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Gas Phase Atomic Hydrogen Induced Carbon−Carbon Bond Activation in Cyclopropane on the Ni(100) Surface

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Abstract: Carbon−carbon bond activation in adsorbed cyclopropane is observed following exposure to gas phase atomic hydrogen on the Ni(100) surface for temperatures as low as 100 K. Exposure to either gas phase atomic hydrogen or deuterium results in formation of adsorbed propyl. In both cases subsequent reaction between adsorbed propyl and coadsorbed hydrogen/deuterium produces propane at 121 K. The activation of a single C−C bond in adsorbed cyclopropane dominates as indicated by the fact that propane is the only product observed. No multiple C−C bond activation which would result in methane or ethane formation was ever observed. These reactions and their mechanisms have been investigated using temperature-programmed reaction (TPR) and vibrational spectroscopy using high-resolution electron energy loss spectroscopy (HREELS). The reactivities of hydrogen and deuterium were indistinguishable during these experiments so we have used the generic term hydrogen or gas phase atomic hydrogen to describe the reactions of both hydrogen and deuterium. The vibrational spectrum of adsorbed cyclopropane indicates weak interaction with the Ni(100) surface at 100 K. This weak interaction results in molecular cyclopropane desorption at 123 K with only a small amount of dehydrogenation. After atomic hydrogen exposure, a new loss feature appears at 383 cm^{-1} in the vibrational spectrum. This new mode corresponds to the Ni−C bond stretching mode of adsorbed propyl, the primary reaction intermediate. Carbon−carbon bond activation in adsorbed cyclopropane also causes substantial reduction in the intensities of cyclopropane's ring deformation modes at 821 and 1006 cm^{-1}. These results clearly indicate that C−C bond activation occurs during exposure to gas phase atomic hydrogen. Isotopic labeling studies reveal that the adsorbed propyl intermediate is hydrogenated by labelled surface hydrogen. Carbon−carbon bond activation in adsorbed cyclopropane has never been observed during adsorption on a surface with preadsorbed hydrogen nor during exposure to nascent hydrogen formed by dissociating molecular hydrogen. A detailed potential energy diagram for the reactions of adsorbed cyclopropane on the Ni(100) surface is developed based on results from these experiments and the literature.

Introduction

Skeletal rearrangement in alkanes is an important catalytic process which requires carbon−carbon bond activation. Despite the fact that C−C bonds are weaker than either H−H or C−H bonds, C−C bond activation is less frequently observed in catalytic reactions by transition metals. This disparity in reactivity is thought to result from inefficient binding of C−C bonds to transition metals during the initial approach, due either to the directional character of carbon p orbitals or steric hindrance caused by tetrahedral bonding of carbon.[1,2]

Recently, quantum chemical model calculations have been used to estimate the energetics for intermolecular C−C bond activation by transition metals. Model calculations have been performed for C−C bond activation by second-row transition metal atoms in ethane, cyclopropane, and cyclobutane.[2] For a given transition metal atom, the calculated activation energy for metal atom insertion into C−C bonds is always the lowest for cyclopropane because of the ring strain present in both the metallacyclobutane product and the cyclopropane reactant.[2] These calculations also suggest that palladium has the lowest barrier for C−C bond activation among the second-row transition metal atoms. The calculated activation energies for palladium atom insertion into the C−C bond are 31.8 kcal/mol for ethane, −1.9 kcal/mol for cyclopropane, and 15.6 kcal/mol for cyclobutane. The activation energy of Ni atom insertion to the C−C bond of cyclobutane is 32.6 kcal/mol.[2]

Model calculations have also been used recently to characterize the unusual reactivity of cyclopropane compared to normal alkanes and other cycloalkanes. Wong et al. have summarized the literature relating the special reactivity of cyclopropane to its thermodynamic and bonding properties.[3] Cyclopropane has significant angular and torsional strain due to the cyclic arrangement of the C−C−C bond and the coplanar arrangement of the carbon atoms which mandates the C−H bonds be eclipsed. The relief of strain associated with ring opening is often invoked to rationalize the high reactivity of the cyclopropyl group. However, ring strain alone is not sufficient to explain the large differences in reactivity observed between cyclopropane and cyclobutane since the amount of ring strain relieved during the ring opening process is similar in both cases.[2] The σ aromaticity of cyclopropane has also been proposed to explain the large difference in reactivity between cyclopropane and cyclobutane. The σ aromaticity of cyclopropane has been reviewed by Dewar[4] and Cremer.[5] Aromatic stabilization results in 17 kcal/mol of stabilization in cyclopropane.[5] For the reactions of cyclopropane with electrophiles, aromaticity is thought to be maintained in the transition state and therefore the activation barrier is low.[4] Thus, in addition to the relieving

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ring strain during ring opening, the fact the cyclopropyl remains essentially intact in the ring-opening transition states accounts for its high reactivity.

Recent experimental studies have shown that the C−C bond in cyclopropane can be activated by transition metal complexes of nickel(0),[6] palladium(0),[7] palladium(II),[8] platinum(0),[9] platinum(II),[10] and iridium(I).[11] Co-condensation of atomic Ni vapor and cyclopropane in an Ar matrix results in spontaneous Ni atom insertion into the C−C bond of cyclopropane at 12 K forming nickelacyclobutane.[12] However, photoactivation is required for insertion of atomic iron into the C−C bond of cyclopropane at 10−15 K in an argon matrix.[13] The high reactivity of cyclopropane has also been demonstrated in the gas phase. Reactions with atomic hydrogen in a gas-phase flow discharge system result in both hydrogen abstraction and C−C bond activation producing methane.[14] Hydrogen abstraction to form cyclopropyl and its subsequent hydrogenation to form propylene is suggested as the initial step of this gas-phase reaction.[14]

The reaction of cyclopropane (1 Torr) with hydrogen (100 Torr) on the Ni(111) and Ni(100) surfaces results in both single C−C bond activation (propane formation) and multiple C−C bond activation (methane and ethane formation).[15] The estimated thermal activation barrier for cyclopropane ring opening on the Ni(100) surface is 15 kcal/mol.[15] The Ni(100) surface has higher reactivities than the Ni(111) surface for both single and multiple C−C bond activation. For the Ni(100) surface, single C−C bond activation is dominant below 465 K while multiple C−C bond activation dominates at higher temperatures. Similar reactivity patterns have been observed in the 1−10-Torr range with excess hydrogen for the Ir(111) and the Ir(110)−(1×2) surfaces since single C−C activation is dominant below 500 K and the more open Ir(110)−(1×2) is more active.[16] Similar patterns were also observed for the Ru(0001) and Ru(11$\bar{2}$0) surfaces in the 1-Torr range with excess hydrogen since the more open Ru(11$\bar{2}$0) surface is more active and increasing temperature favors multiple bond activation.[17]

The reactions of cyclopropane on supported transition metal catalysts lead to C−C bond activation above room temperature in hydrogen atmospheres. On supported Ni catalysts a mixture of methane, ethane, and propane was formed for hydrogen pressures in the 70 to 700 Torr range and temperatures in the 290 to 410 K range.[18] The activation energy of cyclopropane hydrogenolysis on the supported Ni catalysts was reported to be 13 kcal/mol.[18]

No hydrogenation or hydrogenolysis has been observed for cyclopropane adsorbed on transition metal surfaces in the absence of gas-phase cyclopropane and hydrogen. Dehydrogenation is observed during cyclopropane adsorption on the Ir(110)−(1×2) surface at 100 K for exposures of 1.7 L or less.[19] For larger exposures, cyclopropane adsorbs molecularly with an adsorption probability of unity. Preadsorbed hydrogen inhibits dehydrogenation of cyclopropane on the Ir(110)−(1×2) surface but does not induce ring opening or hydrogenation.[19] Cyclopropane adsorbs molecularly on the Ir(111) surface at 100 K and no significant dehydrogenation occurs during subsequent heating.[19] On the Ru(001) surface, cyclopropane interacts very weakly with the surface and desorbs intact at 150 K without dehydrogenation.[20] On this surface, cyclopropane adsorbs with C_s symmetry which corresponds to a slight ring deformation or an inclination of the ring with respect to the surface.

