

1,3- and 1,4-cyclohexadiene reaction intermediates in cyclohexene hydrogenation and dehydrogenation on Pt(111) crystal surface: a combined reaction kinetics and surface vibrational spectroscopy study using sum frequency generation

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Abstract

The hydrogenation and dehydrogenation reactions of cyclohexene on Pt(111) surface were investigated by surface vibrational spectroscopy via sum frequency generation (SFG) both under ultrahigh vacuum (UHV) and high pressure conditions with 10 Torr cyclohexene and various hydrogen pressures up to 590 Torr. Under UHV, cyclohexene on Pt(111) undergoes a change from π/σ -bonded, σ -bonded, and $c\text{-C}_6\text{H}_9$ surface species to adsorbed benzene when the surface was heated. A site-blocking effect was observed at saturation coverage of cyclohexene and caused the dehydrogenation to shift to higher surface temperature. At high pressures, however, none of the species observed in UHV condition were seen. 1,4-cyclohexadiene (CHD) was found to be the major species on the surface at 295 K even in the presence of nearly 600 Torr of hydrogen. Hydrogenation was the only detectable reaction at the temperature range between 300–400 K with 1,3-CHD on the surface as revealed by SFG. Further increasing surface temperature results in a decrease in hydrogenation reaction rate and an increase in dehydrogenation reaction rate with both 1,3-CHD and 1,4-CHD detectable on the surface simultaneously. Monitoring the reaction kinetics and the chemical nature of surface species together allows us to postulate a reaction mechanism: cyclohexene hydrogenates to cyclohexane via a 1,3-CHD intermediate, and dehydrogenates to benzene through both 1,4-CHD and 1,3-CHD intermediates. Both 1,3- and 1,4-CHD dehydrogenate to benzene at sufficiently high temperature on Pt(111). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Dehydrogenation; Sum frequency generation

1. Introduction

Professor Kenzi Tamaru was one of the great builders and leaders of surface chemistry and heterogeneous catalysis in Japan. Through the

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education of his students and through his research he left an indelible mark on science in Japan in general and on Japanese chemistry in particular. It is my privilege to contribute to this issue to honor his contributions.

The dehydrogenation of cyclic alkanes and alkenes to aromatic molecules is one of the key reactions during naphtha reforming [1]. The hydrogenation of olefins is also an important reaction in the chemical technology. The dehydrogenation and hydrogenation of cyclohexene provide us with information on both processes [2,3]. By changing the hydrogen pressure or the temperature the equilibrium shifts towards hydrogenation or dehydrogenation when the reaction is performed over a transition metal catalyst. We explored the mechanisms of these reactions over a platinum single crystal surface of (111) orientation in the 300–570 K temperature and 30–600 Torr pressure range using sum frequency generation (SFG) surface vibrational spectroscopy. Using SFG we have also explored the molecular species that form upon the chemisorption of a monolayer of cyclohexene as a function of temperature and coverage.

Previous surface science studies of cyclohexene chemisorption on Pt(111) in ultra high vacuum (UHV) found that the molecule dehydrogenates to benzene readily above 300 K [4–13]. Evidence for a $c\text{-C}_6\text{H}_9$ intermediate was found from both high resolution electron energy loss spectroscopy (HREELS) and laser induced transient desorption-Fourier transform mass spectrometer (LITD-FTMS) studies during the dehydrogenation of cyclohexene (C_6H_{10}) as well as during cyclohexane (C_6H_{12}) dehydrogenation by abstraction of three hydrogen atoms at 220 K [14,15]. Our studies confirm the findings of others in UHV. We have also explored the dehydrogenation and hydrogenation of 1,3- and 1,4-cyclohexadienes on Pt(111) in UHV. Both 1,3- and 1,4-cyclohexadienes (C_6H_8) species dehydrogenate to benzene readily around room temperature [16].

Our high pressure SFG studies of cyclohexene dehydrogenation and hydrogenation, the first

of its kind, shows that 1,4-cyclohexadiene (CHD) is an important reaction intermediate. Its dehydrogenation produces benzene. 1,3-Cyclohexadiene, which is also present on the surface, is the reaction intermediate mainly responsible for the hydrogenation reaction to produce cyclohexane.

2. Experimental

The experiments were done over a Pt(111) single crystal surface in a UHV-batch reactor dual system, which has been described previously [17]. The UHV chamber was pumped by a turbomolecular pump and an ion pump and had a base pressure lower than 1×10^{-10} Torr. The platinum (111) single crystal was cut, oriented and polished by the normal procedures. An ion gun that can be used to sputter-clean the crystal, a mass spectrometer, and a retarding field analyzer (RFA) for Auger and LEED were installed in the chamber.

