Unusual Hydrogen Effect in Olefin Dehydrogenation: 1-Methylcyclohexene Dehydrogenation Initiated by Excess Hydrogen over Pt(111) Surfaces, a Combined Sum Frequency Generation Spectroscopy and Kinetic Study

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Dehydrogenation and hydrogenation of 1-methylcyclohexene (C_7H_{12}) at 1.5 Torr on Pt(111) in the presence and absence of excess hydrogen were studied using gas chromatography and sum frequency generation vibrational spectroscopy. Kinetic studies showed that the turnover rate (TOR), in molecules per Pt atom per second, for the dehydrogenation to toluene (C_7H_8) in the presence of 15 Torr of H_2 increased continuously, starting at about 350 K. This onset temperature matches the onset temperature of the formation of the methylcyclohexenyl (C_7H_{10} or C_7H_{11}) intermediates observed by SFG experiments, indicating that methylcyclohexenyl is a reactive surface intermediate in the dehydrogenation to toluene. In the absence of hydrogen, the TORs of the hydrogenation/dehydrogenation reactions were negligible at 403 K. When 15 Torr of H_2 was added, the dehydrogenation as well as the hydrogenation reactions began with constant rates (TOR = 0.042 and 0.016, respectively). This observation is consistent with an SFG measurement in which the methylcyclohexenyl intermediate was not detected until 5 Torr of H_2 was added to 1.5 Torr of 1-methylcyclohexene. In light of these results, we discuss the rate-limiting step and the role of excess hydrogen in the 1-methylcyclohexene dehydrogenation reaction.

1. Introduction

Metal-catalyzed hydrocarbon conversion reactions are always carried out in the presence of excess hydrogen. Extensive studies have shown that hydrogen pressure is an important parameter controlling the reaction activity and selectivity in catalytic hydrocarbon conversion processes.[1–8] Hydrogen adsorbed on a catalyst surface slows down the rate of dehydrogenation and fragmentation of hydrocarbon molecules. In recent years, with the application of combined sum frequency generation (SFG) vibrational spectroscopy and reaction kinetics studies, we could explore the molecular details of the effects of hydrogen during catalytic hydrocarbon conversion reactions.[9–12]

In this paper, we describe a surprising effect of excess hydrogen on the dehydrogenation of 1-methylcyclohexene (C_7H_{12}). This reaction was studied on a Pt(111) single-crystal model catalyst surface with use of sum frequency generation (SFG) vibrational spectroscopy along with gas chromatography (GC). Dehydrogenation of methylcyclohexene is one of the major steps in the process of dehydrocyclization of *n*-heptane (C_7H_{16}) to toluene (C_7H_8), which is an important reaction that occurs in the catalytic reforming process for the production of high octane number products, such as toluene, from low octane number hydrocarbons, such as *n*-heptane. Hydrogenation of methylcyclohexene to methylcyclohexane (C_7H_{14}) also occurs during this conversion process; the production of methylcyclohexane is beneficial to diesel or jet fuels.[13] Despite its importance, studies of the adsorption and surface chemistry of methylcyclohexene on metal surfaces are rare, in contrast with the extensive studies for cyclohexene (C_6H_{10}).[14–18]

We report that excess hydrogen initiates both dehydrogenation and hydrogenation of 1-methylcyclohexene on Pt(111). The initiation of dehydrogenation by excess hydrogen is somewhat counterintuitive. To explain this unusual hydrogen effect, we propose a reaction model that excess hydrogen assists the chemisorption of 1-methylcyclohexene, which is a rate-limiting step, by forming methylcyclohexyl (C_7H_{13}). A methylcyclohexyl molecule on the surface undergoes a disproportionation reaction with a weakly adsorbed 1-methylcyclohexene to produce methylcyclohexane and methylcyclohexenyl. The methylcyclohexenyl intermediate converts into toluene via further dehydrogenation.