In our work, reactions of adsorbed cyclopropane with gas-phase atomic hydrogen have been investigated on the Ni(100) surface. Gas-phase atomic hydrogen induces a wide range of surface reactions, which do not occur with adsorbed surface hydrogen. Gas-phase atomic hydrogen induces low-temperature cyclohexene hydrogenation on Ni surfaces,[21] ethylene and benzene hydrogenation on the Cu(111) surface,[22] hydrogen addition to ethylene on the Cu(100) surface,[23] hydrogenation of carbon monoxide on the Ru(001) surface,[24] and hydrogen abstraction from cyclohexane on the Cu(111) surface.[25] Most surface reactions caused by gas-phase atomic hydrogen occur via Eley−Rideal (ER) mechanism.[21−25] The ER mechanism is characterized by the direct reaction of incoming reagent from the gas phase with adsorbed species on impact.

Experimental Section

The experiments were performed in the UHV chamber equipped with instruments for Temperature Programmed Reaction Spectroscopy (TPRS), Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction spectroscopy (LEED), High Resolution Electron Energy Loss Spectroscopy (HREELS), and X-ray Photoelectron Spectroscopy (XPS). All surface analysis instruments were located on the same level so that a simple rotation about the manipulator was sufficient to position the sample in front of each spectrometer or source. The background pressure of the system during the experiments was $\sim 5 \times 10^{-11}$ Torr.

TPR spectra were taken using a Quadrupole Mass Spectrometer (QMS) and a linear heating rate of 3 K/s. The ionizer of the QMS was shielded by a gold plated cylinder with coaxial entrance tube. A low ionization energy (30 eV) was used for TPR experiments since the relative ion yields of hydrogen and deuterium are decreased significantly relative to hydrocarbons. With this decreased sensitivity to hydrogen, investigations of the reaction could be made with a smaller range of Mass Spectrometer (MS) sensitivities. This change significantly decreased the settling time required for each mass scan and improved our signal to noise. The sample was positioned 1 mm in front of this tube for TPR, so that only molecules desorbing from the flat center region of the sample could enter the ionizer through the coaxial tube. The desorption spectra were collected with Hunt Scientific

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Temperature Programmed Analysis software which programs the sample temperature and multiplexes the QMS to monitor a range of masses or up to 26 specific masses.[26] In these experiments, a range of masses was monitored during initial experiments and then selected discrete masses were monitored to provide more detailed information.

HREELS 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 a ~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.

The Ni(100) crystal was attached to an L-shaped manipulator that allows the 3-coordinate displacements and a full 360° rotation about the manipulator axis. The sample was cooled to 98 K with an internal liquid nitrogen reservoir. The sample could be heated up to 1100 K by passing a DC current through two 0.5-mm Ta support wires that were spot welded to the edge of the 1.5 cm diameter Ni crystal disk. A 0.01 mm diameter chromel−alumel (K type) thermocouple spot welded to the back of the crystal was used for temperature measurement. The Ni(100) crystal was cleaned by Ar^+ sputtering followed by annealing to 1000 K, oxygen treatment, and hydrogen treatment. The cleanliness of the surface was verified by AES.

Micro-channel array-directed beam dosers and leak valves were used for reagent dosing. All exposures were performed in front of directed doser assembly which minimizes system contamination. Cyclopropane (Matheson, 99%) was used as received. Hydrogen (Matheson 99.9999%) and deuterium (Matheson 99.5%) were used without further purification both for molecular hydrogen adsorption and for the production of atomic hydrogen. Gas-phase atomic hydrogen was created on a 1800 K tungsten filament by the dissociation of molecular hydrogen at 9.0×10^{-7} Torr. Gas-phase atomic deuterium was produced in the same way. The theoretical limit for the dissociation efficiency is approximately 0.3 per H_2 collision under the experiment conditions used.[27,28] Thus the hydrogen flux from the W filament was a mixture of molecular hydrogen and atomic hydrogen. In this paper, the term “atomic hydrogen” is used for convenience to indicate this mixture of hydrogen atoms and molecular hydrogen. Gas-phase atomic hydrogen and deuterium showed identical reactivities in the experiments we performed. Therefore all vibrational studies were performed with gas-phase atomic hydrogen to avoid compression of the vibrational spectrum due to the isotope effect. TPR experiments were conducted with gas-phase atomic deuterium to differentiate product peaks from the ^{13}C isotope peaks of the reactants. The Ni surface was exposed to the beam of atomic hydrogen in a line of sight geometry. The Ni crystal was positioned ~5 cm away from the end of a 9 cm long W coil during atomic hydrogen dosing. Heating by the radiation from the hot W filament was minimized by housing the W filament in a liquid nitrogen filled Cu cooling block. In this way, the temperature of the Ni crystal in front of the hot W filament could be kept below 110 K. Since an accurate dissociation coefficient is not available from this experiment, exposures of atomic hydrogen are given in terms of exposures of molecular hydrogen to the W filament as measured by an ion gauge. In this work, exposure units are arbitrary and included primarily as a basis for internal comparisons. Exposures are presented in Langmuirs ($1\ L = 1 \times 10^{-6}$ Torr s) based on the background pressure reading from the ion gauge and have not been corrected for large preferential dosing fluxes and ion gauge sensitivity factors.

Results

The reactivities of hydrogen and deuterium were indistinguishable during these experiments. We have indicated the isotope being used, but have generally performed similar experiments with both isotopes to confirm the results. The isotopes used are also clearly identified in all figures. Specific isotopes are clearly identified for the isotope labeling experiments. Generally, TPRS experiments performed with gas-phase atomic deuterium are presented to clarify the results. Gas-phase atomic hydrogen has been used for the vibrational experiments to simplify the spectra and avoid spectral compression caused by the isotope effect.

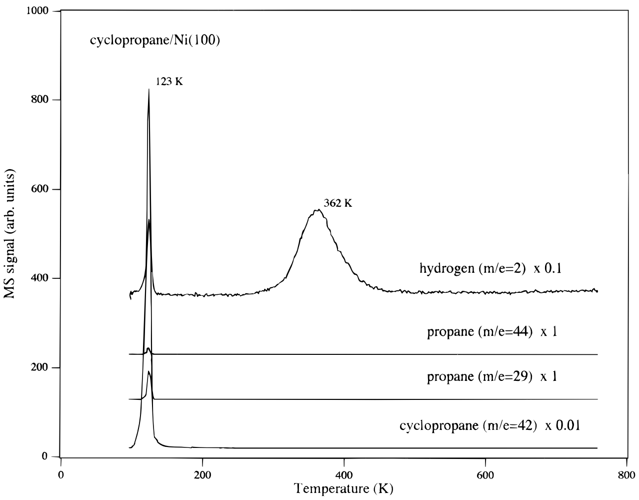

Figure 1. TPR spectra of Ni(100) taken after exposure to 0.024 L of cyclopropane. Most adsorbed cyclopropane desorbs at 123 K without reaction.

