

## Gas-Phase Atomic Hydrogen Induced Carbon–Carbon Bond Activation in Cyclopropane on the Pt(111) Surface

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*Received: January 23, 1998*

Carbon–carbon bond activation in adsorbed cyclopropane is observed following exposure to gas-phase atomic hydrogen on the Pt(111) surface for temperatures as low as 120 K despite the fact that this low index platinum surface generally does not activate C–C bonds. Cyclopropane desorbs molecularly at 140 K. In the presence of coadsorbed hydrogen, no reaction with cyclopropane is observed. In contrast, gas-phase atomic hydrogen reacts with cyclopropane at 120 K to form a propyl intermediate. During subsequent heating, this intermediate is hydrogenated to form propane at 170, 190, and 220 K. As indicated by the lack of methane and ethane formation, no multiple C–C bond activation processes were observed. Reaction mechanisms are proposed for each new TPRS peak observed based upon the products observed, isotope experiments, and comparisons with the literature. The primary 170 K propane peak is caused by surface hydrogenation of an adsorbed propyl formed by C–C bond activation in adsorbed cyclopropane by gas-phase atomic hydrogen. The 190 K propane peak is caused by reaction between adsorbed cyclopropane and a new reactive form of adsorbed hydrogen. The propane peak at 220 K is dominant only for low gas-phase atomic hydrogen exposures and may be associated with a coverage-dependent reaction path. Taken together, these results clearly indicate that the reaction between gas-phase atomic hydrogen and cyclopropane is more complex on the Pt(111) surface than the analogous reaction on the Ni(100) surface where only one propane peak was reported. Prolonged exposures of the clean Pt(111) surface to gas-phase atomic hydrogen at 120 K resulted in an unusually low-temperature state of hydrogen that desorbs below 220 K, causes carbon–carbon bond activation, and has not previously been reported.

### Introduction

Achieving an understanding of carbon–carbon bond activation on metal surfaces is of fundamental importance to the chemical sciences. Many important catalytic processes involve hydrogenolysis, or carbon–carbon bond breaking, of large hydrocarbons to more commercially important fragments.<sup>1</sup> Inducing carbon–carbon bond activation in ultrahigh-vacuum conditions has often proven difficult. One solution has been the generation of intermediates in a high-pressure reactor followed by the transfer of the metal catalyst to UHV for study.<sup>2</sup> Another more recent method is to induce C–C bond activation in vacuo through the reaction of gas-phase atomic hydrogen with adsorbed species.<sup>3</sup> This facilitates the generation of a number of interesting intermediates that may be present at high pressures but are hard to synthesize under vacuum conditions.

Studies involving the reaction of gas-phase atomic hydrogen with adsorbed hydrocarbons include C=C bond hydrogenation in ethylene on the Ni(111)<sup>4</sup> and Cu(111)<sup>5</sup> surfaces, hydrogen addition to methyl on the Ni(111)<sup>6</sup> and Cu(100)<sup>7</sup> surfaces, hydrogen abstraction in cyclohexane on the Cu(111)<sup>8</sup> and Ni(100)<sup>9</sup> surfaces, and deuterium exchange in xylene on the Pt(111)<sup>10</sup> surface. The first case of carbon–carbon activation was observed in cyclopropane by Son et al. on the Ni(100) surface.<sup>3</sup> Cyclopropane and cyclobutane undergo extensive C–C bond activation to form the corresponding alkanes. The larger less strained cyclic hydrocarbons showed no C–C bond activation, and hydrogen abstraction dominated.<sup>9</sup>

This research is part of a larger effort to develop a more detailed understanding of the effects of structure and the

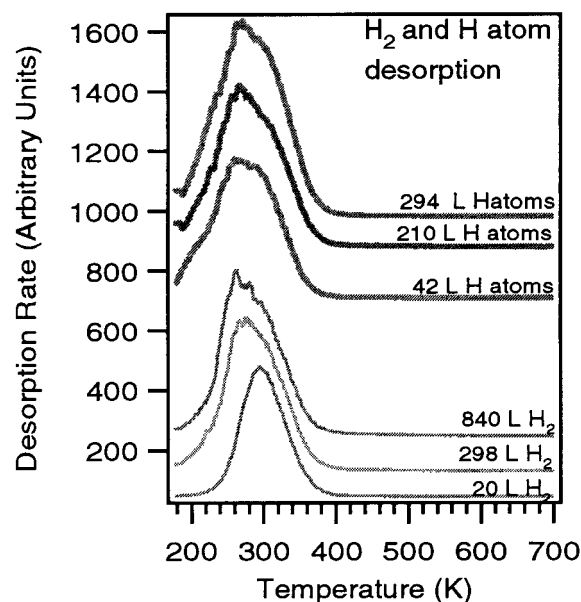
chemical identity of metal surfaces on C–C bond activation. To this end, the reaction of gas-phase atomic hydrogen with cyclopropane adsorbed on Pt(111) has been characterized so that comparisons can be made with similar studies on nickel.

