# Gas Phase Atomic Hydrogen-Induced Hydrogenation of Cyclohexene on the Ni(100) Surface

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Gas phase hydrogen atoms add to adsorbed cyclohexene at 100 K on the Ni(100) surface, resulting in cyclohexane formation during subsequent TPR (temperature-programmed reaction) experiments. No C–C bond activation is observed after exposure to gas phase atomic hydrogen. Vibrational and isotope studies indicate that a cyclohexyl intermediate is formed by the addition of gas phase atomic hydrogen to adsorbed cyclohexene. This adsorbed cyclohexyl is hydrogenated primarily by surface hydrogen to form cyclohexane during subsequent heating. Cyclohexane yields increase with increasing atomic hydrogen exposure, and yields in the 90% range have been observed with large atomic hydrogen exposures. In the presence of only coadsorbed hydrogen, no significant hydrogen addition to adsorbed cyclohexene is observed, and cyclohexene desorption dominates during subsequent TPR experiments. Vibrational spectroscopy indicates that  $\pi$ -bonded cyclohexene with the C=C bond parallel to the surface is the dominant surface species in the presence of coadsorbed surface hydrogen. In contrast, di- $\sigma$ -bonded cyclohexene is the dominant species in the absence of coadsorbed hydrogen. In the absence of coadsorbed hydrogen, dehydrogenation of the adsorbed cyclohexene results in benzene formation with increasing temperature. Adsorbed benzene formed by dehydrogenation has been identified after heating to 390 K in the absence of hydrogen using vibrational spectroscopy.

# Introduction

This study of the reactions between gas phase atomic hydrogen and adsorbed cyclohexene is part of our program to explore the role of hydrogen in C-C bond activation processes. Cyclohexene is a particularly interesting reactant because the complete range of surface reactions including isomerization, hydrogenolysis, hydrogenation, and dehydrogenation can all occur with this cyclic olefin.

Reactions of atomic hydrogen with olefins have been studied extensively in the gas phase.<sup>1</sup> Atomic hydrogen primarily adds to the  $\pi$  bonds forming a vibrationally excited alkyl radical. These excited radicals can undergo either dissociation or collisional stabilization. Limited hydrogen abstraction also occurs during reactions between olefins and gas phase atomic hydrogen. In most cases, the ratio of hydrogen abstraction to hydrogen addition is below 0.1.<sup>1</sup> The activation energy for hydrogen atom addition to alkenes in the gas phase is generally well below 7 kcal/mol. For example, the activation energy for hydrogen atom addition to gas phase propylene is 1.5 kcal/mol in the 77–90 K temperature range.<sup>1</sup>

Reactions of gas phase atomic hydrogen with solid olefins at low temperatures (<150 K) have also been investigated, and hydrogen addition to the double bond to form an alkyl radical is the primary process observed.<sup>2–5</sup> The alkyl radicals produced either react with other alkyl radicals or react with hydrogen atoms depending on the mobility of alkyl radicals in the solid.<sup>5</sup> Reactions between alkyl radicals predominate in solids where diffusion of alkyl radicals is rapid, while reactions with atomic hydrogen dominate when high-viscosity matrices are employed. In both cases, disproportionation and combination of the intermediates result in the formation of the final stable products. The immobilizing effect of the matrix also affects the overall reaction rate.<sup>5</sup> For instance, undiluted solid 1-hexene does not appear to react with atomic hydrogen at 77 K but shows considerable reactivity when diluted with inerts which enhance mobility.<sup>5</sup> The estimated activation energy for hydrogen atom addition to solid olefins is approximately 1.5 kcal/mol.<sup>3</sup> Disproportionation of the alkyl radicals produced appears to proceed without activation energy.

In contrast to H atom reactions with gas phase olefins or solid olefins, reactions of atomic hydrogen with olefinic hydrocarbons adsorbed on the surface have been investigated only recently. Bent and co-workers observed that gas phase atomic hydrogen adds to adsorbed ethylene to form ethyl and to adsorbed benzene to form partially hydrogenated benzene at 110 K on the Cu-(111) surface.<sup>6a</sup> Similar reactions have been also observed for adsorbed ethylene on the Cu(100) surface.<sup>6b</sup> Isotope studies have shown that the resulting ethyl species dissipate energy and accommodate to the surface before decomposition or rearrangement occurs.<sup>6b</sup> The estimated cross section for hydrogen addition to ethylene on the Cu(111) surface is 18 Å<sup>2</sup>, which is an order of magnitude larger than the cross section for hydrogen abstraction from cyclohexane on the same surface.<sup>7,8</sup>