2. Experimental Section

The experimental apparatus for GC and SFG measurements has been previously described.[10,19] All experiments were carried out on a Pt(111) single-crystal surface in a high-pressure/ultra-high-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, where high-pressure catalysis studies were carried out. The HP cell was equipped with a reaction loop that contained a recirculation pump and septum for gas abstraction and GC analysis. For GC measurements, the reactant and product gases in the HP cell were constantly mixed by a recirculation pump. Periodic sampling allowed kinetic measurements of the gas-phase composition.

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°

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and 60°, respectively, with respect to 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 theory of SFG for surface studies has been described in detail previously.[20-22] 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

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

Near resonance with vibrational modes of the adsorbates, 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 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, depends on the Fresnel factor, the surface density of the adsorbates, and the infrared and Raman transition cross sections of the qth vibrational mode. To analyze our SFG spectrum, the SFG signal, I_{SF}, was first normalized to the intensity (I_{IR}) of the incident infrared beam on the surface. This was necessary because gas molecules in the HP cell absorb some portion of the incident infrared beam.

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 or GC measurements. The Pt(111) surface was routinely checked by Auger electron spectroscopy (AES) for cleanliness.

3. Results

3.1. Kinetic Studies of 1-Methylcyclohexene Catalytic Reactions on Pt(111) at Various Temperatures in the Absence and Presence of H$_2$. Kinetic measurements with GC were performed under 1.5 Torr of 1-methylcyclohexene and 750 Torr of Ar with preintroduced H$_2$ at 15 Torr. Observed gas products were methylcyclohexane and toluene. Turnover rates (TORs), in molecules per Pt atom per second, for the hydrogenation to methylcyclohexane and the dehydrogenation to toluene were calculated and plotted as a function of temperature in the temperature range 290−480 K in Figure 1a. The hydrogenation rate rises below 300 K until reaching a maximum at about 370 K. The rate then decreases gradually, while the dehydrogenation rate increases continuously, starting at about
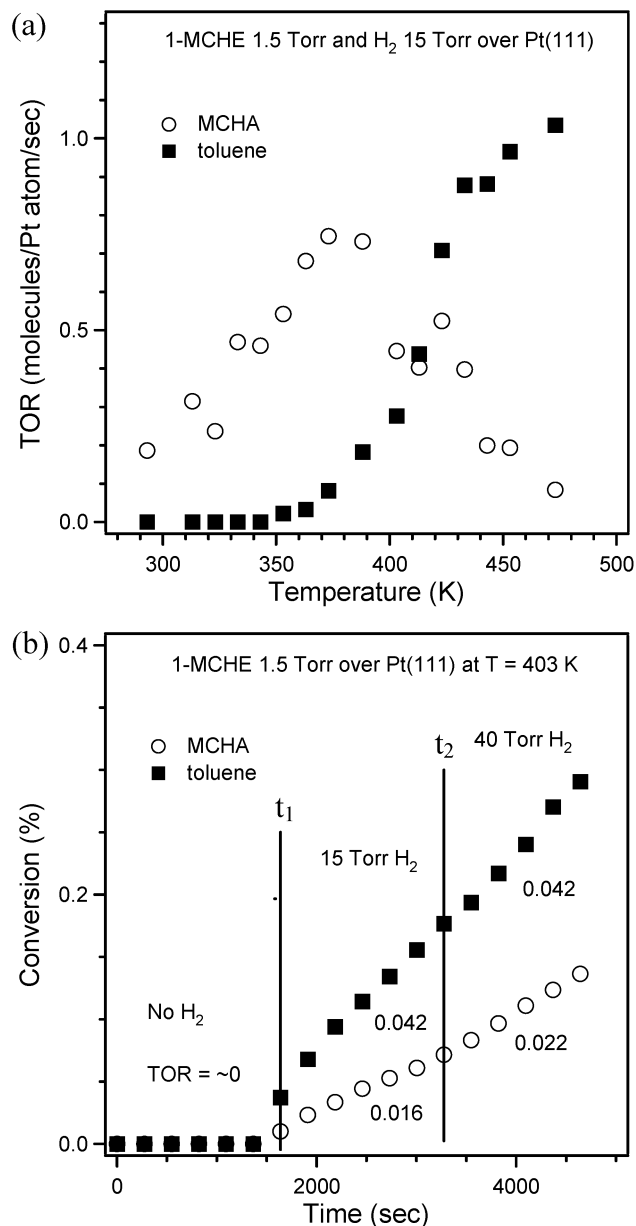