### Experimental Section

All experiments were performed in an ultrahigh-vacuum chamber equipped with turbo, ion, and TSP pumps which combined to give a base pressure of  $5 \times 10^{-10}$  Torr. The system was equipped with a quadrupole mass spectrometer for temperature-programmed reaction spectroscopy (TPRS), Auger electron spectroscopy (AES) to verify surface cleanliness, and an atomic hydrogen source for the production of gas-phase atomic hydrogen.

A Pt(111) crystal oriented within  $0.5^\circ$  of the low index plane was mounted on a ceramic support with two 0.5 mm tantalum wires which allowed heating to 1050 K and liquid nitrogen cooling to 110 K. The sample was attached to an L-shaped manipulator that allows 3-coordinate displacements and  $360^\circ$  rotation. This allowed exact sample positioning in front of all instruments and gas dosers. Temperature was measured with a 0.01 mm chromel–alumel (type K) thermocouple spot-welded to the back of the crystal.

The crystal was cleaned by initial Ar<sup>+</sup> ion sputtering followed by annealing to 1000 K. During experimental runs, carbonaceous impurities generated by cyclopropane decomposition were the major contaminants. These were removed by cycles of oxidation in O<sub>2</sub> at  $8 \times 10^{-8}$  Torr and 700 K for 5 min followed by annealing to 1000 K for 100 s. Auger electron spectroscopy verified that the surface was clean.



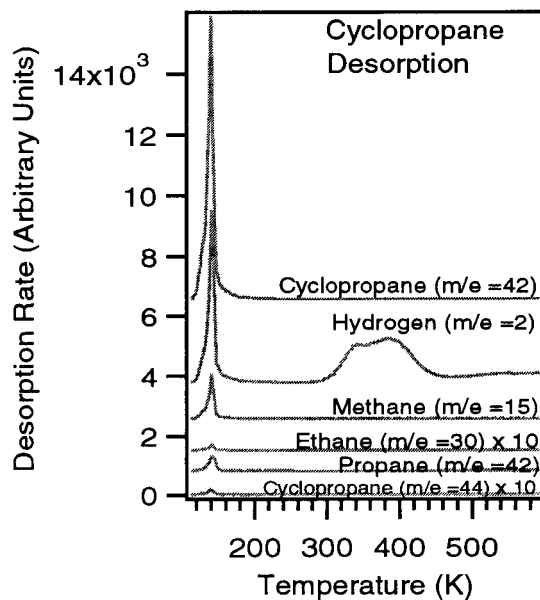
**Figure 1.** Exposure set for gas-phase atomic hydrogen on the Pt(111) surface. Peaks at 300 and 270 K look similar to those achieved with molecular hydrogen exposure. A new hydrogen state is seen as a shoulder near 220 K.

Reactive gases were inlet through a directional dosing system controlled by a leak valve. Hydrogen (Matheson, 99.9999%), deuterium (Matheson, 99.5%), and cyclopropane (Matheson, 99%) were used without further purification. Gas-phase atomic hydrogen was generated by passing molecular hydrogen over a 1800 °C tungsten filament positioned 10 cm from the sample. We refer to the mixture of hydrogen atoms and molecules as gas-phase atomic hydrogen for simplicity. Details of this method of hydrogen atom creation are discussed elsewhere.<sup>11</sup> All exposures are expressed in terms of langmuirs ( $1 \text{ langmuir} = 1 \times 10^{-6} \text{ Torr s}$ ) based on ion gauge pressure readings and have not been corrected for large directional dosing fluxes and ion gauge sensitivity factors.

TPRS spectra were taken with a QMS set with an ionization energy of 30 eV to decrease the yield of hydrogen relative to organics. The mass spectrometer and temperature were controlled with a Hunt Scientific control system allowing the simultaneous detection of up to eight masses with independent control of mass spectrometer electron multiplier sensitivities. Desorption products were identified by prominent features in their fragmentation patterns.<sup>12</sup> For all experiments, a linear heating rate of 5 K/s was used.

## Results

**Interaction of Gas-Phase Atomic Hydrogen on the Pt(111) Surface.** Gas-phase atomic hydrogen induces a new hydrogen desorption feature on Pt(111) in the leading edge of the TPRS desorption spectrum. Figure 1 compares hydrogen TPRS spectra derived from gas-phase atomic and gas-phase molecular hydrogen exposure. The three lower spectra are typical TPRS spectra resulting from the adsorption of molecular hydrogen on the Pt(111) surface. With two overlapping peaks at 270 K  $\beta_1$  and 300 K  $\beta_2$ , these spectra are very similar to previously published results.<sup>13</sup> The upper three spectra are examples of TPRS of the exposure of a clean Pt(111) surface to gas-phase atomic hydrogen. These traces have a distinctive new shoulder at approximately 220 K in the leading edge of the  $\beta_1$  desorption peak. Exposures using up to 800 langmuirs of molecular hydrogen showed no indication of the 220 K shoulder.