We have found that small strained cycloalkanes react readily with gas phase atomic hydrogen on the Ni(100) surface.<sup>9</sup> Hydrogen addition leading to ring opening is dominant for three-, four-, and five-membered cycloalkanes on the Ni(100) surface. This reactivity may be associated with the high p character of the strained C–C bond in these small cycloalkanes. On the other hand, atomic hydrogen addition is not observed for cyclohexane, which has unstrained C–C bonds similar to saturated *n*-alkane's. Instead, hydrogen abstraction dominates in the adsorbed cyclohexane, leading to cyclohexene and cyclohexadiene formation during exposure to gas phase atomic hydrogen.<sup>9</sup>

Cyclohexene is an interesting reactant since the  $\pi$  and  $\pi^*$  orbitals are the primary interaction centers, resulting in nearly parallel adsorption of the unsaturated carbon–carbon bond on the Ni surface.<sup>10,11</sup> As a result, some C–H bonds in CH<sub>2</sub> groups are very close to the surface and susceptible to activation. In fact, dehydrogenation is the dominant thermal process observed for cyclohexene adsorbed on Ni surfaces.<sup>10,11</sup> On the other hand,

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# Hydrogenation of Cyclohexene on the Ni(100) Surface

cyclohexane adsorbs reversibly, and no dehydrogenation is observed on the low-index Ni surfaces.<sup>10</sup> Cyclohexane adsorbs with the carbon ring parallel to the metal surface, and HREELS spectra show a C–H soft mode due to C–H···M interactions involving the axial hydrogens.<sup>12–16</sup>

Recently, we have demonstrated that adsorbed cyclohexene can be hydrogenated to cyclohexane on the Ni(100) surface by both gas phase atomic hydrogen and desorbing bulk hydrogen at a low temperature and pressure.<sup>17</sup> Gas phase atomic hydrogen addition to cyclohexene on the less reactive Cu(100) surface has also been recently characterized.<sup>18</sup> Cyclohexyl formation followed by subsequent  $\beta$ -hydrogen elimination to form cyclohexene is the main reaction observed for cyclohexene adsorbed on this surface. No cyclohexane formation was observed. To the best of our knowledge, the hydrogenation of cyclohexene to cyclohexane has been observed previously only with high pressures of both cyclohexene and hydrogen. Cyclohexene hydrogenation over the Pt(223) stepped surface requires a high pressure with excess hydrogen (H<sub>2</sub>/cyclohexene  $\sim 10$ ).<sup>19</sup> At room temperature, cyclohexene dehydrogenation is dominant in the  $10^{-7}$  Torr pressure range on the Pt(223) surface. Hydrogenation only begins to dominate in the 100 torr pressure range on this rough surface.<sup>19</sup> The activation energy estimated for hydrogenation is 5 kcal/mol at 77 Torr. Disproportionation of cyclohexene is not observed under these high-pressure conditions so no benzene is observed. Catalytic hydrogenation of cyclohexene over supported Ni, Pt, and Pd catalysts also requires atmospheric pressures of hydrogen and temperatures above 300 K.20-23

In this work, a detailed mechanistic study of gas phase atomic hydrogen-induced cyclohexene hydrogenation has been performed using vibrational spectroscopy (HREELS) and isotope experiments. The present work clearly shows that cyclohexene hydrogenation by gas phase atomic hydrogen occurs at 100 K on the Ni(100) surface.

#### **Experimental Section**

The experiments were performed in an ultrahigh-vacuum chamber which has been described previously in detail.<sup>9</sup> The background pressure of the system during the experiments was  $\sim 5 \times 10^{-11}$  Torr. The Ni(100) crystal was cleaned by Ar<sup>+</sup> sputtering followed by annealing to 1000 K, oxygen treatment, and hydrogen treatment. The cleanliness of the surface was verified by AES.

Microchannel array-directed beam dosers and leak valves were used for reagent dosing. Cyclohexene (Aldrich, 99%) was used after being purified by several freeze–pump–thaw cycles. Hydrogen (Matheson, 99.9999%) and deuterium (Matheson, 99.5%) were used without further purification both for adsorption and for the production of atomic hydrogen. The arbitrary exposure units reported have not been corrected for large preferential dosing fluxes and ion gauge sensitivity factors. Exposures are presented in langmuirs (1 langmuir =  $1 \times 10^{-6}$ Torr s) based on the background pressure reading from ion gauge and are intended to be used as a basis for internal comparisons.