Figure 1. (a) Turnover rates (TORs) of the hydrogenation to methylcyclohexane (MCHA) and the dehydrogenation to toluene of 1-methylcyclohexene (1-MCHE) at 1.5 Torr in the presence of 15 Torr of H$_2$ as a function of temperature and (b) the fractional change of methylcyclohexane and toluene in the gas composition as a function of time. In panel b, the H$_2$ pressure was kept at zero at $0 < t < t_1$, 15 Torr at $t_1 < t < t_2$, and 40 Torr at $t > t_2$.

350 K. A similar temperature dependence of TORs has been reported for the hydrogenation of cyclohexene to cyclohexane and the dehydrogenation to benzene on Pt(111).[23]

The effect of excess hydrogen on the conversion rates was studied by a different type of GC experiment. The time evolution of the gas composition was recorded initially in 1.5 Torr of 1-methylcyclohexene at 403 K in the absence of excess hydrogen and, subsequently, H$_2$ was added. Figure 1b shows the change in the gas composition of methylcyclohexane and toluene as a function of time. The catalytic conversions were negligible in a period of $0 < t < t_1$, in which there is no excess hydrogen. When 15 Torr of H$_2$ was added at $t = t_1$, surprisingly, the dehydrogenation as well as the hydrogenation reaction began with constant rates (TOR = 0.042 and 0.016, respectively). The TORs remained the same after a total of 40 Torr of H$_2$ was added at $t = t_2$.
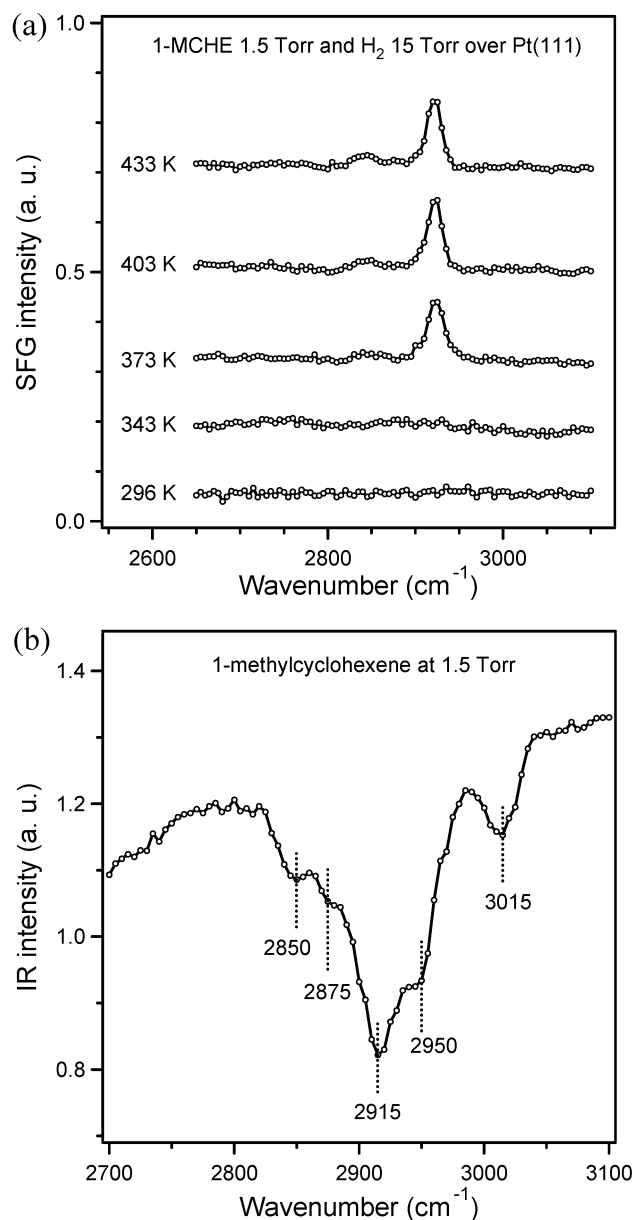
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Figure 2. (a) The temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr of 1-methylcyclohexene and 15 Torr of H_2 and (b) the IR adsorption spectrum of 1-methycyclohexene at 1.5 Torr.