Cyclopropane on the Ni(100) Surface. The interaction of cyclopropane with the surface is weak and most cyclopropane desorbs intact when heated. The TPR spectra in Figure 1 were taken from the Ni(100) surface after exposure to 0.024 L of cyclopropane at 100 K. Molecular desorption of cyclopropane at 123 K clearly dominates during heating. With increasing exposure, the cyclopropane desorption peak increases without saturation within the range of experiments performed. No additional desorption feature has been observed with exposures up to 0.16 L, the highest exposure used. Similar low-temperature molecular desorption of cyclopropane has been previously observed below 160 K on the Ru(001)[29] and Ir(110)[19] surfaces. A very small amount of adsorbed cyclopropane is dehydrogenated on the Ni(100) surface during the TPR experiments producing the hydrogen peak at 362 K. Hydrogen produced by the dehydrogenation is estimated to be less than 0.04 monolayer based on the comparison with the TPRS of saturated monolayer hydrogen. The uncertainty of this coverage estimate is ±2% relative to the saturation hydrogen coverage. No self-hydrogenation or hydrogenolysis has been observed as evidenced by the absence of propane peaks at 44 and 29 amu. The small 29-amu peak at 123 K (<0.05% of desorbing cyclopropane) is caused by fragmentation of cyclopropane. The small 44-amu peak (<0.01% of desorbing cyclopropane) at 123 K is caused by the natural abundance of ^{13}C isotope in the desorbing cyclopropane. The 2-amu peak around 123 K is caused by the fragmentation of cyclopropane in the ionizer since the intensity decreases dramatically as the ionization energy is decreased. A careful analysis of cyclopropane peak shape indicated that the desorption order is one.[30] The peak temperature for cyclopropane does not shift with the increased exposure also indicating that cyclopropane desorption from the Ni(100) surface is first order. The activation energy for cyclopropane desorption is approximately 7 kcal/mol based on the Redhead method[31] assuming first-order desorption and a $10^{12}-10^{13}$ preexponential factor.

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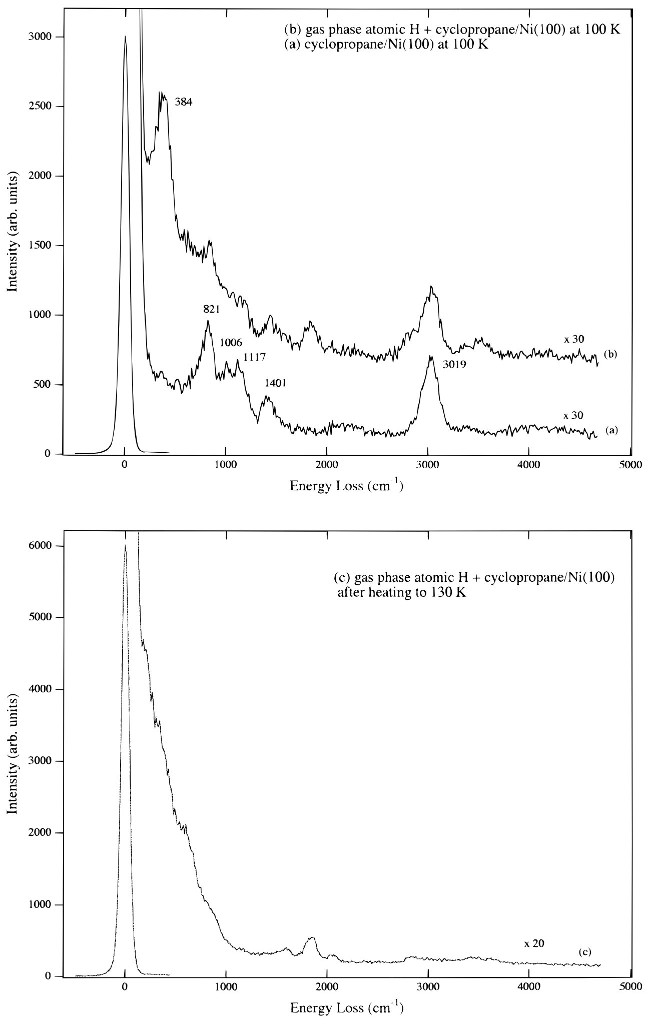

Figure 2. HREELS spectra of cyclopropane taken (a) at 100 K, (b) at 100 K after exposure to gas phase atomic hydrogen, and (c) after heating to 130 K after atomic hydrogen exposure. Spectrum a corresponds to weak adsorption of molecular cyclopropane. The new loss features at 383 cm^{-1} and around 2800 cm^{-1} in spectrum b indicate formation of adsorbed propyl at 100 K.

The HREELS spectrum of adsorbed cyclopropane also offers a strong indication of weak molecular adsorption of cyclopropane on the Ni(100) surface at 100 K. Spectrum a in Figure 2 was taken at the specular angle following a 0.01 L cyclopropane exposure at 100 K. Mode assignments for the peaks observed (Table 1) are based on comparisons with the vibrational spectrum of gas-phase cyclopropane[32] and comparisons with HREELS spectra of cyclopropane on the Ru(001),[33] Pt(111),[34] and Cu(110)[35] surfaces. The HREELS spectrum of cyclopropane shown in Figure 2a parallels the vibrational spectra of the gas-phase cyclopropane molecule. The peaks at 821 and 1006 cm^{-1} correspond to ring-deformation modes. The peak at 1117 cm^{-1} is caused by a ring-stretching mode. The peak at 3019 cm^{-1} is the C−H stretching mode. No indication of C−H mode softening was observed as expected since no C−H mode softening has been reported for cyclopropane on other metal surfaces.[33−35]

Table 1. Vibrational Modes of Gas-Phase Cyclopropane[32] and Cyclopropane Adsorbed on the Ni(100) Surface at 100 K[a]

mode number	gas phase	adphase	description[33−35]
ν_{14}	741		CH$_2$ rock
ν_7	854 (w)		CH$_2$ rock
ν_{11}	866 (vs)	821	ring deform.
ν_5	(975)		CH$_2$ wag
ν_{10}	1028 (vs)	1006	ring deform.
ν_{13}	(1050)		CH$_2$ twist
ν_4	(1125)		CH$_2$ twist
ν_3	1188	1117	ring breathing (stretch)
ν_9	1442 (m)	1401	CH$_2$ scissor
ν_2	1475		CH$_2$ scissor
ν_8	3025 (s)		CH$_2$ sym stretch
ν_1	3027	3019	CH$_2$ sym stretch
ν_{12}	3075		CH$_2$ asym stretch
ν_6	3101(s)		CH$_2$ asym stretch

[a] For the gas phase modes, IR, Raman, and inactive modes (in parentheses) are listed. Approximate transition cross sections for the IR active modes are indicated (vs = very strong, m = medium, w = weak).

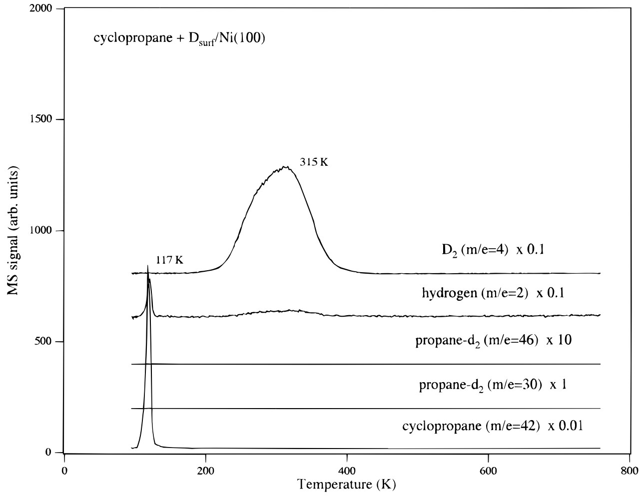

Figure 3. TPR spectra taken from a Ni(100) surface preexposed to 0.5 L of deuterium and then exposed to 0.020 L of cyclopropane at 100 K. Cyclopropane desorbs at 117 K without significant reaction.