Gas phase atomic hydrogen was created on a ~1800 K tungsten filament by the dissociation of molecular hydrogen at  $9.0 \times 10^{-7}$  Torr. Since an accurate dissociation coefficient is not available, exposures of atomic hydrogen are given in terms of exposures of molecular hydrogen to the W filament as measured by an ion gauge.

TPR spectra were taken using a quadrupole mass spectrometer (QMS) and a linear heating rate of 3 or 5 K/s. The desorption spectra were collected with Hunt Scientific software, which



**Figure 1.** TPR spectra of submonolayer cyclohexene adsorbed on the Ni(100) surface. Dehydrogenation is dominant, and only a small amount of cyclohexene desorbs at 181 K. Benzene produced from dehydrogenation desorbs around 440 K.

controls sample temperature and monitors a range of masses or up to 26 specified masses.<sup>24</sup>

Vibrational spectra have been taken using an HREELS spectrometer with a 127° cylindrical deflection monochromator and an identical analyzer. The count rate for the elastic peak was  $10^4-10^6$  counts/s with ~10 meV resolution. The incident beam energy was ~4.5 eV at a pass energy of 0.29 eV. All the spectra were collected in the specular direction at 60° from the surface normal. Spectra were collected with a PC interfaced to the HREELS electronics. The signal was averaged over 25 scans of the chosen energy region, using 1.5 meV steps and a 0.5 s dwell time at each step.

## **Results and Discussion**

Cyclohexene on the Ni(100) Surface. Desorption and dehydrogenation are the main thermal pathways observed for cyclohexene adsorbed alone on the Ni(100) surface. Dehydrogenation is dominant for small coverages, while molecular desorption of cyclohexene increases with increasing surface coverage. The TPR spectra for a submonolayer of cyclohexene formed using an apparent 0.008 langmuir cyclohexene exposure at 100 K on the Ni(100) surface is shown in Figure 1. Only a small amount of cyclohexene desorbs molecularly at 181 K. Dehydrogenation is dominant, resulting in both hydrogen and benzene desorption with increasing temperature. A fraction of the benzene (78 amu) produced by dehydrogenation desorbs around 440 K. The remaining adsorbed benzene dehydrogenates around 460 K, resulting in the high-temperature hydrogen peak. The 78 amu peaks below 200 K are caused by the fragmentation of cyclohexene in the ionizer.<sup>17</sup> The lack of significant cyclohexene disproportionation is clearly indicated by the absence of cyclohexane desorption. Cyclohexene desorption spectra taken for a series of increasing cyclohexene exposures are shown in Figure 2. With increasing cyclohexene exposure, molecular cyclohexene desorption at 181 K increases. For apparent exposures above 0.012 langmuir, desorption from cyclohexene multilayers increases at 140 K.

Benzene adsorption/desorption from this Ni(100) sample is shown in Figure 3 for use as a reference. Molecular benzene desorption is observed at 462 K. Dehydrogenation of benzene results in hydrogen desorption over the 350–500 K temperature range on this surface, as previously reported.<sup>25</sup>

Adsorbed benzene formed by cyclohexene dehydrogenation has also been characterized using vibrational spectra in Figure



**Figure 2.** Thermal desorption of cyclohexene from the Ni(100) surface. Molecular desorption of cyclohexene becomes significant as the surface coverage is increased. Desorption of monolayer cyclohexene occurs at 181 K. Desorption of multilayers appears at 140 K as the exposure is increased.



**Figure 3.** TPR spectra of benzene adsorbed on the Ni(100) at 100 K. Desorption and dehydrogenation of monolayer benzene occur in the same temperature range.

4. Spectrum a corresponds to a multilayer of cyclohexene at 100 K. Spectrum b corresponds to a monolayer of cyclohexene adsorbed on the Ni(100) surface at 100 K. Spectrum c was taken after heating this cyclohexene monolayer to 390 K.

The vibrational spectrum of multilayer cyclohexene (a) is similar to the vibrational spectrum of liquid cyclohexene. Vibrational assignments for multilayer cyclohexene are indicated in Table 1. These assignments are based on those for the vibrational spectra of both liquid phase cyclohexene and cyclohexene adsorbed on the Pt(111) surface.<sup>26</sup> The monolayer HREELS spectrum (b) is very similar to the spectrum of a monolayer formed by annealing a cyclohexene multilayer to 165 K (data not shown).