A passive–active mode locked Nd:YAG laser and nonlinear optical setup were employed in the optical measurements. A visible beam at 532 nm generated by a frequency-doubling crystal, KDP, was used as the visible input in SFG. An infrared beam tunable between 2500 and 4000 cm^{-1} [18] was generated by a LiNbO_3 OPG/OPA stage. The sum frequency output from the Pt crystal was collected by a photomultiplier and a gated integrator.

The SFG technique has been widely used in the interfacial studies due to its surface specificity [19,20]. Briefly, SFG is a second order nonlinear optical process. This process is only allowed in the electric dipole approximation in a medium without centrosymmetry. As a result, the SFG signal in our case is dominated by contribution from the Pt(111) surface and adsorbed layer, where inversion symmetry is necessarily broken.

High pressure catalysis studies were carried out in a batch mode by introducing high pressure gases into the vacuum chamber. Gas pres-

sure was measured by a Baratron gauge that is capable of measuring pressure from 100 mTorr up to 1000 Torr. A recirculation pump was employed to circulate the gas mixture and a septum was used as a sampling port. An HP-5890 series II gas chromatography (GC) with a column that can separate cyclohexadienes, cyclohexene, cyclohexane and benzene was used to follow the gas phase kinetics.

The reactant from Aldrich was further purified by freeze–pump–thaw treatment before introduced into the reactor as a vapor. The typical reaction condition was 10 Torr of cyclohexene and 30–590 Torr of hydrogen. The total pressure was made up to one atmosphere by helium gas. The sample was then heated up to different temperature via a resistive heating. The SFG spectra were taken during the reaction, while the gas phase compositions were analyzed by GC.

3. Results and discussion

3.1. Cyclohexene dehydrogenation in UHV

The SFG spectrum taken at 130 K after a clean Pt(111) surface was exposed to 4 L (L: exposure unit: 1 L = 10^{-6} Torr s) cyclohexene revealed three features at 2875, 2918 and 2958 cm^{-1} (Fig. 1). This spectrum is similar to the Raman spectrum of cyclohexene in liquid phase [21], which has peaks at 2865, 2916 and 2940 cm^{-1} in this frequency range. According to the assignment there, we ascribe 2875 and 2958 cm^{-1} features to C–H stretch modes in CH_2 groups and 2918 cm^{-1} peak to the Fermi resonance of the bending mode of C–H bond [22]. This spectrum remains the same until 200 K. At 217 K, two new peaks in the spectrum were seen at 2860 and 2945 cm^{-1} and the spectral intensity increased by a factor two compared to the previous one. The intensity enhancement suggests a more ordered cyclohexene layer on the surface. The spectral features up-shifted to 2955 and 2863 cm^{-1} as the surface temperature

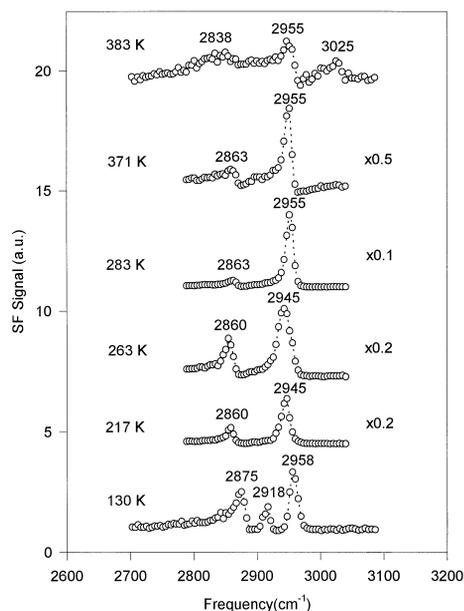


Fig. 1. SFG study of cyclohexene on Pt(111) at different surface temperature.

was raised to 283 K with further enhancement in intensity. This species survived on the surface until 371 K and further decomposition and dehydrogenation [2] occurred above this temperature as evidenced by the greatly attenuated spectral intensity and the appearance of the 3025 cm^{-1} peak, which implies the presence of sp^2 carbon species.

The origin of the SFG spectral features of cyclohexene on the surface needs further discussion. Cyclohexene has a double bond in its molecular structure and has a half chair conformation with C_2 symmetry in a free molecule [21,22]. A stable half chair conformation is shown in Fig. 2. The double bond plays an important role when the cyclohexene molecule interacts with platinum surface. Apparently, cyclohexene donates its π -electron density in the double-bond to the metal as it bonds to the surface. The spectral features observed at 130 K are similar to those of free cyclohexene molecules [21], therefore a molecular cyclohexene species is suggested. Due to the different electronic coupling with the carbon ring in the axial and equatorial positions, the equatorial

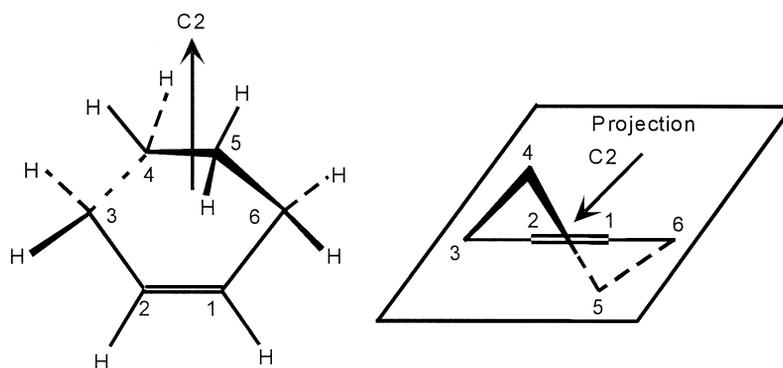


Fig. 2. The half chair conformation of cyclohexene.