Cyclopropane Coadsorbed with Surface Hydrogen. Coadsorbed surface hydrogen does not induce any significant reaction in adsorbed cyclopropane during TPR experiments. Figure 3 is the thermal desorption spectrum of cyclopropane on the Ni(100) surface preexposed to 1.1 L of molecular deuterium. In the presence of coadsorbed surface deuterium, the desorption temperature of cyclopropane decreases by 6 deg to 117 K. No C−C bond activation by surface deuterium has been observed. Coadsorbed surface deuterium clearly inhibits dehydrogenation of adsorbed cyclopropane and results in a substantial decrease in the amount of hydrogen formed during the TPR experiment. Isotope exchange between surface deuterium and adsorbed cyclopropane is not significant. The intensity of the 43-amu peak observed was approximately 4% of that for the 42-amu peak, which corresponds to the natural abundance of the ^{13}C isotope of cyclopropane. A very weak broad 2-amu peak appears between 220 and 380 K. Considering peak size and peak position, we believe this small hydrogen peak is due to the fragmentation of deuterium. A similar 2-amu peak has been observed for the desorption of surface deuterium on the Ni(100) surface. As discussed earlier, the 2-amu peak at 117 K is caused by the fragmentation of cyclopropane in the

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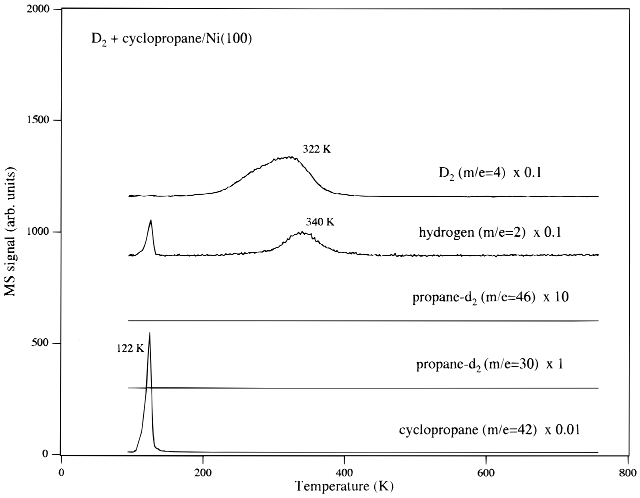

Figure 4. TPR spectra taken from the Ni(100) surface preexposed to 0.024 L of cyclopropane then exposed to 81 L of D_2. No hydrogenation by gas-phase molecular deuterium or nascent surface deuterium is observed.

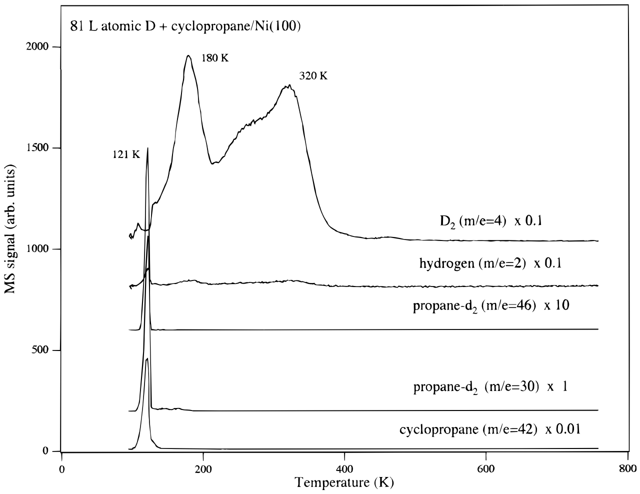

Figure 5. TPR spectra taken from the Ni(100) surface preexposed to 0.024 L of cyclopropane then exposed to 81 L of gas-phase atomic deuterium. Propane-d_2 is formed at 121 K by C−C bond activation.

ionizer. Increasing the amount of deuterium preexposure to 3.6 and 6.3 L did not make any significant change in the reaction.

Cyclopropane Exposed to Gas-Phase Molecular Hydrogen. Dissociative adsorption of molecular hydrogen on the Ni(100) surface is an exothermic process which liberates 23 kcal/mol.[36] Dissociating gas-phase molecular hydrogen on surfaces partially covered with cyclopropane might result in reaction prior to thermal accommodation of the adsorbed H atoms formed. Figure 4 shows the TPRS of cyclopropane postexposed to 81 L of molecular deuterium. No indication of C−C bond activation is shown. No peak corresponding to either propane-d_1 (45 amu) or propane-d_2 (46 amu) was observed. Molecular cyclopropane desorption at 122 K is the dominant thermal process. Dehydrogenation of a small amount of cyclopropane still occurs resulting in hydrogen desorption at 340 K from the surface.

Cyclopropane Exposed to Gas-Phase Atomic Hydrogen. Incoming hydrogen atoms from the gas phase induce C−C bond activation in cyclopropane on the Ni(100) surface at 100 K. Figure 5 shows the TPR spectra of adsorbed cyclopropane exposed to gas-phase atomic deuterium. Doubly deuterated propane (46 amu) is formed and desorbs at 121 K. The amount of propane product increases with the increased deuterium atom exposure (Figure 6). Unreacted cyclopropane desorbs from the surface at 121 K. No methane or ethane (or their deuterated counterparts) was ever observed during exposures to gas-phase atomic hydrogen (deuterium). No significant amount of deuterated cyclopropane is produced from the reaction with atomic deuterium. The intensity of the 43-amu peak after atomic deuterium exposure was basically identical in size to the 43-amu peak from the ^{13}C isotope of cyclopropane. Auger analysis after these experiments indicates that no residual carbon remains on the surface. During the exposure to atomic deuterium, the surface is saturated with adsorbed deuterium and bulk deuterium is also formed. The broad deuterated propane desorption feature at 128−194 K is caused by the reaction of cyclopropane with desorbing bulk deuterium formed during atomic deuterium exposure. For comparison, the reactivity of bulk deuterium alone is shown in Figure 8. The deuterium peak at 180 K in Figure 5 corresponds to the desorption of approximately 0.5 monolayer equivalents of bulk deuterium, which has been formed during atomic deuterium exposure. The deuterium peaks at 270 and 320 K are caused by the desorption of a full monolayer of adsorbed deuterium also formed during the atomic deuterium exposure. A sharp decrease in intensity of the deuterium desorption peak at 121 K is observed. The area of this dip is proportional to the amount of propane-d_2 formed at 121 K as shown in Figure 7.

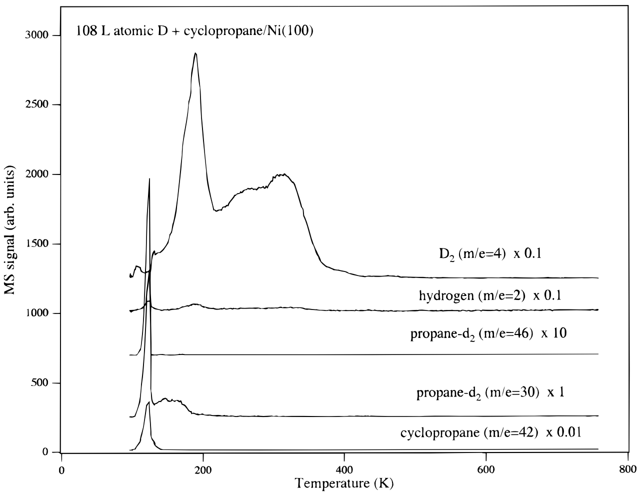

Figure 6. TPR spectra taken from the Ni(100) surface preexposed to 0.023 L of cyclopropane then exposed to 108 L of gas-phase atomic deuterium. The yield of propane-d_2 observed at 121 K increases with the increased deuterium atom exposure.

Propane formation at 121 K is not caused by desorbing bulk deuterium since C−C bond activation by desorbing bulk deuterium occurs at a higher temperature. C−C bond activation in the 128 to 194 K temperature range has been previously observed in the reaction with desorbing bulk deuterium alone.[37] Figure 8 shows the TPR spectra of cyclopropane reacting with bulk deuterium in the absence of gas-phase atomic deuterium. Due to the desorption temperature difference between cyclopropane and bulk hydrogen, only a small amount of cyclopropane reacts with bulk deuterium.