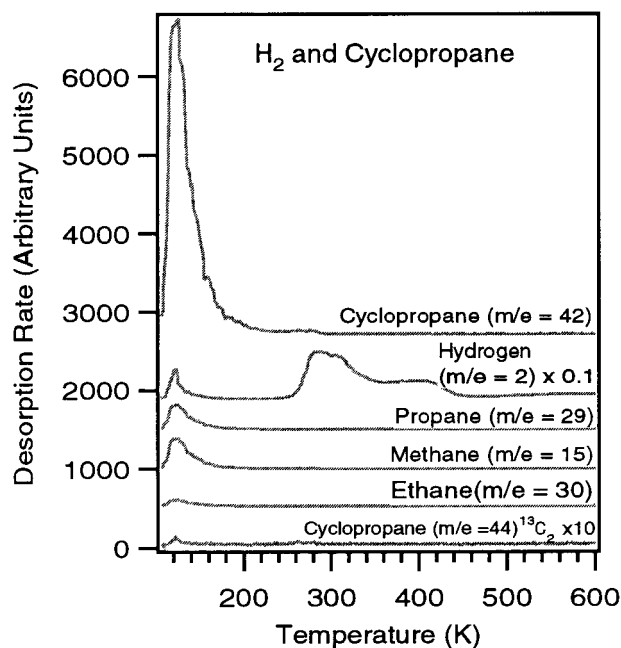


**Figure 2.** Molecular cyclopropane desorption occurs at 140 K. Some decomposition is evidenced by high-temperature hydrogen peaks starting at 350 K. No disproportionation to form propane or other desorbing organics is observed.

Therefore, this feature must be associated with exposure to gas-phase atomic hydrogen. As indicated later in this paper, this new low-temperature state displays an increased reactivity compared to the surface states obtained by molecular hydrogen adsorption. Figure 1 also shows that gas-phase atomic hydrogen populates the Pt(111) surface more efficiently than molecular hydrogen. Comparison of like exposures of gas-phase atomic and molecular hydrogen shows that a 40% increase in coverage can be obtained with gas-phase atomic hydrogen.

**Desorption of Cyclopropane.** Cyclopropane adsorbs weakly on the Pt(111) surface, and most of the adsorbed cyclopropane desorbs molecularly with a minor amount of decomposition occurring. No methane, ethane, or propane formation is observed during these TPRS experiments. The TPRS spectra shown in Figure 2 are the result of a 0.36 langmuir exposure of cyclopropane at 120 K. As can readily be seen from the figure, molecular desorption at 140 K dominates. The cyclopropane desorption temperature compares well with previous results for Pt(111)<sup>14</sup> and is similar to results obtained on Ni(100),<sup>3</sup> Ru(001),<sup>15</sup> and Ir(110)<sup>15</sup> surfaces. Aside from desorption, a small amount of the cyclopropane dehydrogenates with increasing temperature. This is evidenced by the two clear higher temperature hydrogen peaks at 350 and 390 K and a very broad peak extending up to 750 K which is apparent at higher sensitivity scales. Comparing the amount of hydrogen produced by cyclopropane dehydrogenation with the amount of hydrogen in the Pt(111) hydrogen  $\beta_2$  peak indicates that approximately 0.05 monolayers of cyclopropane undergoes dehydrogenation. No self-hydrogenation or hydrogenolysis is evidenced by the lack of methane, ethane, and propane formation. The small traces in the methyl ( $m/e = 15$ ), ethane ( $m/e = 28$ ), and propane ( $m/e = 29$ ) at 140 K are caused by fragmentation of cyclopropane in the mass spectrometer. The peak at 140 K in the 44 amu peak ( $<0.01\%$  of the cyclopropane parent) agrees well with the natural abundance of  $^{13}\text{C}_2$  cyclopropane isotope. With increasing cyclopropane exposures up to 1.76 langmuirs, no additional desorption features were observed.

**Cyclopropane and Coadsorbed Hydrogen.** The presence of coadsorbed hydrogen lowers the desorption temperature for molecular cyclopropane from 140 to 130 K; however, no

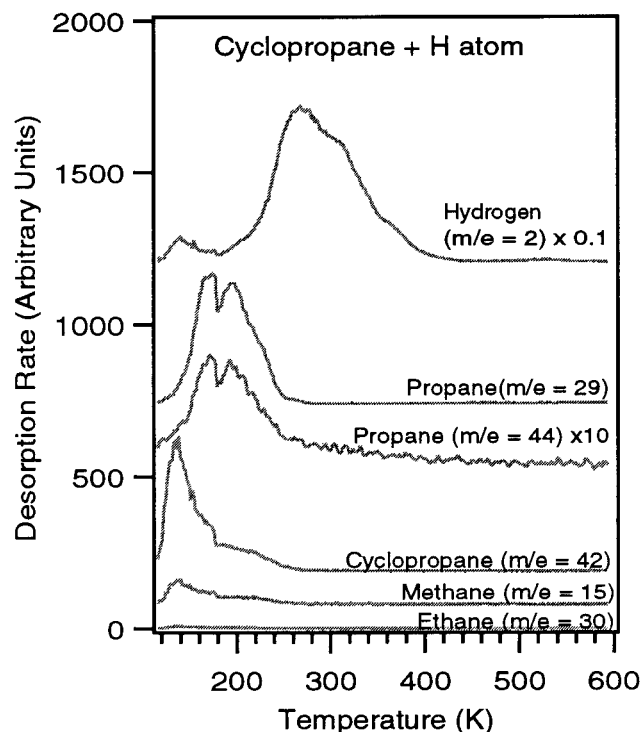


**Figure 3.** Coadsorbed hydrogen and cyclopropane induce no C–C bond activation. Molecular cyclopropane desorption is shifted to a lower temperature of 130 K.