C–H appears at higher stretching frequency [23,24]. This spectrum is also nearly identical to the Raman spectrum of deuterated cyclohexene-3,3,6,6- d_4 with a small shift in frequencies [22]. In the substituted molecule, the signal comes from CH_2 groups at the C_4 and C_5 positions (Fig. 2). Therefore, the SFG features observed at 130 K can then be more specifically assigned to C–H bonds at C_4 and C_5 .

The lack of seeing any features from CH_2 groups at C_3 and C_6 and CH groups at C_1 and C_2 can be rationalized if these C–H bonds parallel to the surface and the metal surface selection rule prohibits us from seeing any of the stretching transitions [25,26]. The molecular identity of this species implies that the double bond is barely perturbed or only partially hybridized, therefore a π/σ hybridized cyclohexene species is proposed. This has also been found by Henn et al. [2], who proposed the formation of a molecular di- σ species.

This molecular species is stable below 200 K. It converts to a new species around 217 K as evidenced by the two new peaks at 2860 and 2945 cm^{-1} . This result fits very well to a di- σ cyclohexene species, as proposed by others at this temperature [2]. The shift in frequencies of the two features is probably due to the electronic effect as the hybridization of the double bond has changed from sp^2 to sp^3 . The π/σ cyclohexene probably interacts with metal surface via a side-on geometry and causes the

carbon ring to tilt away from the surface normal. As the hybridization of the double bond carbons changes from sp^2 to sp^3 , the carbon ring of the di- σ species will lie closer to the surface normal, and hence gives stronger SFG signal.

Further dehydrogenation occurs at 283 K. The observed new species can be assigned as a π -allyl $c\text{-C}_6\text{H}_9$ species on the surface according to other studies of cyclohexane and cyclohexene decomposition on the same surface [2,14,15]. This assignment is consistent with our spectral results since the stronger peak at 2955 cm^{-1} can be attributed to the equatorial C–H stretching in the $c\text{-C}_6\text{H}_9$ species. In this intermediate $c\text{-C}_6\text{H}_9$ (shown in Fig. 3), the equatorial C–H on the C_6 position carbon is nearly vertical since half the carbon ring is nearly perpendicular to the surface. This shows the stepwise tilting of the carbon ring toward the metal sur-

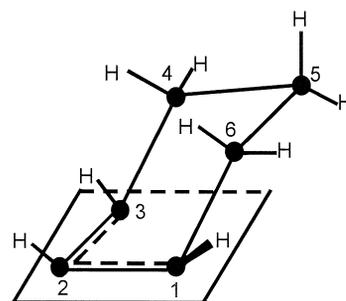
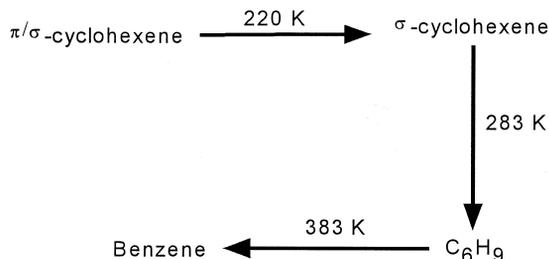


Fig. 3. The possible C_6H_9 species of cyclohexene dehydrogenation on Pt(111).

face as it dehydrogenates to the final product—benzene.

The observed temperature of benzene formation is higher than reported by others [2]. This is probably due to a higher coverage of cyclohexene on the surface in our study. High coverage could cause the dehydrogenation of the $c\text{-C}_6\text{H}_9$ species to shift to higher temperature. This upshift of the temperature where dehydrogenation occurs is apparently due to a site-blocking effect and has been observed in other hydrocarbon molecule decomposition on Pt(111) [27]. Since the sites needed for dehydrogenation of the C_6H_9 species are not readily available at high coverage, this affects the chemistry in the decomposition pathway. Only at higher temperature, the species desorbs or decomposes and make available the necessary dehydrogenation sites. Based on the above discussion, a reaction pathway can be proposed as below:



3.2. The vibrational spectra of 1,3-CHD and 1,4-CHD on Pt(111) in UHV

An SFG spectrum of 1 L 1,3-CHD on Pt(111) at 130 K is depicted in Fig. 4a. Four peaks at 2830, 2875, 2900 and 3020 cm^{-1} and a shoulder at 2770 cm^{-1} appear in the spectrum. The 2830, 2875 and 2900 cm^{-1} features can be assigned to the C–H stretch modes of CH_2 and the 3020 cm^{-1} peak to the CH stretch mode of the C=C–H group of 1,3-CHD on the surface, since they correspond well with those in the infrared spectrum of the same molecule in the gas phase [28,29]. An infrared spectrum of 1,3-CHD in the liquid phase is also shown for comparison (Fig. 4b). The close coincidence in

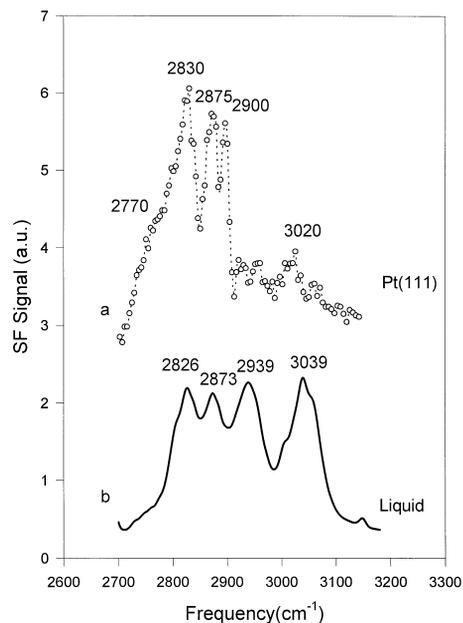


Fig. 4. (a) A typical SFG spectrum of monolayer 1,3-CHD on Pt(111) at 130 K; (b) infrared spectrum in liquid phase.

frequencies between the SFG features and the infrared peaks indicates that 1,3-CHD adsorbs intact on the surface. The non-planar conformation of the 1,3-CHD molecule with two CH_2 groups pointing in opposite directions hinders the interaction between its π -electrons and the d-orbitals of surface Pt metal atoms, and could probably result in a tilted configuration of the adsorbed 1,3-CHD molecule on the surface. This geometry has a significant consequence on the chemistry of 1,3-CHD upon annealing.

Fig. 5a represents an SFG vibrational spectrum of 1 L exposure of 1,4-CHD on Pt(111) at 130 K. Only a sharp peak at 2770 cm^{-1} with a peakwidth of $\sim 12\text{ cm}^{-1}$ at the half maximum was observed. This spectrum is very different from the infrared spectrum of the liquid 1,4-CHD (Fig. 5b). It has been shown that 1,4-CHD adsorbs molecularly on the surface below 230 K [30]. This molecule in gas phase has a nearly planar configuration with its π -orbitals perpendicular to the molecular plane. Therefore, the molecule should adsorb flat on the surface to facilitate the interaction between its π -electrons and the d-orbitals of the surface Pt atoms.

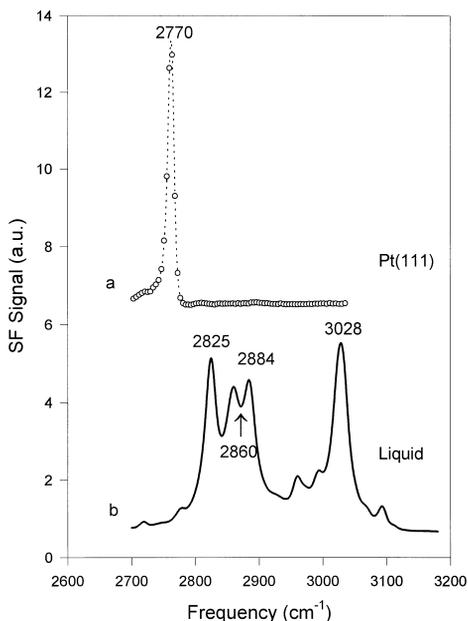


Fig. 5. (a) A typical SFG spectrum for monolayer 1,4-CHD on Pt(111) at 130 K; (b) infrared spectrum of liquid phase 1,4-CHD.

The spectral result can be explained by the flat adsorption geometry or a ‘quatra- σ -bonding’ [30]. The C–H bonds in C=C–H group are in the molecular plane and parallel to the surface, thus give no SFG signal due to the selection rule on metal surface [25,26]. The feature observed in the spectrum is then assigned to the C–H stretch mode in CH₂ group. The axis of the CH₂ group points along the metal surface, therefore, only the asymmetric CH stretch mode of the CH₂ group has non-zero dipole moment along the surface normal and contributes to the signal.