Compared to the multilayer spectrum (a), the peaks at 662 and ~1600 cm<sup>-1</sup> are absent in the monolayer spectrum (b). The disappearance of the 1600 cm<sup>-1</sup> C=C stretching mode in the monolayer spectrum suggests that cyclohexene's double bond is parallel to the surface based on the surface dipole selection rule. Parallel adsorption of cyclohexene's unsaturated carbon-carbon bond on Ni and Pt surfaces has been observed previously.<sup>10,11</sup> In a parallel configuration the double bond may interact with the surface either by forming a  $\pi$  bond or by forming a  $\eta^2$ -di- $\sigma$  bond. The peak at 662 cm<sup>-1</sup> is caused by a



**Figure 4.** HREELS spectra of (a) multilayer cyclohexene on the Ni(100) surface at 100 K, (b) monolayer cyclohexene on the Ni(100) surface at 100 K, and (c) cyclohexene heated to 390 K on the Ni(100) surface. These spectra were taken at the specular angle.

TABLE 1: Assignments of HREELS Peaks for Cyclohexene Adsorbed on the Ni(100) Surface at 100  ${\rm K}^a$ 

cyclohexene (ad)/mono	cyclohexene (ad)/multi	cyclohexene (liq)	description
	415	452	C-C-C+C-C-H bend
	662	720	C-C-H+C=C-C bend
860	909	878	C-C stretch
		917	C-C-H bend
		1038	C-C stretch + $C-C-H$ bend + $CH_2$ rock
1083	1082		-
		1138	C-C-H bend
1243	1280	1264	$C-C-H$ bend + $CH_2$ twist
1305	1341	1321	C-C-H bend
		1392	$C-C-H$ bend + $CH_2$ wag
1441	1415	1438	CH <sub>2</sub> scissor
		1447	
		1456	
	1600	1653	C=C stretch
		2840	CH <sub>2</sub> asym stretch
		2860	-
		2882	
2937	2909	2898	
		2929	CH <sub>2</sub> sym stretch
		2940	
		2960	
		2993	
		3022	

<sup>*a*</sup> Energies of corresponding IR peaks for liquid cyclohexene<sup>26</sup> are included for comparison. Peak energies are given in cm<sup>-1</sup>.

C=C-C bending mode.<sup>26,27</sup> Therefore, the absence of this peak in the monolayer spectrum suggests that  $\eta^2$ -di- $\sigma$  bonding is dominant for monolayer cyclohexene. Similar changes in the intensity of the bending modes have been observed for cyclohexene on the Pt(111) surface where the  $\eta^2$ -di- $\sigma$  bonding configuration is thought to dominate.<sup>26a</sup> The 662 cm<sup>-1</sup> bending mode reappears in the presence of coadsorbed hydrogen, suggesting that  $\pi$  bonding becomes dominant due to the decreased interaction observed in the presence of coadsorbed hydrogen.

The peak around 860 cm<sup>-1</sup> in Figure 4b is caused by a C–C stretching mode. The appearance of the C–C stretching mode for adsorbed cyclohexene indicates that some of the C–C bonds in adsorbed cyclohexene are tilted with respect to the surface, although the C=C bond is paralleled to the surface. A tilted geometry would result in axial hydrogens which are not pointed toward the surface.<sup>10,11</sup> This tilted geometry is consistent with the absence of C–H soft modes for adsorbed cyclohexene.



**Figure 5.** TPR spectra of cyclohexene coadsorbed with surface hydrogen on the Ni(100) surface. Most cyclohexene desorbs below 200 K without reaction.

TABLE 2: Comparison of Vibrational Modes betweenAdsorbed Cyclohexene Annealed at 385 K and AdsorbedBenzene;<sup>28</sup> Strongest IR Modes of Gas Phase Benzene<sup>35,36</sup>Are Also Included (Peak Energies in cm<sup>-1</sup>)

cyclohexene(ad) at 385 K	benzene(ad) <sup>28</sup> at room temp	benzene (g) <sup>35,36</sup>	mode	description
792	766	673	$v_4$	C-H(out-of-plane) bend
1090	1008	1038	$v_{14}$	C-H(in-plane) bend
1398	1452	1486	$v_{13}$	C-C stretch
2980	3024	3063	$v_{12}$	C-H stretch