hydrogen addition is observed. No methane, ethane, or propane formation is observed during these TPRS experiments. The products formed during TPRS of coadsorbed hydrogen (5 langmuirs) with 0.36 langmuir of cyclopropane are shown in Figure 3. Molecular desorption of cyclopropane at 130 K dominates. For methane ( $m/e = 15$ ), ethane ( $m/e = 30$ ), and propane ( $m/e = 29$ ), only cyclopropane mass spectroscopic fragments at 130 K are observed. Therefore, the presence of coadsorbed surface hydrogen does not promote the hydrogenolysis of cyclopropane. The lower temperature hydrogen desorption peak near 300 K is caused by desorption of the coadsorbed hydrogen. Again, a small amount of cyclopropane dehydrogenation is evidenced by the two smaller hydrogen peaks at 350 and 390 K. For hydrogen exposures up to 300 langmuirs, no hydrogenation or hydrogenolysis products are observed. The TPRS are similar to Figure 3 except that the 300 K hydrogen peak increases with increasing exposure.

**Cyclopropane and Gas-Phase Atomic Hydrogen.** Gas-phase atomic hydrogen induces C–C bond activation in cyclopropane on the Pt(111) surface below 170 K. Propane formation provides clear evidence for this new reaction channel; however, no ethane and methane are formed. The products of the exposure of 210 langmuirs of gas-phase atomic hydrogen to adsorbed cyclopropane (0.36 langmuir) are shown in Figure 4. The 29 amu propane trace exhibits three desorption peaks at 170, 190, and 220 K. Since molecular propane desorption from the Pt(111) surface occurs below 110 K, these must be reaction-limited desorption peaks.<sup>16</sup> Therefore, addition of two gas-phase hydrogen atoms to form propane cannot be responsible for these peaks; instead, reaction of adsorbed intermediates derived from cyclopropane must be responsible for the propane formation peaks observed.

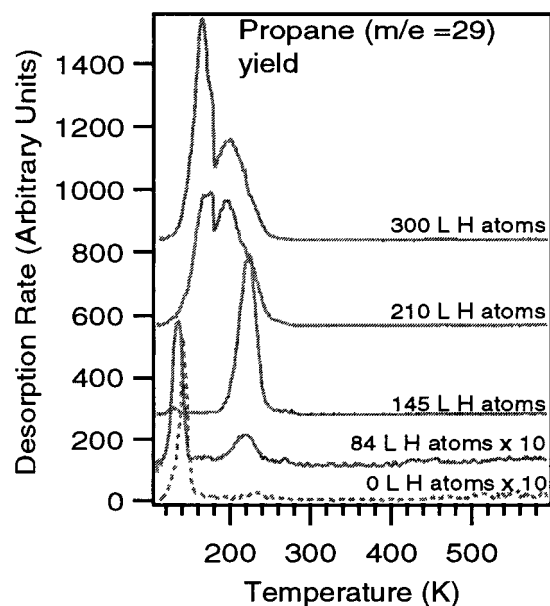
The other desorption products observed in Figure 4 are cyclopropane and hydrogen. Cyclopropane desorption occurs at 130, 170, and 220 K. The low-temperature cyclopropane peak is indicative of desorption of cyclopropane in the presence of coadsorbed hydrogen as shown in Figure 2. The 170 and 220 K cyclopropane peaks are only observed following exposure of adsorbed cyclopropane to gas-phase atomic hydrogen (com-



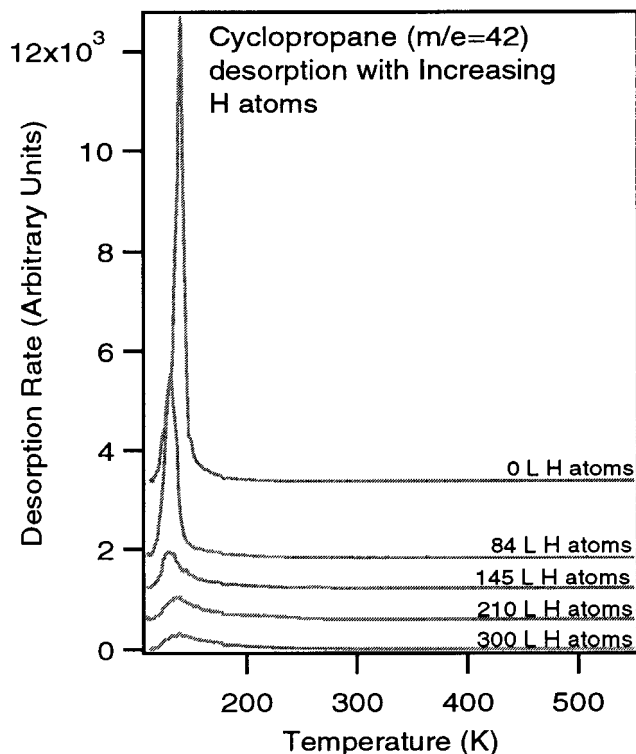
**Figure 4.** Gas-phase atomic hydrogen exposure to adsorbed cyclopropane induces C–C bond activation as evidenced by three propane desorption features at 170, 190, and 220 K. Note the amount of molecular cyclopropane desorption is greatly reduced compared to Figure 2. A new cyclopropane desorption state is evidenced by a shoulder at 170 K. Selective, single C–C bond activation occurs. No methane, ethane, or other desorbing organics are formed.