Hydrogen abstraction is not significant during atomic hydrogen (or deuterium) exposures to cyclopropane adsorbed on the Ni(100) surface. The vibrational results show no indication of hydrogen abstracted products. The HREELS spectrum taken at 130 K after desorption of the propane product shows no

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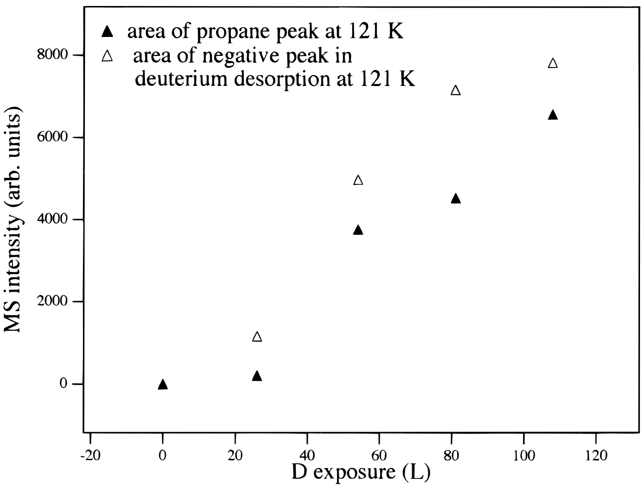

Figure 7. Propane yield at 121 K vs the integrated area of the negative D_2 dip at the same temperature. The decrease in the amount of D_2 desorbed is proportional to the propane yield at 121 K.

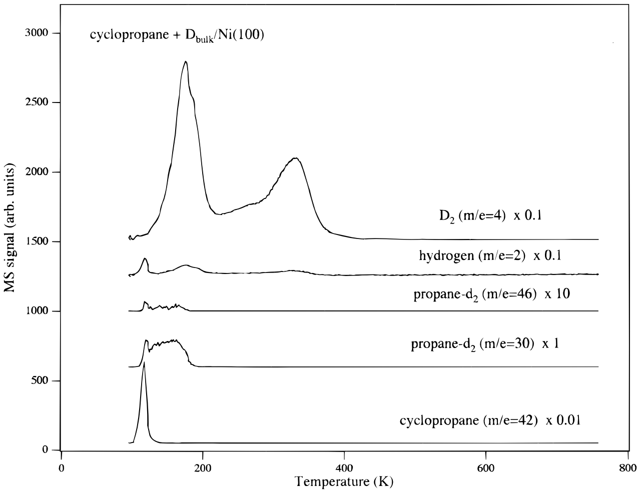

Figure 8. TPR spectra following a 0.032-L exposure of cyclopropane to the Ni(100) crystal containing 1 monolayer equivalent of bulk hydrogen and 1 monolayer of surface hydrogen in the absence of gas-phase atomic hydrogen exposure. A small amount of propane-*d_2* is formed over the 128−194 K temperature range, well above the 121 K propane peak temperature observed following reaction with gas-phase atomic hydrogen.

indication of strongly adsorbed hydrogen-abstracted organic products (Figure 2c). The formation of deuterated cyclopropane is not significant during atomic deuterium exposure indicating that abstraction followed by rehydrogenation of the reactant is not significant. Hydrogenation of hydrogen-abstracted products after C−C bond activation could lead to the formation of propylene. Adsorbed propylene desorbs at a higher temperature[38] than weakly adsorbed cyclopropane so we can easily distinguish gas-phase cyclopropane and propylene despite the similarity in their MS fragmentation patterns.[39] In these experiments, no hydrocarbon desorption has been observed at a higher temperature than the desorption temperature of cyclopropane. In the gas-phase reactions of cyclopropane with atomic hydrogen, hydrogen abstraction followed by hydrogen addition and isomerization are believed to dominate,[14] and methane is the dominant hydrocarbon product observed. In these studies on the Ni(100) surface, methane formation has never been observed. Taken together these observations indicate that hydrogen abstraction during atomic hydrogen exposure of cyclopropane is not significant. Hydrogen abstraction has been observed in reactions with larger cycloalkanes adsorbed on this surface, and the dehydrogenation of the hydrogen-abstracted species was observed in follow-up TPR experiments.[40] For cyclopentane adsorbed on the Ni(100) surface, both C−C bond activation and hydrogen abstraction occur during atomic hydrogen exposure.[40] In the reaction with adsorbed cyclohexane, hydrogen abstraction has also been observed using TPRS.[40]

HREELS spectra taken from a monolayer of cyclopropane after atomic H exposure clearly show that gas-phase atomic hydrogen is directly activating the adsorbed cyclopropane at 100 K (Figure 2). Spectrum b in Figure 2 was taken at 100 K right after hydrogen atom exposure of adsorbed cyclopropane. A new peak appears around 383 cm^{-1} due primarily to the Ni−C stretching mode[41−43] of adsorbed propyl. A C−H soft mode is also observed around 2800 cm^{-1} which is consistent with propyl formation. The C−H soft modes of adsorbed alkyls have been previously observed on several Cu surfaces[44−47] and explained by the softening of α-CH bonds. The intensities of cyclopropane's ring-deformation modes at 821 and 1006 cm^{-1} and ring-stretching mode at 1117 cm^{-1} are reduced after exposure to atomic hydrogen suggesting a decrease in the concentration of adsorbed cyclopropane. The small intensity of methyl's symmetric deformation mode around 1385 cm^{-1} (Figure 2b) suggests that the terminal methyl group of propyl is likely to have a tilted orientation with respect to the surface normal.[44−47] The peak at 1434 cm^{-1} may be caused by the antisymmetric deformation mode of the methyl group as well as the CH_2 scissoring mode. Spectrum c in Figure 2 was obtained after heating the sample used for spectrum b to 130 K to desorb cyclopropane and propane. Most loss features disappear after heating to 130 K, as expected. Small peaks corresponding to background CO adsorption appear during spectral acquisition. The increased background intensities below 1200 cm^{-1} are caused by the vibrational modes of surface hydrogen and bulk hydrogen. Surface hydrogen modes appear in the ranges of 530−630 and 1100−1200 cm^{-1}.[48−51] The vibrational peak for bulk hydrogen in a Ni crystal appears around 800 cm^{-1}.[48,49] As seen in Figure 5, the desorption temperature of both surface hydrogen and bulk hydrogen is higher than 130 K.

Atomic Deuterium Exposure of Cyclopropane Coadsorbed with Surface Hydrogen. In order to characterize the reaction mechanism, a series of isotope-labeling experiments have been performed which focus on the role of adsorbed surface hydrogen in the reaction. When cyclopropane coadsorbed with hydrogen is exposed to gas-phase atomic deuterium, singly deuterated propane is the primary reaction product (Figure 9a). The

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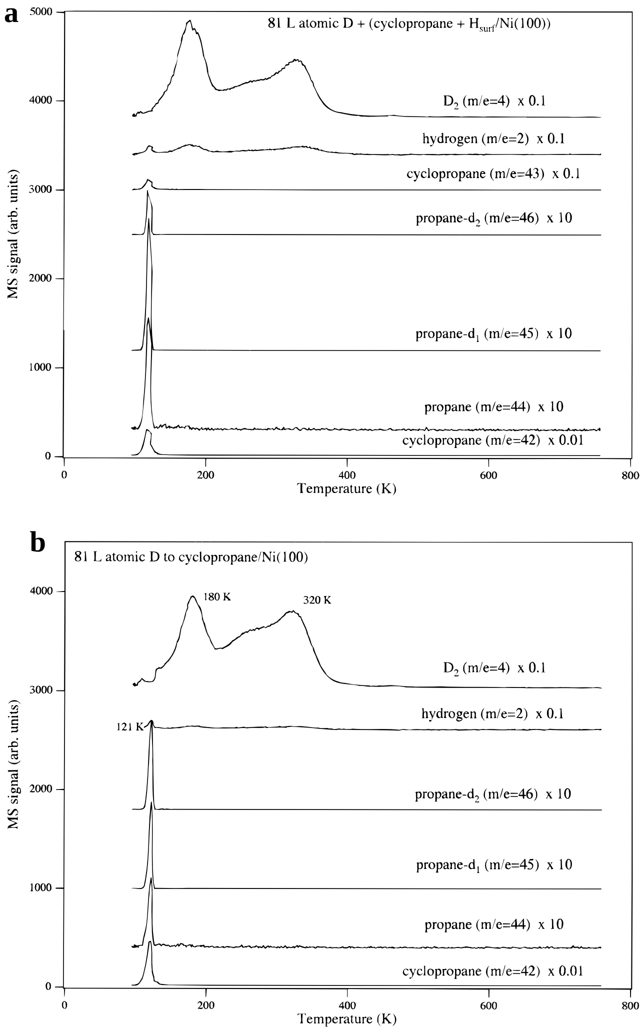