Spectrum c in Figure 4 taken after flashing adsorbed cyclohexene to 390 K is very similar to the spectrum of benzene adsorbed on the Ni(100) surface.<sup>28</sup> Peak assignments for spectrum c are indicated in Table 2. With heating the most significant changes observed are the appearance of a strong peak at 792 cm<sup>-1</sup> and the increase of C–H stretching energy to 2980 cm<sup>-1</sup>. The 792 cm<sup>-1</sup> peak corresponds to benzene's C–H out-of-plane bending mode.<sup>28</sup> The increase of the C–H stretching energy up to 2980 cm<sup>-1</sup> is caused by the sp<sup>2</sup> hybridization of the benzene formed. As expected, this C–H stretching energy is smaller than the 3024 cm<sup>-1</sup> energy reported for a complete monolayer of benzene.<sup>28</sup> A similar energy increase with increasing surface coverage has been previously reported for benzene for benzene on the Pt(111) surface.<sup>29</sup>

Cyclohexene Coadsorbed with Surface Hydrogen. Molecular cyclohexene desorption is dominant for cyclohexene coadsorbed with hydrogen on the Ni(100) surface (Figure 5). No significant amount of hydrogenation by surface hydrogen has been observed. The small 56 amu hydrogenation peak near 250 K is likely to be associated with reactive surface defects.<sup>30</sup> Desorption of dehydrogenated products is not observed in the presence of coadsorbed surface hydrogen/deuterium. The 78 amu peak at 181 K is caused by the fragmentation of cyclohexene. However, the hydrogen peak around 460 K clearly indicates that dehydrogenation of residual adsorbed organic occurs at an elevated temperature. Apparently a small fraction of the adsorbed cyclohexene remains on the surface and dehydrogenates with increasing temperature even in the presence of coadsorbed hydrogen/deuterium. The sharp low-temperature hydrogen peak around 260 K clearly indicates that coadsorbed cyclohexene affects the desorption energetics of surface hydrogen.

Isotope exchange occurs below 181 K for cyclohexene coadsorbed with deuterium on the Ni(100) surface (Figure 6).



**Figure 6.** TPR spectra of cyclohexene coadsorbed with surface deuterium on the Ni(100) surface. Isotope exchange between adsorbed cyclohexene and surface deuterium has been observed.



**Figure 7.** HREELS spectra of (a) monolayer cyclohexene on the Ni(100) surface at 100 K and (b) cyclohexene coadsorbed with surface hydrogen. The C=C-C bending mode appears at 673 cm<sup>-1</sup> in the presence of coadsorbed hydrogen. These spectra were taken at the specular angle.

Comparisons between the hydrogen (2 amu) and deuterium (4 amu) peaks indicate that the sharp hydrogen peak at 260 K is associated primarily with hydrogen exchanged out of cyclohexene. The 83 amu peak at 181 K represents 17% of the 82 amu peak at the same temperature and is larger than natural abundance of [<sup>13</sup>C]cyclohexene. Therefore, cyclohexene- $d_1$  must be the main cause of the 83 amu peak at 181 K. The 83 amu peak at 140 K represents ~2% of the corresponding 82 amu peak and is consistent with natural abundance of [<sup>13</sup>C]-cyclohexene. The amount of hydrogen produced by exchange cannot be determined directly because of large cross section variations between hydrogen and deuterium. With our mass spectrometer, the ion yield for deuterium (4 amu) was approximately 40% relative to hydrogen (2 amu).

Cyclohexene interaction with the surface is modified substantially in the presence of coadsorbed hydrogen as highlighted by the vibrational spectra in Figure 7. In the presence of coadsorbed hydrogen, a new peak appears at 673 cm<sup>-1</sup>, and the intensities of the peaks in the region of 1100-1500 cm<sup>-1</sup> are increased. On the basis of the comparisons with the IR spectrum of liquid cyclohexene,<sup>27</sup> we believe that the peak at 673 cm<sup>-1</sup> is caused by a C=C-C deformation mode. This peak suggests that the C=C bond in cyclohexene is not disturbed significantly by adsorption in the presence of coadsorbed



Figure 8. TPR spectra of monolayer cyclohexene after exposure to 95 langmuirs of atomic hydrogen at 100 K. Cyclohexane is produced and desorbs at 178 K. No benzene formation is observed.

hydrogen. The increased intensities of the peaks appearing between 1100 and 1500 cm<sup>-1</sup> due to the C–C–H and CH<sub>2</sub> bending modes indicate that the cyclohexene's hydrogens become less strongly bound to the surface in the presence of coadsorbed hydrogen.