The frequency of the peak, 2770 cm⁻¹, is about 50–100 cm⁻¹ red-shifted from the C–H stretch modes found for 1,4-CHD in gas phase (i.e., symmetric stretch 2825 cm⁻¹ and anti-symmetric stretch 2875 cm⁻¹, respectively [28,29]). The red-shift indicates bond weakening. This is probably due to the strong electron-withdrawal effect from the surface Pt atoms, and consequently, the electron density in the two C–H bonds flows to the surface Pt atoms and weakens the bond between C and H. Even larger C–H bond weakening effect (red-shifted

by 200 cm⁻¹) was observed during cyclohexane adsorption on Pt(111) due to hydrogen bonding with metal surface atoms [13].

The temperature dependence of SFG spectra of 1,4-CHD on Pt(111) is presented in Fig. 6. 1,4-Cyclohexadiene does not dehydrogenate significantly below 260 K as one can conclude from the spectra. Above 300 K, the signal from adsorbed 1,4-CHD disappeared completely. This is due to the dehydrogenation of 1,4-CHD to benzene at this temperature, as has been revealed by bismuth postdosing thermal desorption mass spectroscopy (BPTDS) studies on the same system [30]. The weak feature at 3030 cm⁻¹ is probably from the adsorbed benzene fragments. The dehydrogenation happens via a hydrogen-abstraction mechanism instead of β -hydrogen elimination from the CH₂ group as indicated by the activation energy measurements [9,30].

The temperature dependence of the SFG spectra of adsorbed 1,3-CHD shown in Fig. 7 is

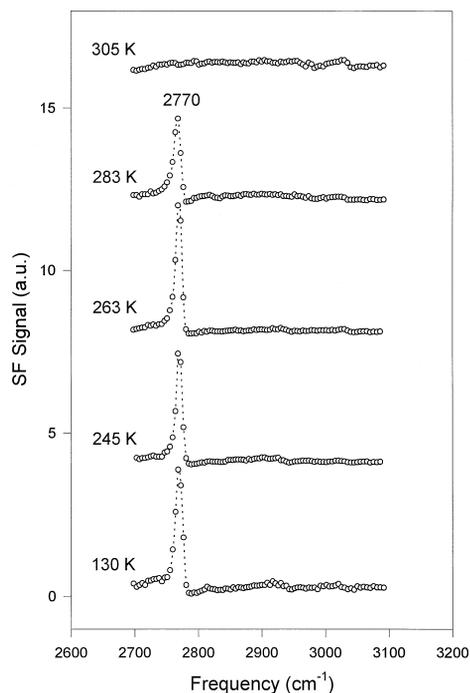


Fig. 6. Temperature dependence of SFG spectrum of 1,4-CHD on Pt(111) under ultrahigh vacuum.

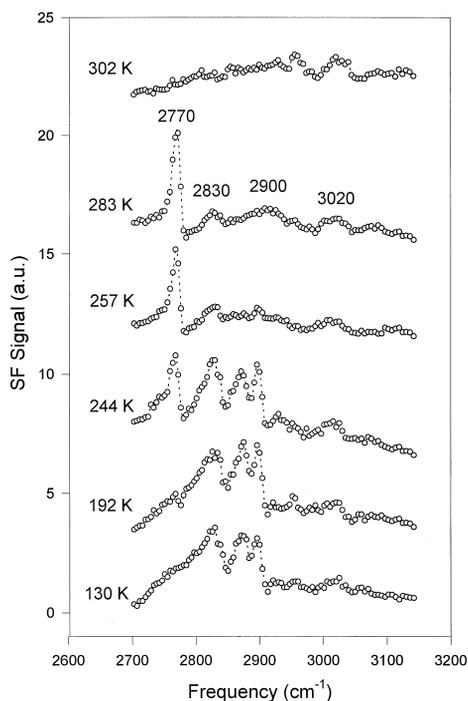


Fig. 7. SFG spectra for 1,3-CHD on Pt(111) at different temperatures.

more complex. With increase of temperature, the 2770 cm^{-1} feature grows while those characteristic of the adsorbed 1,3-CHD decrease. At 283 K , the 2770 cm^{-1} peak becomes the major feature in the spectrum, but it disappears above 300 K , leaving a weak feature at 3030 cm^{-1} that signifies the presence of benzene as the final product in the thermal evolution [11,30]. The 2770 cm^{-1} peak is identical to that for the adsorbed 1,4-CHD in Fig. 7. This is a clear evidence that 1,4-CHD is present on the Pt surface before 1,3-CHD completely dehydrogenates to benzene.