3.2. SFG Vibrational Spectra of Surface Species upon Adsorption of 1-Methylcyclohexene on Pt(111) at Various Temperatures in the Absence and Presence of H_2. SFG experiments were performed to identify surface intermediates during the 1-methylcyclohexene catalytic reactions. Figure 2a shows the temperature-dependent SFG spectra of the surface species on Pt(111) in 1.5 Torr of 1-methylcyclohexene and 15 Torr of H_2. The sample temperature was initially kept at 296 K, and then increased in a stepwise manner for each SFG measurement. In the C−H stretching region of 2600−3200 cm^{-1}, no SFG peak appeared until 373 K at which point two major bands were shown at 2845 and 2925 cm^{-1}. The intensity of the two bands remained the same upon heating to 433 K. The bands at 2845 and 2925 cm^{-1} are typical symmetric and asymmetric C−H stretches of a CH_2 group, respectively.[24−29] We emphasize that the onset (about 360 K) of the appearance of the peaks in the SFG spectrum (Figure 2a) matches the onset of the production of toluene in the GC results (Figure 1a). This

indicates that the surface species responsible for the SFG spectrum is a reactive surface intermediate in the process of 1-methylcyclohexene dehydrogenation to toluene.

For comparison with the SFG spectrum, an IR absorption spectrum of 1-methylcyclohexene in the gas phase is shown in Figure 2b. The IR absorption spectrum was obtained simultaneously during an SFG measurement. A key difference from the SFG spectrum is that the IR spectrum shows discernible bands for a vinylic C−H stretch (C=C−H, 3015 cm^{-1}) and CH_3 stretches (symmetric at 2875 cm^{-1} and asymmetric at 2950 cm^{-1}).[24,25,30] These bands are all absent in the SFG spectrum in Figure 2a.

The absence of the vinylic C−H stretch indicates that 1-methylcyclohexene was either π-bonded with its vinylic C−H stretch parallel to the metal surface or σ-bonded by breaking the π-bond in the molecule. The latter was proven to be true for the following reasons. In general, with increasing temperature π-bonded alkenes readily desorb due to their weak bonding to the surface, or they will convert into strongly di-σ-bonded species.[24] For instance, π-bonded ethylene (C_2H_4) on Pt(111) converts into di-σ-bonded ethylene below 52 K,[31] and π-bonded cyclohexene (C_6H_{10}) desorbs or converts into di-σ-bonded cyclohexene between 100 and 200 K.[32] We examined the adsorption strength of the surface species by comparing SFG spectra at low and high pressures. A SFG spectrum was initially taken at 403 K in 1.5 Torr of 1-methylcyclohexene and 15 Torr of H_2, after which the sample was cooled to 300 K and the HP reaction cell was evacuated. Afterward another SFG spectrum was taken at 300 K and below 5×10^{-9} Torr. We found that there was no change in the SFG spectrum (two bands at 2845 and 2925 cm^{-1}) before and after the evacuation. This indicates that the surface species responsible for the SFG spectrum was σ-bonded to the surface rather than weakly π-bonded.