Cyclohexene Exposed to Gas Phase Atomic Hydrogen. Gas phase atomic hydrogen hydrogenates adsorbed cyclohexene at 100 K, and cyclohexane is produced during subsequent TPR experiments. The TPR spectra in Figure 8 indicates that cyclohexane is formed at 178 K with a yield of approximately 90% after adsorbed cyclohexene was exposed to 95 apparent langmuirs of gas phase atomic hydrogen.<sup>31</sup> A small amount of unreacted cyclohexene desorbs at the same temperature. The observed cyclohexane formation is mainly caused by cyclohexene hydrogenation initiated by gas phase atomic hydrogen. Hydrogenation of cyclohexene by bulk hydrogen occurs at the desorption temperature of bulk hydrogen and can easily be distinguished from addition of gas phase atomic hydrogen.<sup>17</sup> The small high-temperature hydrogen peak above 400 K indicates that a small amount of residual hydrocarbon dehydrogenation is occurring at an elevated temperature after exposure to gas phase atomic hydrogen.

The fact that no noncyclic alkanes desorb with increasing temperature indicates that hydrogen-induced C-C bond activation cannot be observed with adsorbed cyclohexene (Figure 8). No benzene desorption has been observed after reaction of monolayer cyclohexene with gas phase atomic hydrogen, suggesting that hydrogen abstraction is not a primary reaction pathway of monolayer cyclohexene (Figure 8). Abstraction from adsorbed cyclohexene could also result in the formation of dehydrogenated species which would be dehydrogenated above 400 K.<sup>25</sup> No increase in the hydrogen peaks above 400 K is observed after reaction with gas phase atomic hydrogen as indicated by direct comparison of Figures 8 and 5, which were both run with 30 eV ionization energy. We propose that competition between adsorption of gas phase atomic hydrogen on the Ni surface and abstraction from the adsorbed organic appears to play an important role in controlling the reaction selectivity. Adsorption of gas phase atomic hydrogen on the Ni surface is a *nonactivated* exothermic process ( $\Delta H \sim -64$ kcal/mol).9 However, hydrogen abstraction from cyclohexene is activated by more than 9 kcal/mol of activation energy32 and is less exothermic ( $\Delta H \sim 23$  kcal/mol).<sup>33</sup> These energetics which strongly favor adsorption apparently preclude abstraction as a dominant reaction pathway for the adsorbed monolayer.



**Figure 9.** TPR spectra of multilayer cyclohexene on a hydrogenprecovered Ni(100) surface taken after exposure to 141 langmuirs of atomic hydrogen at 100 K. Cyclohexane is produced and desorbs above 122 K. Benzene formation caused by hydrogen abstraction is observed above 354 K.

Both hydrogenation and hydrogen abstraction are observed following reaction of multilayer cyclohexene with gas phase atomic hydrogen. The TPR spectra in Figure 9 were taken for a multilayer of cyclohexene adsorbed on the hydrogen-preexposed Ni(100) surface after exposure to 141 langmuirs of atomic hydrogen. A hydrogen-preexposed surface was used to inhibit thermal dehydrogenation of cyclohexene. In this figure, hydrogen abstraction is clearly indicated by both benzene desorption above 355 K and residual hydrocarbon dehydrogenation above 400 K. Hydrogenation of multilayer cyclohexene is indicated by cyclohexane desorption at the multilayer desorption temperature of 141 K. Cyclohexane produced by hydrogenation desorbs at 141 and 175 K. With increased atomic hydrogen exposures, the total cyclohexane yield increases (data not shown). The amount of benzene produced does not show any strong correlation with cyclohexane yield. Therefore, we propose that benzene formation results from hydrogen abstraction by gas phase atomic hydrogen rather than from disproportionation of cyclohexene.

The changes in the vibrational spectra with atomic hydrogen exposure at 100 K (Figure 10) clearly indicate that cyclohexene is hydrogenated by gas phase atomic hydrogen. Spectrum a in Figure 10 was taken from a monolayer of cyclohexene at 100 K. Spectrum b was obtained after exposing a monolayer of cyclohexene to 95 apparent langmuirs of atomic hydrogen. A reference vibrational spectrum c of monolayer cyclohexane is shown in Figure 10 for comparison. The dashed inset in spectrum c shows that cyclohexane's soft modes at 2600 cm<sup>-1</sup> are not observed in the presence of coadsorbed hydrogen. After adsorbed cyclohexene is exposed to gas phase atomic hydrogen, the energies and relative intensities of several vibrational modes are modified, and new low-energy vibrational modes appear as indicated in Table 3. These new modes at 399 and 460 cm<sup>-1</sup> correspond closely to C-C-C bending and torsional modes in monolayer cyclohexane<sup>12</sup> and clearly indicate saturation of carbon-carbon bonds in cyclohexene during atomic hydrogen exposure. The intensity of the peak at 460 cm<sup>-1</sup> appears to include a contribution from Ni-C stretching mode, suggesting that adsorbed hydrogenated species may be interacting directly with the Ni surface. The C-H stretching mode is also shifted to a lower energy (2895  $\text{cm}^{-1}$ ) after exposure to gas phase atomic hydrogen, indicating a higher degree of carbon saturation. The intensities of the peaks corresponding to the CH<sub>2</sub> scissoring