pare Figures 2 and 3). The hydrogen TPRS trace exhibits several features between 130 and 650 K. The hydrogen peaks below 250 K are attributed to fragmentation of propane and cyclopropane. The hydrogen peaks at 270 and 300 K are the  $\beta_1$  and  $\beta_2$  desorption-limited peaks which result from high hydrogen exposures.<sup>13</sup> The hydrogen peaks above 350 K are caused by dehydrogenation of a small amount of irreversibly adsorbed hydrocarbon species derived from cyclopropane, as noted previously. No multiple C–C bond activation was observed. Both the methyl (15 amu) and ethane (30 amu) TPR spectra have features only at 130 K corresponding to cyclopropane fragmentation in the mass spectrum. Earlier published work indicated that when *gas-phase cyclopropane* is exposed to gas-phase atomic hydrogen, propene and cyclopropyl radicals are formed.<sup>17</sup> Consequently, the possibility of propene formation was investigated. Careful analysis of mass spectrum cracking patterns at 27, 29, 39, 41, and 42 amu (not shown) show that propene is not one of the desorption products.

With increasing hydrogen atom exposure, propane yield increases. Figure 5 shows propane formation as a function of gas-phase atomic hydrogen exposure. For low doses of gas-phase atomic hydrogen, only the 220 K propane peak is observed. With increasing exposure, this peak decreases, and the two propane peaks at 170 and 190 K become dominant. Cyclopropane desorption spectra from this same set of experiments are shown in Figure 6. As hydrogen exposure increases, the cyclopropane desorption peaks at 130 decreases, the 170 K peak increases, and the 220 K peak remains unchanged for all hydrogen atom exposures. After a 298 langmuir exposure to gas-phase atomic hydrogen, the highest exposure used for these experiments, 90% of the original cyclopropane is removed by a combination of mechanisms discussed below. The unvarying size of the 220 K peak is consistent with hydrogenation of

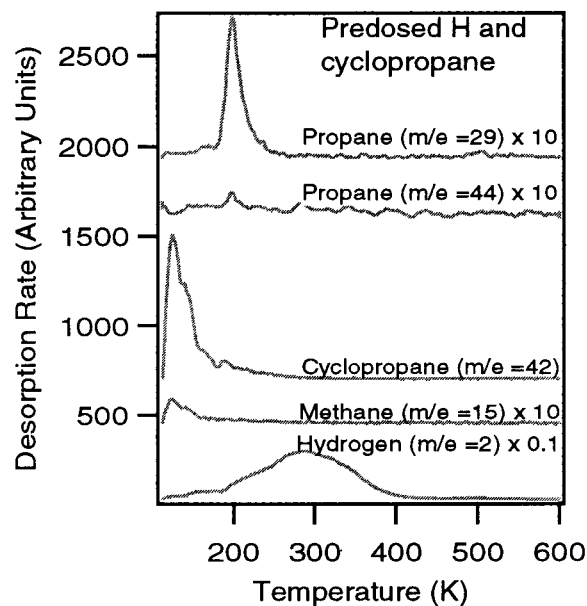


**Figure 5.** Increasing gas-phase atomic hydrogen exposure increases propane formation. At low H atom doses, a propane peak at 220 K is observed. As exposure increases, this peak grows, reaches a maxima, and then decreases. Concurrently, two new features at 170 and 190 K increase with increasing exposure. The 170 K peak becomes the dominant feature at high exposures.



**Figure 6.** The amount of molecular cyclopropane desorption decreases as gas-phase atomic hydrogen exposure increases. After a 290 langmuir H atom exposure, only 10% of the original cyclopropane remains. Two new cyclopropane desorption features at 170 and 230 K are observed. The 170 K feature increases with gas-phase atomic exposure, while the 230 K peak remains constant.

cyclopropyl groups formed on surface defect sites. Correlation of the cyclopropane 220 K peak with surface defects is further supported by recent unpublished studies of cyclopropane adsorption on a rough Pt foil.<sup>18</sup> Two cyclopropane desorption features are observed at 140 and 220 K. The low-temperature peak on the foil is again associated with cyclopropane desorption



