohexane to benzene is initiated by the dissociative adsorption of cyclohexane (C_6H_{12}), leading to the formation of the cyclohexyl (C_6H_{11}) intermediate. Studies[15,38,39] on alkyl halide adsorption and reactions on metal surfaces have suggested that the thermal chemistry of cyclohexyl, like other alkyls on transition metal surfaces, is dominated by β-hydride elimination, the elimination of a hydrogen atom from the carbon adjacent to that bonded to the surface. We speculate that a cyclohexene (C_6H_{10}) intermediate, formed by β-hydride elimination from a cyclohexyl intermediate, subsequently loses one hydrogen atom at the γ-position to form a

π-allyl c-C_6H_9 intermediate. As shown in Figure 2a, the formation of the π-allyl c-C_6H_9 intermediate is facile at 310 K in the absence of excess hydrogen.

Now we discuss a rate-limiting step in the dehydrogenation processes of high-pressure cyclohexane to benzene on Pt(111) in the presence of high-pressure hydrogen. We first consider the adsorption and reactions of cyclohexene (C_6H_{10}) on Pt(111). Cyclohexene on Pt(111) is not only one of the possible intermediates in cyclohexane (C_6H_{12}) conversion to benzene but also a reactant molecule to be hydrogenated to cyclohexane. Our previous SFG studies[28] showed that, upon adsorption of 1.5 Torr of cyclohexene (C_6H_{10}) on Pt(111), π-allyl c-C_6H_9 exists as a major surface species in the temperature range of 310−400 K. At above 400 K, π-allyl c-C_6H_9 coexists with 1,3-cyclohexadiene (C_6H_8).[28] The dehydrogenation of π-allyl c-C_6H_9 was found to be irreversible with temperature. By contrast, this study showed that upon adsorption of 1.5 Torr of cyclohexane (C_6H_{12}) with 15 Torr of H_2, a major surface intermediate is cyclohexyl (C_6H_{11}) in the temperature range of 296−453 K. Previously observed surface intermediates such as π-allyl c-C_6H_9, 1,3-cyclohexadiene (C_6H_8), and cyclohexene (C_6H_{10}) were not observed in this temperature range. Moreover, the SFG band intensities of the cyclohexyl intermediate change reversibly with the temperature (Figure 3), implying that the dehydrogenation of cyclohexane to cyclohexyl and its backward reaction−hydrogenation of cyclohexyl−is reversible in that temperature range.

These observations strongly suggest that dehydrogenation of cyclohexyl to form cyclohexene is a rate-limiting step in the cyclohexane catalytic conversion to benzene on Pt(111) in the presence of excess hydrogen. The dehydrogenation of cyclohexyl to cyclohexene competes with the backward reaction: hydrogenation of cyclohexyl, followed by desorption in the form of cyclohexane. According to the calculations by Koel et al.,[31] an activation energy (12 kcal/mol) for the cyclohexyl conversion to adsorbed cyclohexene is lower than an activation energy (17 kcal/mol) of the dehydrogenation to adsorbed cyclohexane. The presence of excess hydrogen, however, may inhibit the dehydrogenation and enhance the hydrogenation process.

5. Concluding Remarks

In this work, SFG surface vibrational spectroscopy allows us to monitor a reactive surface intermediate during high-pressure cyclohexane catalytic reactions on Pt(111). We have shown that cyclohexyl (C_6H_{11}) exists as a reactive surface intermediate during the reactions in the presence of excess hydrogen. The dehydrogenation of cyclohexane to cyclohexyl and its backward reaction, hydrogenation of cyclohexyl, were found to be reversible in the temperature range of 296−453 K. It was also observed that the dehydrogenation of cyclohexyl is prohibited by excess hydrogen. This work demonstrates the capability of SFG vibrational technique to examine key elementary steps during high-pressure catalytic reactions in the presence of excess hydrogen.

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