**Figure 10.** HREELS spectra of (a) monolayer cyclohexene on the Ni-(100) surface at 100 K, (b) monolayer cyclohexene on the Ni(100) surface taken after exposure to 95 langmuirs of atomic hydrogen at 100 K, and (c) monolayer cyclohexane on the Ni(100) surface at 100 K. The dashed line attached to spectrum c is a part of HREELS spectrum for cyclohexane coadsorbed with hydrogen on the Ni(100) surface. These spectra were taken at the specular angle.

TABLE 3: Comparison of Vibrational Modes of AdsorbedCyclohexene Exposed to Gas Phase Atomic Hydrogen andCyclohexane Adsorbed on the Ni(100) Surface at 100 K;Vibrational Modes (IR and Raman) of Gas PhaseCyclohexane<sup>35,37</sup> Are Also Listed<sup>a</sup>

H+ cyclohexene(ad)	cyclohexane(ad)	mode	gas phase	description
399	393	$v_6$	383	C-C-C bend, torsion
460	480	$v_{16}$	523 (w)	C-C-C bend
843	850	$v_5$	802	C-C stretch
		$v_{23}$	785	CH2 rock
		$v_{31}$	863	C-C stretch
1041	1023	$v_{15}$	1030 (m)	CH2 rock
		$v_{22}$	1027	C-C stretch
1276	1257	$v_{21}$	1266	CH2 twist
		$v_{29}$	1261	CH2 twist
1374	1331	$v_{20}$	1347	CH2 wag
		$v_{28}$	1355	CH2 wag
1424	1431	$v_3$	1465	CH <sub>2</sub> scissor
		$v_{14}$	1437 (m)	CH <sub>2</sub> scissor
		$v_{19}$	1443	CH <sub>2</sub> scissor
		$v_{27}$	1457	CH <sub>2</sub> scissor
	2653			softened C-H stretch
2895	2888	$v_1$	2930	CH2 asym stretch
		$v_{12}$	2915 (m)	CH2 asym stretch
		$v_{25}$	2933	CH <sub>2</sub> asym stretch
		$v_2$	2852	CH <sub>2</sub> sym stretch
		$v_{13}$	2860 (m)	CH <sub>2</sub> sym stretch
		$v_{18}$	2897	CH <sub>2</sub> sym stretch
		$v_{26}$	2863	CH <sub>2</sub> sym stretch

<sup>*a*</sup> IR-active modes are given with their intensities (vs = very strong, m = medium, and w = weak). Peak energies are given in cm<sup>-1</sup>.

mode  $(1424 \text{ cm}^{-1})$  are also increased after atomic hydrogen exposure. All these observations are consistent with cyclohexene hydrogenation by gas phase atomic hydrogen at 100 K. The hydrogenated product is believed to be adsorbed cyclohexyl based on both these spectroscopic results and isotope experiments described in the next paragraph. An adsorbed cyclohexyl intermediate is not likely to be further hydrogenated by gas phase atomic hydrogen since hydrogen abstraction rather than hydrogen addition dominates in sp<sup>3</sup>-hybridized carbon during atomic hydrogen exposure.<sup>34</sup> The absence of the C–H soft mode in spectrum b may be caused by the presence of coadsorbed hydrogen or may be caused by a different orientation



**Figure 11.** TPR spectra of multilayer cyclohexene adsorbed on a hydrogen-presaturated Ni(100) surface taken after exposure to 139 langmuirs of atomic deuterium. Singly deuterated cyclohexane- $d_1$  is the main hydrogenated product observed.



**Figure 12.** A schematic diagram for the proposed reaction mechanism of cyclohexene hydrogenation on the Ni(100) surface. Gas phase atomic hydrogen adds to cyclohexene at 100 K to form cyclohexyl. This intermediate is hydrogenated preferentially by surface hydrogen to form cyclohexane.

for cyclohexyl compared to adsorbed cyclohexane. The C–H soft mode are not observed for cyclohexane coadsorbed with surface hydrogen (dashed line in spectrum c). The decreased intensities of the peaks corresponding to C–C stretching mode at ~843 and ~1041 cm<sup>-1</sup> in spectrum b suggest that the cyclohexyl group may be oriented more nearly parallel to the surface than the cyclohexene ring.