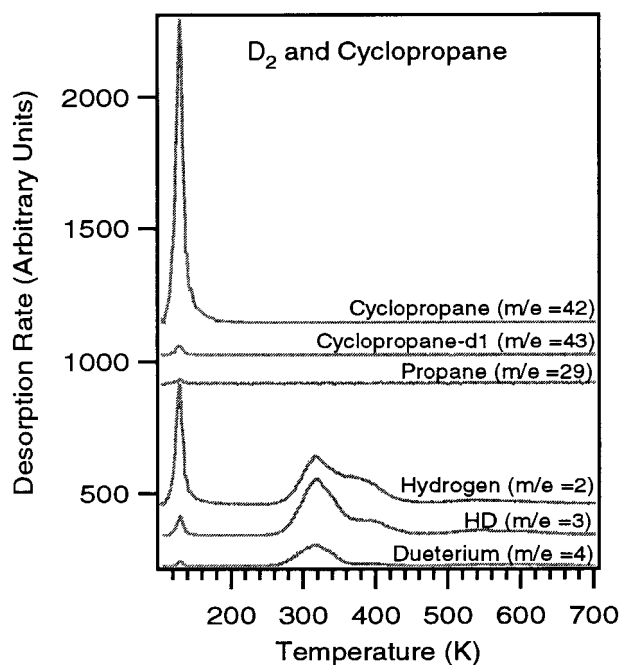
**Figure 7.** Preadsorbed gas-phase atomic hydrogen on the Pt(111) surface reacts with postadsorbed cyclopropane to form propane, which desorbs at 190 K during heating. Aside from molecular cyclopropane desorption, no other desorbing organic products are observed. The size of the  $\beta_3$  hydrogen shoulder at 220 K is reduced by reaction with cyclopropane (compare size of hydrogen shoulder with Figure 1).

from the (111) planes of the foil. The 220 K peak is associated with desorption from defects. On this rough foil surface, the large concentration of defects causes the 220 K peak to be more intense than the 140 K peak. Based on these comparisons, the 220 K cyclopropane is clearly associated with surface defects.

Preadsorbed gas-phase atomic hydrogen causes propane formation at 190 K. The desorption products resulting from the pre dosing of 210 langmuirs of gas-phase atomic hydrogen followed by the adsorption of 0.36 langmuir of cyclopropane are shown in Figure 7. In the propane TPR spectra (29 and 44 amu), one desorption feature at 190 K is observed. In the cyclopropane (42 amu) TPR spectrum, molecular desorption at 130 K is observed in agreement with results in Figure 3. The hydrogen TPRS trace contains the hydrogen desorption peaks discussed in Figures 2 and 3. Along with the  $\beta_1$  and  $\beta_2$  peaks at 270 and 300 K, the new 220 K shoulder observed in Figure 1 is also present. The presence of the 220 K shoulder is correlated with the propane peak at 190 K. After reaction with cyclopropane, the shoulder is greatly reduced compared to a control experiment using gas-phase atomic hydrogen on a clean Pt(111) surface. If the low-temperature hydrogen shoulder is removed by heating to 220 K for 100 s, then no propane is observed. This indicates that propane formation can be induced by this new low-temperature hydrogen species.

**Cyclopropane and Coadsorbed Surface and Gas-Phase Atomic Deuterium.** When cyclopropane is coadsorbed with deuterium, no deuterium exchange or incorporation is observed. The products of the coadsorption of 5 langmuirs of deuterium with 0.36 langmuir of cyclopropane are shown in Figure 8. Molecular desorption of cyclopropane at 130 K is the major desorption product. No cyclopropane- $d_1$  ( $m/e = 43$ ) or higher species are observed. As shown by a combination of  $H_2$ , HD, and  $D_2$  species desorbing at temperatures over 300 K, surface deuterium combines with hydrogen derived from cyclopropane dehydrogenation at elevated temperatures.

Gas-phase atomic deuterium exposure induces extensive deuterium exchange and incorporation in adsorbed cyclopropane. The products of the exposure of 0.36 langmuir of cyclopropane



**Figure 8.** Coadsorption of cyclopropane with deuterium does not cause isotopic exchange. As seen in Figure 2, the major feature is molecular cyclopropane desorption at 130 K.

to 210 langmuirs of gas-phase atomic deuterium are shown in Figure 9. Products with masses ranging from cyclopropane- $d_1$  to propane- $d_8$  are observed. For both the deuterated cyclopropane and propane species, two desorption peaks at 170 and 220 K are observed. For masses greater than 49 amu, the desorption peaks can no longer be caused by cyclopropane. For these deuterated propane species ( $>49$  amu), the relative intensity of the 220 K peak is greater than that of the 170 K peak.

The right side of Figure 9 shows the  $H_2$ , HD, and  $D_2$  TPR spectra following exposure to gas-phase atomic deuterium. The