Figure 9. TPR spectra taken (a) after 81-L exposure of gas-phase atomic deuterium to cyclopropane coadsorbed with surface hydrogen on the Ni(100) surface. Propane-d_1, not propane-d_2, is the main reaction product indicating that adsorbed propyl is hydrogenated by surface hydrogen. TPR spectra taken (b) after a 81-L exposure of gas-phase atomic deuterium to the Ni(100) surface preexposed to 0.024 L of cyclopropane. Note the relative size of the propane fragments in the primary propane-d_2 reaction product observed.

decrease of the deuterium desorption rate at the propane formation temperature (121 K) is not significant in this case. Singly deuterated propane rather than doubly deuterated propane is the main reaction product as evidenced by the fact that the propane-d_1 (45 amu) peak is three times as large as the 46-amu (propane-d_2) peak. This intensity ratio indicates that approximately 2.1 times as much propane-d_1 as propane-d_2 is formed after correcting for fragmentation. In the reference spectrum of propane, the intensity of the M − 1 ion of propane is 0.87 relative to the intensity of the parent molecular ion.[37] The large intensity of the 44-amu peak is also consistent with the fact that singly deuterated propane is the primary product. In Figure 9a, the 44-amu peak has an intensity 0.84 of the 45-amu (propane-d_1) peak resulting from the M − 1 fragment of propane-d_1, the M − 2 fragment of propane-d_2, and the M + 2 ion of naturally occurring double ^{13}C cyclopropane. When adsorbed cyclopropane is exposed to gas-phase atomic deuterium in the absence of preadsorbed hydrogen, propane-d_2 (46 amu) is the primary reaction product and the decrease of the deuterium desorption rate at 121 K is clearly observable (Figure 9b). The fragmentation patterns observed in this case are consistent in detail with the fragmentation patterns observed when propane-d_1 is the primary product. The 45-amu peak at 121 K has 87% of the intensity of the 46-amu peak, and corresponds to the M − 1 ion of propane-d_2. The intensity of the 44-amu peak is consistent with contributions primarily from the M − 2 ion of propane-d_2 and the natural abundance of the ^{13}C isotope in the desorbing cyclopropane. In the reference mass spectrum of propane, the intensity of the M − 2 ion is 0.23 relative to the intensity of the molecular ion.[39] The TPRS spectrum of cyclopropane adsorbed alone shows that the peak size of 44 amu, the double ^{13}C isotope of cyclopropane, is 0.1% of the 42-amu peak of cyclopropane (Figure 1).

Discussion

Adsorbed Cyclopropane. Molecular cyclopropane adsorbs weakly as indicated by both TPRS and vibrational spectroscopy. TPRS of cyclopropane adsorbed alone indicates that most cyclopropane desorbs without dissociation at 123 K. Only a very small amount of surface hydrogen (<0.04 monolayer) is produced by dehydrogenation. No dehydrogenation is observed when cyclopropane is adsorbed on a hydrogen precovered surface. Since similar total amounts of cyclopropane desorb when cyclopropane is adsorbed alone and adsorbed on a hydrogen precovered surface, dehydrogenation is not a significant reaction. The similarity observed between the vibrational spectrum of gas-phase molecular cyclopropane and the vibrational spectrum of adsorbed cyclopropane also indicates that the adsorbed cyclopropane interacts weakly with the surface. No C−H soft modes are observed in the vibrational spectrum of adsorbed cyclopropane indicating that no specific Ni−H(−C) interactions are occurring. The similarity of the vibrational data for cyclopropane on Ni(100) to a more detailed vibrational study of cyclopropane adsorbed on the Ru(001) surface[20] suggests that cyclopropane's ring is adsorbed in a tilted configuration on the Ni(100) surface with no detectable specific chemical interactions. Cyclobutane desorbs from this surface at 140 K[40] indicating that the interaction between cyclobutane and the Ni(100) surface is slightly larger than the interaction between cyclopropane and the surface. This small increase in interaction energy observed for cyclobutane suggests that the weak interactions are quite similar. By inference this result suggests that the σ aromaticity of cyclopropane does not play an important role in the bonding with the surface. In both cases no specific chemical interaction with the surface is occurring. The large C−H bond energy of cyclopropane limits dehydrogenation ensuring weak adsorption despite the fact that Ni is extremely active for C−H bond activation. Among single crystal transition metal surfaces studied, only the very open reconstructed Ir(110)−(1×2) induces C−H bond activation in adsorbed cyclopropane at 100 K.[19]

No significant Ni insertion or thermally induced ring opening is observed on the clean Ni(100) surface. As indicated above, cyclopropane is weakly adsorbed and desorbs from the surface at 123 K, therefore in these TPRS studies only reactions which occur below 123 K can be observed. However, Ni insertion is observed at 12 K in Ar matrix studies with Ni gas. Ni vapor has 102 kcal/mol of potential energy relative to Ni solid[52] which may facilitate Ni atom insertion to the C−C bond of cyclopropane. Ni atom insertion is also observed after 48 h at 333 K for the reaction of methylenecyclopropane with methyl arcrylate in the presence of the Ni(0) complex (bis(acrylonitrile)-nickel(0)).[6] To the best of our knowledge, no insertion reactions have been reported for Ni multinuclear clusters. Taken together these results suggest that steric accessibility as well as the

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(52) *CRC Handbook of Chemistry and Physics*, 69th ed.; Weast, R. C., Ed; CRC Press: Boca Raton, FL, 1989; p F-182.

potential energy of Ni atom may play an important role in controlling the reactions of cyclopropane with Ni.

Coadsorbed Hydrogen and Cyclopropane. Coadsorbed hydrogen does not activate the C−C bond in cyclopropane on the Ni(100) surface during TPR experiments. A comparison between the activation energies of hydrogenation and desorption presented in the next section clearly indicates that molecular desorption should be preferred relative to hydrogenation by coadsorbed surface hydrogen. The small amount of dehydrogenation observed in the absence of preadsorbed hydrogen is largely inhibited by preadsorbed hydrogen. In contrast, post-adsorbed hydrogen does not inhibit dehydrogenation. These results suggest that preadsorbed hydrogen occupies surface defect sites and blocks dehydrogenation. Coadsorption with hydrogen decreases cyclopropane's desorption temperature from 123 to 117 K indicating that the interaction with the surface is decreased slightly. Preadsorbed cyclopropane was exposed to adsorbing molecular hydrogen to search for potential reactions which might be induced by the "hot" nascent hydrogen produced during dissociation. No detectable C−C bond activation by adsorbing molecular hydrogen was observed.

C−C Bond Activation Induced by Gas-Phase Atomic Hydrogen. The appearance of adsorbed propyl formed by reaction of gas-phase atomic hydrogen with adsorbed cyclopropane indicates that gas-phase atomic hydrogen induces C−C bond activation in adsorbed cyclopropane to form propyl at 100 K. The adsorbed propyl has been identified based on the appearance of a Ni−C stretching mode and the C−H soft mode after atomic hydrogen exposure. The results of isotopic experiments clearly indicate that the adsorbed propyl, the intermediate, is hydrogenated primarily by surface hydrogen to form propane. Formation of propane-d_1 as the primary product of the reaction of gas-phase atomic deuterium with cyclopropane coadsorbed with hydrogen clearly indicates that surface hydrogen is involved in the reaction, although adsorbed hydrogen alone cannot initiate the reaction. Hydrogenation of adsorbed propyl by surface hydrogen has been previously observed by Zaera et al. during the reactions of propyl iodide on clean and deuterium precovered Ni(100) surfaces.[53] This hydrogenation reaction occurs at 160 K since the hydrogenation is rate limited by C−I bond activation in the propyl iodide. In fact, hydrogenation of alkyl adsorbates by surface hydrogen is a common reaction for alkyl halides and has been demonstrated for the reactions of several alkyl iodides on Ni(100),[53,54] Pt(111),[55] and Cu(110)[56] surfaces.