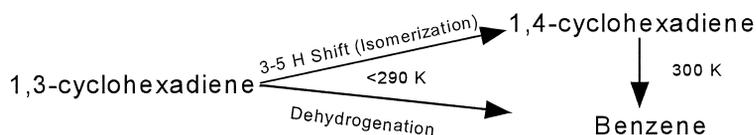
1,4-CHD formation can either occur through a rearrangement of the hydrogen atoms in 1,3-CHD molecules or by a dehydrogenation–

hydrogenation process. However, we did not observe any 1,4-CHD formation on this surface in the benzene and hydrogen coadsorption experiments, and this excludes the possibility of the existence of the dehydrogenation–hydrogenation process. The slight increase in intensity of the high frequency weak features in the SFG spectrum during 1,3-CHD thermal evolution implies that dehydrogenation to benzene is also a possible reaction pathway. Therefore, the dehydrogenation and the isomerization surface reactions occurring upon warming are in competition. A scheme of the two reaction branches is shown below (Scheme 1):

3.3. Hydrogenation and dehydrogenation reactions at high pressures

High pressure reaction studies were carried out typically at 10 Torr vapor pressure of cyclohexene with various hydrogen pressures up to near 600 Torr in the temperature range of $300\text{--}560\text{ K}$. Approximately 0.1% of 1,4-CHD and benzene were present in the gas phase after both cyclohexene and hydrogen were introduced into the chamber at 295 K as found by GC, although there was no such detectable species in the reactant. No further dehydrogenation was observed at this condition and only a slow hydrogenation with a rate of ~ 5 molecules per platinum site per second was obtained, which is comparable to the hydrogenation rate of 1,4-CHD on the same surface, which was done at similar condition.

The prominent feature in surface SFG spectrum is at 2765 cm^{-1} at 295 K in the presence of 10 Torr cyclohexene and various hydrogen pressures in the range of $20\text{--}590\text{ Torr}$ (Fig. 8). This feature was attributed to 1,4-CHD on the



Scheme 1.

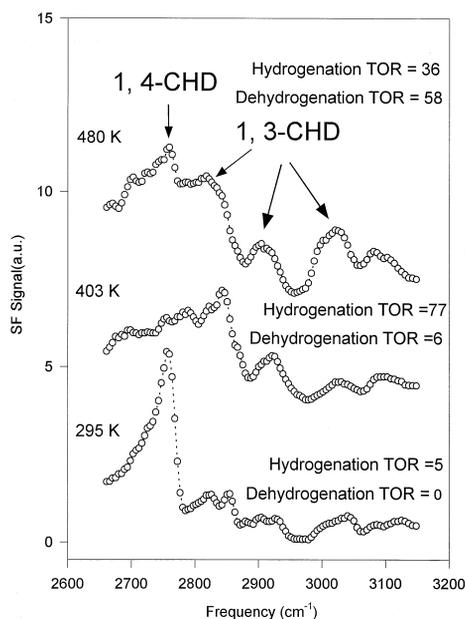


Fig. 8. The temperature dependence of SFG spectrum of high pressure cyclohexene conversion on Pt(111) at 10 Torr cyclohexene/100 Torr hydrogen, TOR is the abbreviation of turnover rate.

surface. The weak peaks in the spectrum were from 1,3-CHD. The assignment of the spectrum was made by comparison to the CHDs' spectra in UHV and the spectra of CHDs at high pressures (Fig. 12). Interestingly, there was no evidence for C_6H_{10} and $c-C_6H_9$ species on the surface, which are the important species in cyclohexene dehydrogenation in UHV condition (Fig. 1).

Above 300 K, the 2765 cm^{-1} peak disappeared (spectrum at 403 K in Fig. 8) and the weak features in the spectrum at 295 K representing 1,3-CHD became stronger and dominated the spectrum. The vibrational SFG spectrum remains unchanged in the temperature range of 300 to 400 K. Further increasing the surface temperature to 480 K, the feature represent 1,4-CHD appeared in the spectrum again in addition to the features from 1,3-CHD. This spectrum indicates that both 1,3-CHD and 1,4-CHD coexist on the surface during high pressure reaction.

The reaction kinetics were also measured as a function of both temperature and hydrogen pres-

sure. The hydrogenation rate was greatly enhanced with increasing surface temperature and reached its maximum rate of 77.6 molecules/site/s around 400 K at 10 Torr cyclohexene/100 Torr H_2 . The temperature dependence of the reaction rate of 10 Torr cyclohexene/100 Torr H_2 was depicted in Fig. 9. Above 400 K, dehydrogenation became observable and suppressed hydrogenation reaction. The maximum dehydrogenation rate of 58 molecules/site/s was obtained at 480 K (Fig. 9).

The hydrogen pressure dependence of the reaction rates was depicted in Fig. 10. The reaction exhibits almost first order in hydrogen pressure below 200 Torr and the order dependence declines as the pressure increased. This implies that a saturation of hydrogen on the surface is approaching at high hydrogen pressure. It should be noted that at 403 K, the dehydrogenation almost exhibits zero order dependence on hydrogen pressure. This is probably due to the low probability of desorption of benzene that slows down dehydrogenation at this temperature [11].