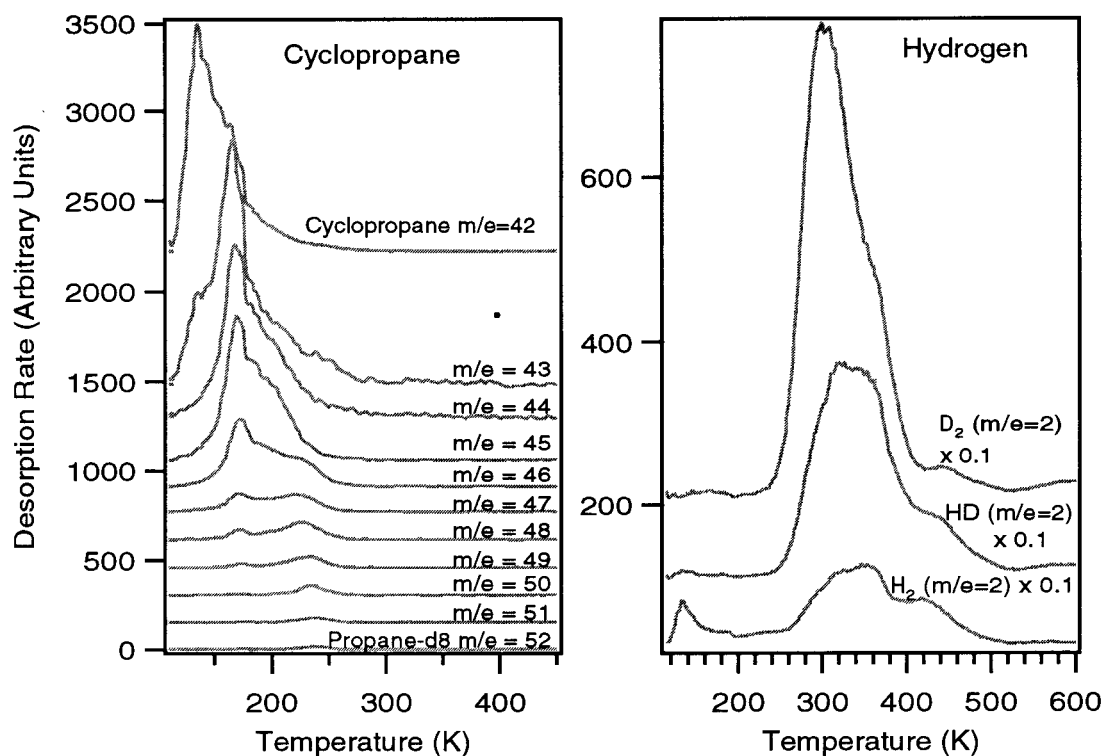
relative intensities of the isotopic hydrogen species desorbing over 300 K are different than those observed for coadsorbed cyclopropane and deuterium. When cyclopropane is exposed to gas-phase atomic deuterium,  $D_2$  is the dominant hydrogen isotopic species desorbing near 300 K. Furthermore, an increased amount of surface hydrogen ( $H_2$ ) desorption is observed at 300 K which increases with increasing gas-phase atomic deuterium exposure. These data indicate that gas-phase atomic deuterium can induce hydrogen abstraction in the adsorbed cyclopropane.

## Discussion

Carbon-carbon bond activation in adsorbed cyclopropane is observed following exposure to gas-phase atomic hydrogen on the Pt(111) surface for temperatures as low as 120 K. Gas-phase atomic hydrogen induces cyclopropane ring opening to form propane by three separate mechanisms. To the best of our knowledge, this is the first study of carbon-carbon bond activation with gas-phase atomic hydrogen on platinum surfaces.

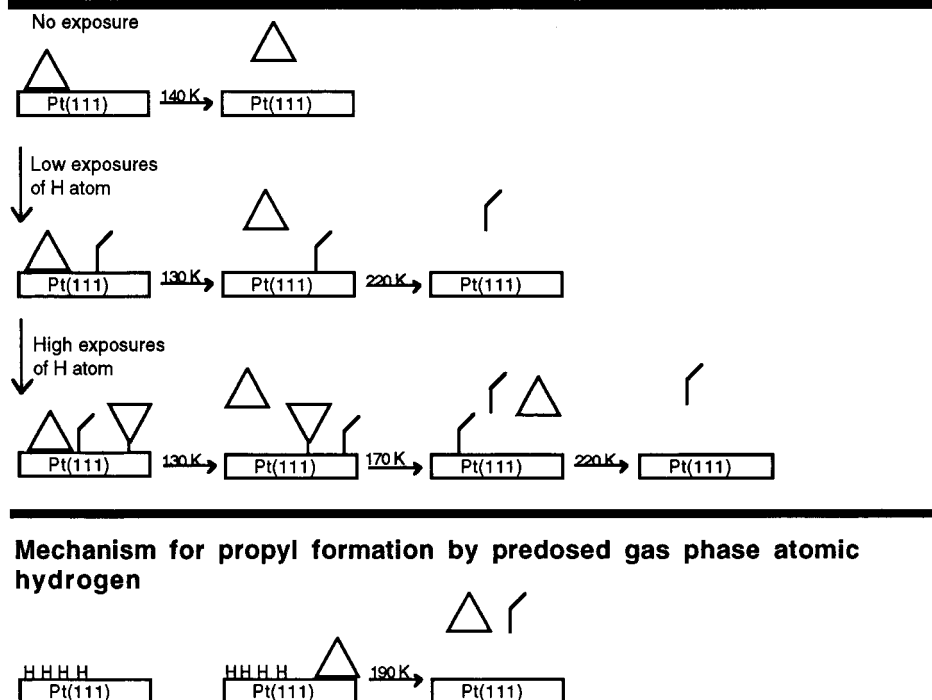
A mechanism consistent with the data for the interaction of gas-phase atomic hydrogen with cyclopropane on the Pt(111) surface can be deduced by examination of the data. First, the results of the interaction of cyclopropane with surface hydrogen will be discussed. Then, the formation and reactivity of the new adsorbed hydrogen surface state will be briefly discussed. Finally, the primary discussion is focused on organic intermediates formed by exposure of adsorbed cyclopropane to gas-phase atomic hydrogen.