Mechanistic studies with isotopic hydrogen clearly show that the surface intermediate formed by addition of gas phase atomic hydrogen primarily adds a single surface hydrogen to form cyclohexane. Figure 11 shows the TPR spectra taken from cyclohexene coadsorbed with hydrogen after exposure to 139 langmuirs of atomic deuterium. Singly deuterated cyclohexane $d_1$  (m/e = 85), not doubly deuterated cyclohexane- $d_2$  (m/e = 86), is the main hydrogenation product. Therefore, surface hydrogen must be involved in the hydrogenation process, although surface hydrogen alone cannot hydrogenate cyclohexene. Cyclohexene- $d_1$  (m/e = 83), cyclohexane (m/e = 84), and cyclohexane- $d_2$  (m/e = 86) are also formed in addition to the primary cyclohexane- $d_1$  product, indicating that some exchange also occurs. The intensity of the cyclohexane- $d_2$  peak at 170 K suggests that a small fraction of the deuterated intermediate may react with desorbing bulk deuterium.<sup>17</sup>

On the basis of these results, we propose a two-step mechanism for cyclohexane formation from adsorbed cyclohexene (Figure 12): (i) gas phase atomic hydrogen adds to adsorbed cyclohexene to form adsorbed cyclohexyl at 100 K;

(ii) the produced cyclohexyl is hydrogenated primarily by surface hydrogen to form cyclohexane.

#### **Summary and Conclusions**

Hydrogenation of cyclohexene is observed on the Ni(100) surface at 100 K during the exposure to gas phase atomic hydrogen. The formation of a cyclohexyl intermediate is indicated by both vibrational spectroscopy and isotope labeling experiments. The appearance of ring deformation modes and Ni-C stretching mode in the vibrational spectrum suggests cyclohexyl formation during atomic hydrogen exposure. Isotope experiments indicate that this cyclohexyl intermediate is singly hydrogenated to cyclohexane primarily by the surface hydrogen during subsequent TPR experiments. Hydrogen addition is the dominant process for both monolayer and multilayer cyclohexene during atomic hydrogen exposures. The absence of desorbing *n*-alkane products indicates that C-C bond activation is not an important process during reaction of gas phase atomic hydrogen with adsorbed cyclohexene. Hydrogen abstraction is significant with only multilayer cyclohexene. Surface hydrogen does not react with coadsorbed cyclohexene on the Ni(100) surface. Molecular desorption is the dominant thermal process for cyclohexene in the presence of coadsorbed hydrogen. Vibrational spectroscopy indicates that  $\pi$ -bonded cyclohexene with the C=C bond parallel to the surface is the dominant surface species in the presence of coadsorbed surface hydrogen. In contrast, di- $\sigma$ -bonded cyclohexene is the dominant species in the absence of coadsorbed hydrogen. In the absence of coadsorbed hydrogen, dehydrogenation of the adsorbed cyclohexene results in benzene formation with increasing temperature. Adsorbed benzene formed by dehydrogenation has been identified using vibrational spectroscopy after heating to 390 K in the absence of hydrogen. A fraction of this benzene desorbs at 440 K, with the remainder being dehydrogenated with increasing temperature.

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(31) For the estimation of cyclohexane yield, fragmentation patterns of desorbing cyclohexene and cyclohexane were obtained with 30 eV of ionization energy. Based on these fragmentation patterns, the 56 amu fragment corresponds to 20% of the total cyclohexane fragments and the 67 amu fragment is 26% of the total cyclohexene fragments. Ionization efficiencies of the two molecules were assumed to be the same for the yield estimation.

(32) The activation energy for hydrogen abstraction from cyclohexane in gas phase is 9 kcal/mol (Grief, D.; Oldershaw, G. A. J. Chem. Soc., Faraday Trans. 1 **1982**, 78, 1189). The activation energy for hydrogen abstraction from cyclohexene is expected to be larger than this value.

(33) This estimate is based on the standard formation enthalpies of di- $\sigma$ -bonded cyclohexene (-18 kcal/mol) and tri- $\sigma$ -bonded cycloallylic radical (-41 kcal/mol) on the Pt(111) surface. Standard formation enthalpies of these two species were provided by Bruce Koel.

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