Since the dehydrogenation reaction rate is zero as revealed by gas composition analysis in

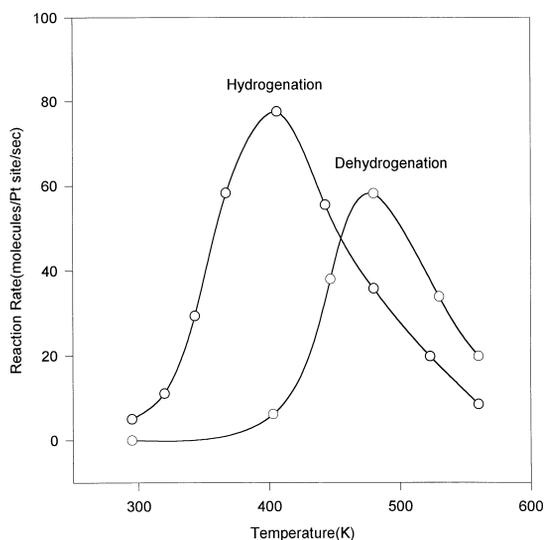


Fig. 9. The temperature dependence of hydrogenation and dehydrogenation reactions on Pt(111) at 10 Torr cyclohexene/100 Torr hydrogen.

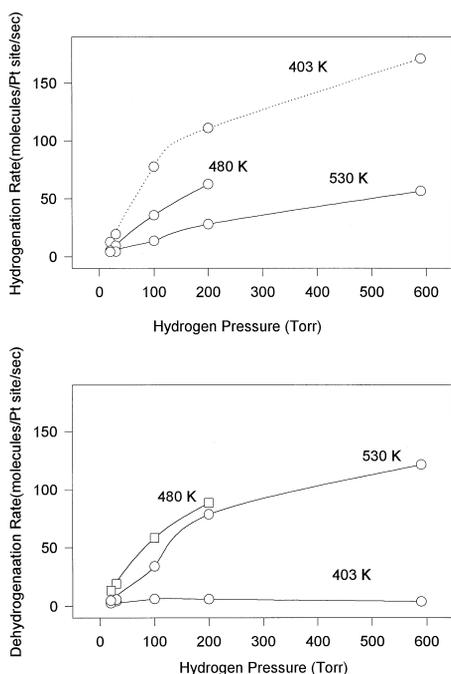


Fig. 10. The hydrogen pressure dependence of both hydrogenation and dehydrogenation reactions at constant pressure of cyclohexene (10 Torr).

the temperature range between 300 K to 400 K, we can make the approximation that only hydrogenation occurs in this temperature range. Thus the Arrhenius law can be applied to the hydrogenation reaction. An activation energy of 8.9 kcal/mol for the hydrogenation reaction at a reaction condition of 10 Torr cyclohexene and 100 Torr of hydrogen was obtained from the Arrhenius plot as shown in Fig. 11. This activation energy is reasonable for the hydrogenation of cyclohexene. Segal et al. [31] obtained an activation energy of ~ 8 kcal/mol for this reaction in studies over supported platinum catalysts. The measured hydrogenation rate drops quickly above 400 K, while the dehydrogenation rate increased rapidly (Fig. 11).

The Arrhenius behavior of the hydrogenation in this range (300–400 K) implies that the number of surface active sites for hydrogenation does not change in any significant manner in the temperature range investigated (300–400 K).

Indeed, 1,4-CHD has relatively larger SFG cross section than that of 1,3-CHD on Pt(111) surface since 1,4-CHD has stronger SFG intensity than 1,3-CHD does at comparable coverage [16], and its absence in the spectrum indicates that the surface concentration of this species is very low. This allows us to conclude that 1,3-CHD is the likely surface reaction intermediate species during cyclohexene hydrogenation. The evidence found at room temperature that 1,4-CHD on the surface inhibits reactions as a full monolayer coverage is reached [11] excludes the possibility that it is an intermediate for hydrogenation in this temperature range.

To confirm the above conclusion, we carried out the hydrogenation of both 1,3- and 1,4-CHD at 295 K as shown in Fig. 12a and b. As expected, 1,3-CHD hydrogenates very fast with a rate of ~ 100 molecules/site/s, while a much lower rate of only ~ 5 molecules/site/s was obtained for 1,4-CHD at 295 K. This correlation between the adsorbed surface species and their hydrogenation kinetics supports the above conclusion that 1,3-CHD is the intermediate in cyclohexene hydrogenation.