The absence of the CH_3 stretching bands may arise from one of the following reasons. One possibility is that the CH_3 group was dehydrogenated to the CH_2 group, which was σ-bonded to the metal surface. The symmetric band of the CH_2 group may blue shift by interaction with the surface to coincidentally overlap the band at 2925 cm^{-1}. The blue shift of the CH_2 symmetric stretch was reported in the cases of ethylene and 1-hexene on Pt(111) where the symmetric stretch of the CH_2 group σ-bonded to Pt(111) was shown at 2900−2920 cm^{-1} in the RAIRS and SFG spectra.[9,33,34] Another possibility is that the CH_3 group was physisorbed with its 3-fold rotational symmetry axis parallel to the surface. As a result, the asymmetric stretch of the CH_3 group may red shift to coincidentally overlap the band at 2925 cm^{-1}. The red shift of the CH_3 asymmetric stretch was reported in the case of n-hexane on Pt(111) where the asymmetric stretch of the CH_3 group contacting the surface was shown at about 2930 cm^{-1} in the RAIRS spectra.[35,36]

In Figure 3, we examined the influence of excess hydrogen on the SFG vibrational spectra at 403 K. In this experiment, SFG spectra were taken while the pressure of H_2 in the reaction cell was increased in a stepwise manner from 0 to 40 Torr in 1.5 Torr of 1-methylcyclohexene. No SFG bands were observed until 5 Torr of H_2 was added. The SFG bands increased slightly at 15 Torr of H_2 and their intensity remained the same at 40 Torr of H_2. This result indicates that excess hydrogen on the surface plays a critical role to initiate the formation of the surface intermediate on Pt(111). Another experiment found that in the absence of excess hydrogen, no SFG band was detected in the temperature range 293−453 K and under 1.5 Torr of 1-methylcyclohexene.
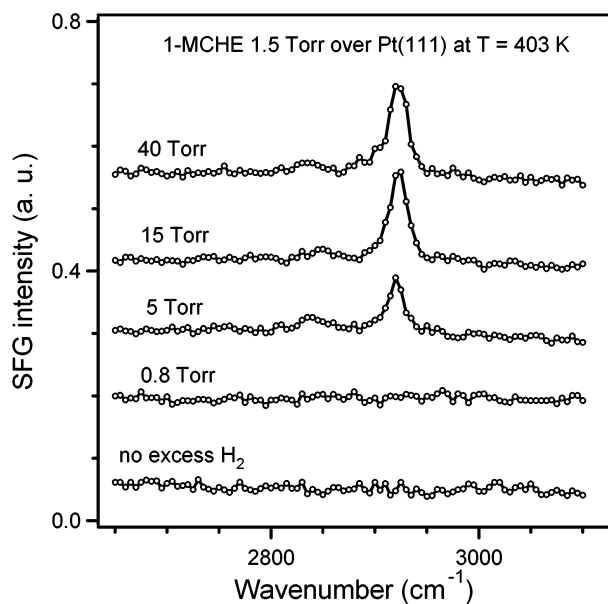
Figure 3. SFG spectra of surface species on Pt(111) at 403 K under 1.5 Torr of 1-methylcyclohexene with varying H_2 pressure.

4. Discussion

4.1. Molecular Identification of the Surface Species Responsible for the SFG Spectra. As described above, SFG experiments were performed to identify surface intermediates during the catalytic reactions of 1-methylcyclohexene at 1.5 Torr on Pt(111). In the presence of excess hydrogen, no SFG bands appeared until the surface temperature was increased to ~373 K, at which temperature two major bands were shown at 2845 and 2925 cm^{-1}. The intensity of the two bands remained the same upon heating to 433 K. Interestingly, the onset temperature of the appearance of the SFG spectrum matches the onset temperature of the toluene production in the gas phase, indicating that the surface species responsible for the SFG spectrum is a reactive surface intermediate in the process of 1-methylcyclohexene dehydrogenation to toluene. Here we attempt to identify the molecular structure of the surface species.