The hydrogenation of adsorbed propyl intermediate by surface hydrogen also causes the abrupt "dip" or depletion peak in the deuterium TPR spectrum during cyclopropane formation at 121 K. The abrupt decrease of the deuterium desorption rate during propane-d_2 desorption suggests that propyl hydrogenation by surface deuterium produces empty surface sites. Desorbing bulk hydrogen refills the empty surface sites generated by the propyl hydrogenation resulting in abrupt decrease in the deuterium desorption rate. The replenishment of the surface adsorption site by desorbing bulk hydrogen has been observed previously on the Ni(111)[48] and Ni(100)[57] surfaces. This intensity decrease of deuterium during deuterated propane formation is not observed for the reaction performed on the hydrogen-pretreated surface since the propyl being formed is hydrogenated primarily by preadsorbed hydrogen.

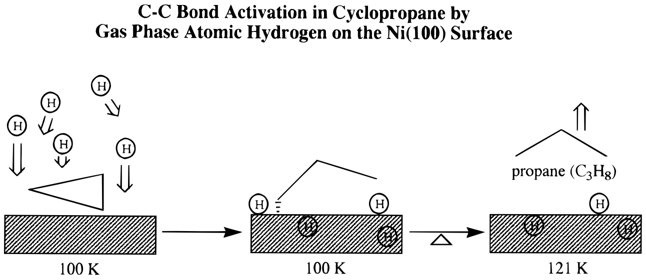

Figure 10. The reaction mechanism for the cyclopropane hydrogenation observed during these experiments. Gas-phase atomic hydrogen addition to adsorbed cyclopropane activates the C−C bond to form propyl, the primary reaction intermediate. This adsorbed propyl is hydrogenated by surface hydrogen in a subsequent heating process to form propane which desorbs from the surface.

Based on the disparity between the temperatures for bulk hydrogen desorption and propane desorption, we feel that hydrogenation of propyl by desorbing bulk hydrogen is not significant. During TPRS experiments, propane desorbs first at 121 K and bulk hydrogen desorbs at 180 K suggesting that most adsorbed propyl is hydrogenated and desorbs as propane below the temperature where bulk hydrogen diffuses out of the bulk and becomes available for reaction. Previously, hydrogenation of cyclohexene on the Ni(100) surface[21] and methyl and ethylene on the Ni(111) surface[49] by desorbing bulk hydrogen have been observed at ∼180 K, the peak temperature of bulk hydrogen desorption.

Ethane and methane formation are not observed in the reaction of cyclopropane with gas-phase atomic hydrogen indicating that the propyl intermediate does not undergo further C−C bond activation steps despite favorable reaction energetics. The absence of C−C bond activation in the adsorbed propyl suggests that the relief of ring strain is an important factor in gas-phase atomic hydrogen induced C−C bond activation in adsorbed cyclopropane.

As indicated in the Results section, no significant hydrogen abstraction from adsorbed cyclopropane has been observed during hydrogen or deuterium atom exposure. This lack of hydrogen abstraction seems reasonable when the strength of C−H bonding in cyclopropane is considered. The C−H bond in cyclopropane has a 106 kcal/mol bond dissociation energy, which is similar to that of methane and 11 kcal/mol higher than a secondary C−H bond in *n*-propane.[58] This observation is consistent with the high activation energy (11.7 kcal/mol) for hydrogen abstraction in the gas-phase reaction of cyclopropane with hydrogen atoms.[14]

The results of this experimental study lead us to propose the reaction mechanism illustrated in Figure 10. Gas-phase atomic hydrogen initiates the ring opening in adsorbed cyclopropane by an Eley−Rideal mechanism and propyl is formed as the primary reaction intermediate. Propyl is then hydrogenated preferentially by surface hydrogen producing propane during subsequent heating.

Energetics of the Cyclopropane Reactions. A potential energy diagram for cyclopropane−hydrogen reactions on the Ni(100) surface in vacuum is shown in Figure 11. Most of the adsorption and activation energies used have been determined experimentally on the Ni(100) surface. Specific sources for the experimental values are indicated later in this section. For

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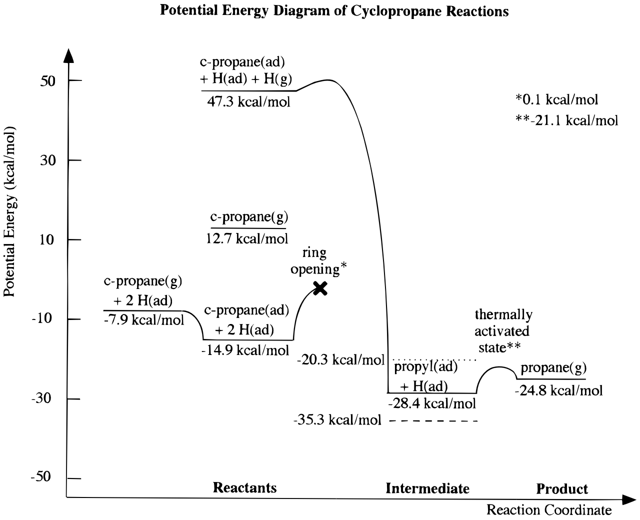

Figure 11. The standard formation enthalpy diagram for cyclopropane and primary reaction intermediates interacting with hydrogen on the Ni(100) surface. The specific sources for these experimental energies are indicated in the text. The left side illustrates that cyclopropane desorption is expected to dominate over hydrogenation by coadsorbed hydrogen. The standard formation enthalpy of the primary reaction intermediates, adsorbed propyl and an adsorbed hydrogen atom, is −28.4 kcal/mol as illustrated in the right side.

adsorption and reactions where energies have not or cannot be directly measured, the energetics have been estimated by combining theoretical estimates and measured standard formation enthalpies for gas-phase species. For instance, the standard formation enthalpy of the adsorbed species has been estimated by subtracting the binding energy of the gas-phase species from the formation enthalpy of this same gas-phase species (often radicals). Carter and Koel have demonstrated that this method produces a good estimate for standard formation enthalpies of a wide range of adsorbed species on metal surfaces.[59] In the following discussion, the term “formation enthalpy” is used to mean “standard formation enthalpy (ΔH_f°)”.

The left part of Figure 11 shows the formation enthalpy of cyclopropane coadsorbed with two surface hydrogen atoms on the Ni(100) surface and the pathways for desorption and the high-pressure thermal path for C−C bond activation. The estimated formation enthalpy of adsorbed cyclopropane is 5.7 kcal/mol, based on a binding energy of 7 kcal/mol from this work and a formation enthalpy of 12.7 kcal/mol of gas-phase cyclopropane.[60] Gas-phase atomic hydrogen has a formation enthalpy of 52.1 kcal/mol.[52] The binding energy of atomic hydrogen on the Ni(100) surface is 62.4 kcal/mol relative to gas-phase atomic hydrogen.[61] Based on these estimates, the formation enthalpy of adsorbed hydrogen atom is −10.3 kcal/mol. This value is consistent with the 11.5 kcal/mol desorption energy observed for hydrogen.[36] The thermal activation energy measured for cyclopropane ring opening on the Ni(100) surface in an atmosphere containing both cyclopropane and hydrogen has been measured to be 15 kcal/mol.[15] However, the activation barrier for molecular cyclopropane desorption from the Ni(100) surface is only 7 kcal/mol. Therefore, cyclopropane desorption is clearly energetically favored and should dominate in these TPRS experiments. These expectations are consistent with the experimental result that no C−C bond activation is observed during TPRS experiments with coadsorbed surface hydrogen and molecular cyclopropane.