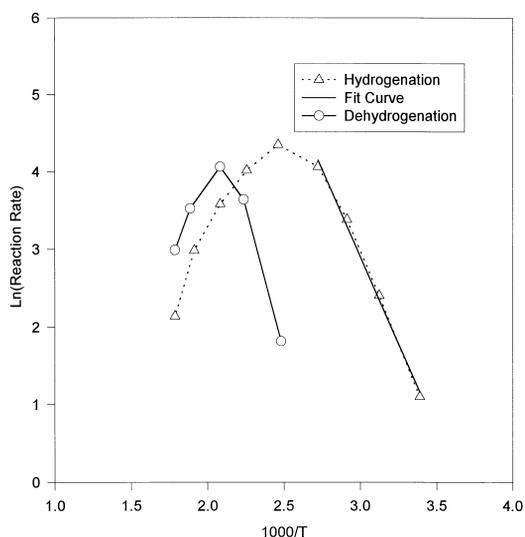


Fig. 11. An Arrhenius plot of the hydrogenation and dehydrogenation reactions of cyclohexene at 10 Torr cyclohexene/100 Torr hydrogen. An activation energy of 8.9 kcal/mol was obtained.

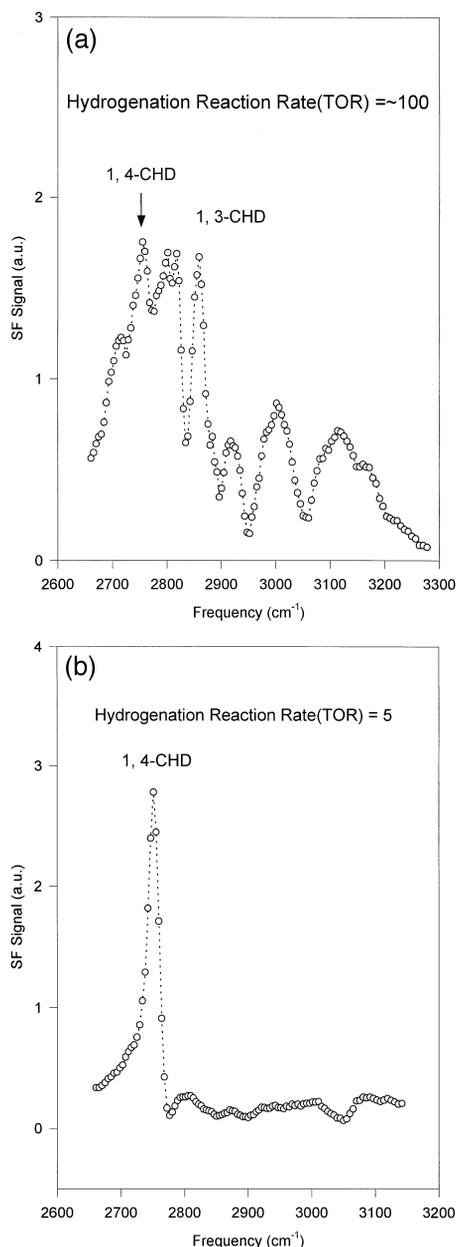
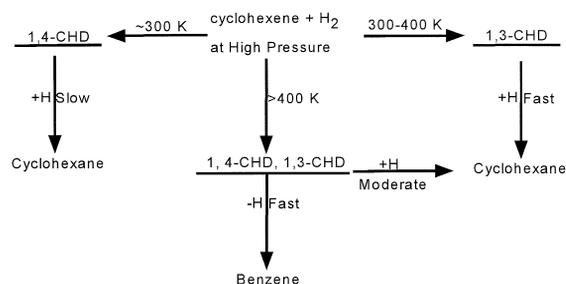


Fig. 12. In situ SFG spectrum of high pressure hydrogenation of (a) 1,3- and (b) 1,4-CHD over Pt(111), TOR is the abbreviation of turnover rate.

Above 400 K, the platinum surface carries out both hydrogenation and dehydrogenation. The dehydrogenation rate reached its peak at 480 K. This shift must be related to the active surface sites that change from reforming hydro-

genation to carrying out dehydrogenation. The steep drop of hydrogenation rate from the Arrhenius behavior can also partly be attributed to the fact that 1,3-CHD is unstable at high temperature and it either dehydrogenates to benzene or rearranges to its 1,4-isomer and contributes directly or indirectly to the dehydrogenation reaction path.

Both hydrogenation and dehydrogenation reaction rates decrease as the temperature is raised above 500 K. This could be due to the deactivation of the surface as the carbonaceous species accumulated. It could also be possible that the adsorption rate of the cyclohexene limited the reactions. A reaction mechanism can be suggested as follows:



4. Conclusions

Cyclohexene dehydrogenates to benzene through π/σ , di- σ and c-C₆H₉ species under UHV condition on Pt(111) surface upon heating. At high pressures with 10 Torr cyclohexene and 30–590 Torr hydrogen, 1,4-CHD and 1,3-CHD are the major surface species under all experimental conditions explored in this study. 1,3-CHD was found to be the dominant surface species during the hydrogenation reaction in the temperature range of 300–400 K and appears to be the reaction intermediate. Above 400 K, the surface carries out both hydrogenation and dehydrogenation reactions, and both 1,3- and 1,4-CHD coexist on the Pt(111) surface as found by SFG spectroscopy. This indicates that both CHDs are precursors for benzene formation.

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