To that end, it is useful to review the prior work on the adsorption and reactions on Pt(111) for C_6 cyclic hydrocabons with chemical and structural similarities to 1-methylcyclohexene, such as cyclohexene and 1-methylcyclohexane. Cyclohexene adsorption on Pt(111) at low pressures (<10^{-6} Torr) has been studied with various surface analytical techniques, such as thermal desorption spectroscopy (TDS),[15] bismuth postdosing TDS (BPTDS),[15,16] laser-induced thermal desorption (LITD),[17] high-resolution electron energy loss spectroscopy (HREELS),[17,37] and reflection-absorption infrared spectroscopy (RAIRS).[14] Briefly, cyclohexene exists in a di-σ form on Pt(111) at 100 K. It converts to π-allyl c-C_6H_9 below 200 K.[14,16] At about 300 K, π-allyl c-C_6H_9 converts to benzene. Further heating induces desorption and decomposition of benzene.[14,16,17] Cyclohexene surface reactions on Pt(111) at high pressure (1.5 Torr) were also studied by sum frequency generation (SFG) vibrational spectroscopy in our laboratory.[10] Various surface species were observed during the reactions in the temperature range 303–483 K. Upon adsorption at 303 K, cyclohexene is dehydrogenated to form 1,4-cyclohexadiene (C_6H_8). At 323 K, this species converts to the π-allyl c-C_6H_9 intermediate. At temperatures higher than 423 K, benzene coexists with π-allyl c-C_6H_9 on the surface. It should be noted that the π-allyl c-C_6H_9 species is an important reactive intermediate in both low- and high-pressure conditions.

CHART 1

1-methylcyclohexene
(C_7H_{12})

methylcyclohexenyl
(C_7H_{10})
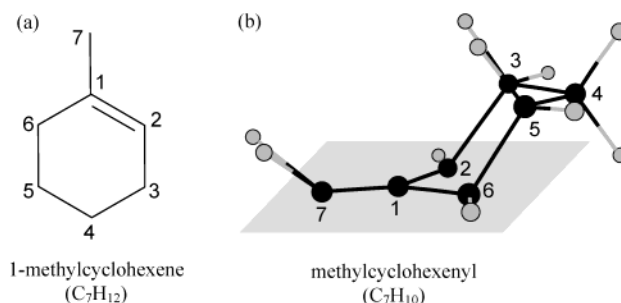
The existence of a π-allyl species as a major reactive intermediate was also reported in the dehydrogenation of methylcyclohexane on Pt(111) in UHV environments.[38,39] According to the studies by Xu et al.[38,39] using TDS, BPTDS, and HREELS, methylcyclohexane is molecularly adsorbed on Pt(111) at 100 K. Adsorbed methylcyclohexane is dehydrogenated at 230 K to form the π-allyl c-C_6H_8-$CH_{3,a}$ species where the CH_3 group contacts the surface. The π-allyl species is further dehydrogenated at ~335 K to the adsorbed benzyl species (c-C_6H_5-$CH_{2,a}$).

On the basis of these prior studies, it is reasonable to consider π-allyl-type species as the species responsible for the SFG spectrum in Figure 2a. Indeed, the SFG spectrum in Figure 2a is almost the same as that of π-allyl c-C_6H_9 in terms of the positions and relative intensities of the two bands. We suggest methylcyclohexenyl as the surface species responsible for the SFG spectra. Chart 1 illustrates one possible molecular structure of methylcyclohexenyl species, π-allyl c-C_6H_8-$CH_{2,a}$, along with the molecular formula of 1-methylcyclohexene. Each carbon atom in Chart 1 was labeled from C_1 to C_7 as an aid in the following discussion. The methylcyclohexenyl intermediate lacks a CH_3 group by forming a σ-bond to the surface at the C_7 position, and a vinylic C–H group by forming two σ-bonds to the surface at the C_1 and C_2 positions. An additional σ-bond to the surface via dehydrogenation is expected at the C_6 position. Another possible molecular structure of methylcyclohexenyl is that with the CH_3 group remaining intact on the surface (π-allyl c-C_6H_8-$CH_{3,a}$). As addressed in the previous section, our SFG spectra cannot distinguish the blue shift of the $CH_{2,a}$ group in π-allyl c-C_6H_8-$CH_{2,a}$ from the red shift of the $CH_{3,a}$ group in π-allyl c-C_6H_8-$CH_{3,a}$.