In the presence of gas-phase atomic hydrogen the situation changes substantially since formation of adsorbed propyl from adsorbed cyclopropane and gas-phase atomic hydrogen is energetically favored. Based on these experimental results, no significant thermal activation energy (less than 6 kcal/mol) is required to activate a C−C bond in cyclopropane by gas-phase atomic hydrogen since the reaction occurs at 100 K. The experimental observation that adsorbed propyl is formed during exposure of adsorbed cyclopropane to gas-phase atomic hydrogen indicates that this reaction is also kinetically accessible on the Ni(100) surface. As far as we know, no information is currently available regarding the kinetic accessibility of C−C bond activation on other surfaces.

The middle part of Figure 11 shows the experimentally determined formation enthalpy of the surface reaction intermediates, an adsorbed propyl and an adsorbed hydrogen atom (solid line). The dashed line and the dotted line show the theroetical estimates based on the method of Carter and Koel as discussed above. The mechanistic data discussed in this paper clearly indicate that adsorbed surface hydrogen adds to adsorbed propyl to form gas-phase propane at 121 K. This detailed mechanistic information allows us to analyze the formation enthalpy of the intermediate state (solid line) by matching the transition states for the two opposing thermally activated processes: (1) hydrogenation of adsorbed propyl by adsorbed hydrogen to form gas-phase propane and (2) gas-phase propane dissociation to form adsorbed propyl and adsorbed hydrogen. The activation energy of propyl hydrogenation from this work and the activation energy of propane dissociation from literature[62] have been used for our estimate.

The estimated activation energy of propyl hydrogenation from this work is 7 kcal/mol based on the Redhead method with a preexponential factor 10^{13} and first-order kinetics. First-order kinetics are reasonable since the mobility of adsorbed hydrogen with a diffusion activation energy of 3.5 kcal/mol[63] should be much larger than the mobility of adsorbed propyl at these low temperatures. The thermal bath experiments performed at 0.01 Torr of propane on the Ni(100) surface indicate that the activation energy of propane dissociation to adsorbed propyl and adsorbed hydrogen is 3.7 ± 1.0 kcal/mol.[62] Based on these estimates the standard formation enthalpy of the intermediate state is −28 kcal/mol (solid line).

Quantum mechanical estimates of the binding energy of alkyl groups on metal surfaces predict a formation enthalpy of −35 kcal/mol for the intermediate state (dashed line). The binding energy of methyl on a Ni cluster with a (100)-like site is theoretically estimated to be 46 kcal/mol referenced to gas-phase methyl radical.[64] If the binding energy of propyl is not much different from this value, the formation enthalpy of adsorbed propyl on the Ni(100) surface is estimated to be −25 kcal/mol based on the 21 kcal/mol formation enthalpy of a gas-phase propyl radical.[65] The formation enthalpy of the intermediate state becomes therefore −35 kcal/mol using the formation enthalpy of an adsorbed hydrogen atom of −10.3 kcal/mol.

Estimation based on experimental studies of alkyl halide reactions results in a formation enthalpy of −20 kcal/mol (dotted line) for the intermediate state as shown in Figure 11. The binding energy estimated for ethyl coadsorbed with iodide on

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the Ni(100) surface is 31 ± 3 kcal/mol referenced to gas-phase ethyl radical.[66] Using this experimental estimate for binding energy of propyl results in the formation enthalpy of −10 kcal/mol for an adsorbed propyl and −20 kcal/mol for an adsorbed propyl and a hydrogen atom on the clean Ni(100) surface.

We believe that our experimental estimate presented here is more representative of the energy of adsorbed propyl on the hydrogen covered Ni(100) surface than either of the previous estimates discussed. The intermediate value of −28 kcal/mol obtained from this work for adsorbed propyl plus adsorbed hydrogen is however clearly consistent with the previous estimates. We expect the quantum mechanical estimate reported here to provide a lower bound for the standard formation enthalpy of adsorbed propyl since the binding energy for propyl is expected to be somewhat smaller than the binding energy of methyl used for this estimate. In addition, propyl formed at 100 K may not be sufficiently mobile to find the minimum energy adsorption site used for this calculation. We also expect that the experimental estimate based on alkyl halide reactions here provides an upper bound for the standard formation enthalpy of adsorbed propyl since coadsorbed halides may decrease the binding energy for propyl.

Molecular beam measurements have also been made regarding translational activation of dissociative propane chemisorption to form adsorbed propyl and hydrogen on the Ni(100) surface.[67] Translational activation has an activation barrier of 11.9 kcal/mol,[67] which is a much larger activation energy than the thermally induced dissociation energy of 3.7 ± 1.0 kcal/mol.[62] The agreement between the experimental and the estimated standard formation enthalpy of the intermediate state discussed above indicates that the transition state observed during translational activation in the reverse reaction is apparently not accessed during hydrogenation of adsorbed propyl by coadsorbed hydrogen. Instead, a transition state very similar to that for the thermally activated dissociation appears to dominate. Translational activation may require pathways with large prefactors which can occur within the short times characteristic of energetic collisions. On the other hand, reactions of coadsorbed species may access pathways with small prefactors and much smaller activation barriers characteristic of extended reaction times which can be accessed by coadsorbed species which can collide many times before reaction.

The experimental results of this work have clearly established that propyl hydrogenation occurs by reaction between adsorbed propyl and coadsorbed hydrogen. A review of thermodynamic and kinetic considerations in the literature suggests that the addition of surface hydrogen to adsorbed propyl should dominate relative to addition of gas-phase atomic hydrogen to the adsorbed propyl intermediate. The primary potential reactions between adsorbed propyl and gas-phase atomic hydrogen are as follows: (1) hydrogen addition to propyl, (2) hydrogen abstraction from propyl, and (3) hydrogen addition to the metal surface without inducing any reaction in propyl. In the reaction of gas-phase atomic hydrogen with a saturated alkyl species on the surface, abstraction rather than addition generally dominates.[68] The calculated reaction enthalpy for propane formation from adsorbed propyl and gas-phase atomic hydrogen is −51.9 kcal/mol; however, addition of atomic hydrogen to the metal surface is even more favorable with an enthalpy of −62.4 kcal/mol. Kinetically, addition of gas-phase atomic hydrogen to the metal surface is favored relative to hydrogen abstraction from adsorbed propyl since addition to the metal surface is basically not activated, while hydrogen abstraction from adsorbed propyl has a 10−11 kcal/mol activation energy.[68] Based on this discussion, hydrogen addition to the metal surface should dominate relative to both hydrogen addition and abstraction from propyl. In our experiments, no indication of hydrogen abstraction from propyl was ever observed.

Desorbing bulk hydrogen is another possible hydrogen source for propyl hydrogenation. However, desorbing bulk hydrogen does not seem to cause hydrogenation of adsorbed propyl since cyclopropane desorption is essentially complete before significant bulk hydrogen desorption occurs, as discussed in the previous section.

Summary and Conclusions

Carbon−carbon bond activation has been observed at 100 K in adsorbed cyclopropane on the Ni(100) surface during gas-phase atomic hydrogen/deuterium exposure. After atomic hydrogen exposure, a new loss feature appears at 383 cm^{-1} in the vibrational spectrum. This new mode corresponds to the Ni−C bond stretching mode of adsorbed propyl, the primary reaction intermediate. Carbon−carbon bond activation in adsorbed cyclopropane also causes substantial reduction in the intensities of cyclopropane's ring-deformation modes at 821 and 1006 cm^{-1}. Isotopic labeling experiments indicate that this propyl intermediate is hydrogenated by coadsorbed hydrogen to form propane at 121 K during TPRS experiments. The vibrational spectrum of adsorbed cyclopropane indicates weak interaction with the Ni(100) surface at 100 K. This weak interaction results in molecular cyclopropane desorption at 123 K without significant dehydrogenation. Carbon−carbon bond activation in adsorbed cyclopropane has never been observed in the reaction with preadsorbed hydrogen nor during exposure to nascent hydrogen formed by dissociating molecular hydrogen. A detailed potential energy diagram for the reactions of adsorbed cyclopropane on the Ni(100) surface is presented based on previous literature results and results from these experiments.

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