It is worth examining the possibility that the SFG spectrum in Figure 2a originates from the products 1-methylcyclohexane and toluene. When SFG experiments were conducted on 1-methylcyclohexane or toluene under various conditions, at low and high pressures and in the temperature range 300–450 K, no noticeable SFG bands were detected in the C–H stretching region 2650–3100 cm^{-1}.

It should be stressed that the methylcyclohexenyl structure in Chart 1 is analogous to the adsorption structure of π-allyl c-C_6H_9 on Pt(111).[10,11,35] With use of the same analysis as was made in the case of the SFG spectrum of π-allyl c-C_6H_9, CH_2 groups at the C_3, C_4, and C_5 positions in Chart 1 can contribute to the SFG bands. Particularly, the transition dipole vector of the asymmetric stretch of the CH_2 group at the C_4 position is nearly perpendicular to the metal surface, giving rise to the strong SFG signal at 2925 cm^{-1}. In contrast, the transition dipole vector of the symmetric stretch is nearly parallel to the metal surface, giving rise to no SFG signal for the symmetric stretch due to the IR surface selection rule. Consequently, the SFG band at 2845 cm^{-1} is attributed to the symmetric C–H stretches at the C_3 and C_5 positions.

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4.2. Elucidating the Mechanism of the Hydrogen-Assisted Dehydrogenation. Our combined GC and SFG results have shown that the methylcyclohexenyl is a reactive surface intermediate in the production of toluene from 1-methylcyclohexene. Surprisingly, it was found that excess hydrogen on the surface is necessary to initiate the formation of the methylcyclohexenyl intermediate and to produce toluene via further dehydrogenation. Now we discuss a rate-limiting step in the formation of toluene and the unusual hydrogen effect on the rate-limiting step.
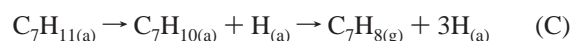
We first compare 1-methylcyclohexene with cyclohexene for their surface intermediates and surface reactions on Pt(111) in the presence of excess hydrogen. Under cyclohexene at 1.5 Torr with H_2 at 15 Torr, the SFG spectrum of π-allyl c-C_6H_9 was observed at 300 K, which is 50 K lower than the onset of the benzene production in the gas phase.[10] In contrast, under 1-methylcyclohexene at 1.5 Torr with H_2 at 15 Torr, the SFG spectrum of 1-methylcyclohexenyl was not observed until about 360 K, which is the onset of the toluene production in the gas phase. This comparison leads us to conclude that the formation of methylcyclohexenyl on the surface is a slow step in the dehydrogenation of 1-methylcyclohexene to toluene.

Next, we consider the elementary steps preceding the dehydrogenation reaction: π-bonded and σ-bonded adsorptions of 1-methylcyclohexene on Pt(111). Referring to the cases of cyclohexene[16,32] and ethylene,[31,40] it is expected that 1-methylcyclohexene is initially π-bonded to the surface. The weakly π-bonded molecule may desorb reversibly or convert into the di-σ-bonded one at elevated temperature. Although no SFG band was observed below about 360 K in the presence of excess hydrogen, we believe that there exist weakly π-bonded molecules on the surface. It appears, nevertheless, that the surface coverage of the weakly adsorbed molecules was low, below the SFG detection limit. In the case of weakly π-bonded ethylene on Pt(111), its surface coverage was estimated to be only 4% at 295 K under 35 Torr of ethylene with 100 Torr of hydrogen.[9]

The conversion from the π-bonding to the di-σ-bonding, followed by dehydrogenation, is facile for cyclohexene adsorbed on Pt(111). In the absence of excess hydrogen, cyclohexene on Pt(111) readily forms a di-σ-bonded species even at 95 K and converts into π-allyl c-C_6H_9 as low as 200 K.[16] In contrast, our SFG measurements for 1-methylcyclohexene in the absence of excess hydrogen showed no evidence that either the di-σ-bonded form or methylcyclohexenyl exist in the temperature range 293–453 K. This indicates that the conversion from π-bonding to di-σ-bonding is a rate-limiting step for 1-methylcylochexene. It is likely that steric hindrance by the methyl group prohibits 1-methylcyclohexene from forming a di-σ-bonded adsorbate on Pt(111).

Finally, we suggest that excess hydrogen on the surface can activate a different reaction pathway to the formation of methylcyclohexenyl. Chemisorption of 1-methylcyclohexene can be achieved by its hydrogenation to form methylcyclohexyl, $C_7H_{13(a)}$, in the presence of excess hydrogen (reaction A). Öfner et al. have reported that ethyl (C_2H_5) formation from weakly π-bonded ethylene (C_2H_4) on a hydrogen-precovered Pt(111) is facile, and the complete hydrogenation of ethylene to ethane requires an activation energy of only 6 kcal/mol.[40] A methylcyclohexyl intermediate then undergoes a disproportionation reaction with weakly π-bonded 1-methylcyclohexene to form a methylcyclohexane, $C_7H_{14(g)}$, and a dehydrogenated species, $C_7H_{11(a)}$ (reaction B). The C_7H_{11} intermediate is dehydrogenated to $C_7H_{10(a)}$, followed by further dehydrogenation to form

adsorbed toluene that eventually desorbs into the gas phase ($C_7H_{8(g)}$, reaction C):

$$C_7H_{12(\pi)} + H_{(a)} \rightarrow C_7H_{13(\sigma)} \qquad (A)$$

$$C_7H_{13(\sigma)} + C_7H_{12(\pi)} \rightarrow C_7H_{14(g)} + C_7H_{11(a)} \qquad (B)$$

$$C_7H_{11(a)} \rightarrow C_7H_{10(a)} + H_{(a)} \rightarrow C_7H_{8(g)} + 3H_{(a)} \qquad (C)$$

where the subscripts (π), (σ), and (a) represent weakly π-bonded, σ-bonded, and strongly chemisorbed molecules, respectively, and (g) represents product molecule in the gas phase. This reaction mechanism predicts the production of both methylcyclohexane and toluene by excess hydrogen, which is consistent with the GC result shown in Figure 1b, where post-introduction of hydrogen initiated the production of both methylcyclohexane and toluene.

It is worth considering a different possibility for the hydrogen-assisted chemisorption of 1-methylcyclohexene. Excess hydrogen might aid in removing adsorbed hydrocarbon fragments, which inhibit the chemisorption of the reactant, from the surface by hydrogenation. The kinetic studies of benzene hydrogenation by Chou et al.[41,42] reported that benzene hydrogenation over Pd-based catalysts was greatly increased by increasing hydrogen pressure. In this case excess hydrogen helped in removing the adsorbed phenyl groups formed by C–H bond scission of benzene that inhibit the adsorption of benzene. Regarding this mechanism, some questions remain. For instance, it is not clear why no SFG spectrum was observed for adsorbed hydrocarbon fragments, if there were hydrocarbon fragments on the surface. It is also not clear why the inhibition of adsorption by hydrocarbon fragments was not observed in the cyclohexene dehydrogenation. For cyclohexene dehydrogenation on Pt(111), the SFG spectra of surface species were observed regardless of the presence of excess hydrogen.[10]

5. Concluding Remarks

We have shown an unusual hydrogen effect on the dehydrogenation of an olefin that excess hydrogen commences the dehydrogenation of 1-methylcyclohexene to form toluene. This hydrogen-induced dehydrogenation may play an important role in reforming reactions of olefinic compounds on platinum-based catalysts, especially when their adsorption is a rate-limiting step due to steric hindrance that can be caused by bulky functional groups.

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