No propane formation from cyclopropane occurs in the *absence* of gas-phase atomic hydrogen on the Pt(111) surface under ultrahigh-vacuum conditions. Figures 2 and 3 clearly show that cyclopropane does not self-hydrogenate and coadsorbed surface hydrogen does not activate the C-C bond. Although cyclopropane is a highly strained molecule that readily undergoes hydrogenation in high-pressure catalytic systems, it

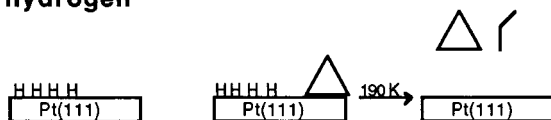


**Figure 9.** Gas-phase atomic deuterium causes extensive D incorporation in adsorbed cyclopropane. Propane species ranging from  $d_1$  to  $d_8$  are observed. Intense features at 170 K for 43 and 44 amu evidence the formation of a new reaction-limited high-temperature cyclopropane state.

### Mechanism for propyl formation from the exposure of gas phase atomic hydrogen to cyclopropane on Pt(111)



### Mechanism for propyl formation by predosed gas phase atomic hydrogen



**Figure 10.** Proposed mechanisms for the interaction of gas atomic hydrogen with cyclopropane adsorbed on the Pt(111) surface. Low exposures of gas-phase atomic hydrogen cause propyl formation which is hydrogenated at 220 K to form propane. Large gas-phase atomic hydrogen exposures cause both propyl and cyclopropyl formation. At 170 K, these intermediate species hydrogenate to form propane and cyclopropane which desorb in addition to the 220 K reaction channel. In all cases, unreacted cyclopropane desorbs below 140 K.

desorbs from the Pt(111) surface before sufficient thermal energy is available to induce hydrogenation.<sup>19</sup> From a Redhead analysis of the cyclopropane desorption peak in the presence of coadsorbed hydrogen, a desorption energy of 7.6 kcal/mol for cyclopropane can be estimated. Since on a Pt catalyst the heat of hydrogenation is reported to be 12 kcal/mol, propane formation under UHV is unfavorable.<sup>20</sup> Therefore, to study C—C bond activation in this system, either high pressures or energetic forms of hydrogen are needed.

A new hydrogen surface state is observed at 220 K, and an increased sticking coefficient is observed following exposure of gas-phase atomic hydrogen to a clean Pt(111) surface (Figure 1). Following the nomenclature of published hydrogen TPD results, we identify the new peak as the  $\beta_3$  state. The desorption temperature for this new state is similar to several well-known subsurface hydrogen states on the Ni(100),<sup>21</sup> Ni(111),<sup>6</sup> and Cu(110)<sup>22</sup> surfaces. In addition, this new form of hydrogen activates adsorbed cyclopropane as previously observed for the subsurface state on nickel. Together these comparisons suggest that this new state may be a subsurface hydrogen state on the Pt(111) surface. However, we cannot unambiguously identify the new state as a subsurface hydrogen state based on this evidence alone. Our current experimental data are also consistent with a more reactive high coverage state of hydrogen. Further spectroscopic studies are required to make a definitive assignment. High coverages of surface hydrogen can rapidly be achieved with exposure to gas-phase atomic hydrogen. Equivalent saturation of the hydrogen  $\beta_1$  and  $\beta_2$  states can be achieved with approximately one-fourth of the exposures required by dosing molecular hydrogen. This result suggests that gas-phase atomic hydrogen has a larger sticking coefficient than the 0.1 reported for molecular hydrogen on the Pt(111) surface.<sup>13</sup>

Predosed gas-phase atomic hydrogen reacting with postdosed cyclopropane causes propane formation at 190 K (Figure 7). This propane formation pathway is correlated with the new  $\beta_3$  hydrogen state discussed above. On Ni(100) the overlap of the leading edge of the subsurface hydrogen and the trailing edge of the cyclopropane desorption peaks resulted in C—C bond activation during TPRS studies.<sup>3</sup> A similar reaction mechanism is proposed for the interaction of the hydrogen  $\beta_3$  state with adsorbed cyclopropane on the Pt(111) surface.

When gas-phase atomic hydrogen is exposed to cyclopropane on the Pt(111) surface, propane peaks at 170, 190, and 220 K as well as a new cyclopropane peak at 170 K are observed (Figure 4). The 190 K propane peak results from the reaction of cyclopropane with the hydrogen  $\beta_3$  peak as discussed above. Therefore, the other new desorption peaks result from direct interaction of gas-phase atomic hydrogen with cyclopropane to form several surface intermediates.

The new 170 K cyclopropane desorption peak is consistent with the hydrogenation of a cyclopropyl intermediate. Deuterated cyclopropane at 43 and 44 amu is clearly observed at 170 K during experiments with gas-phase atomic deuterium (Figure 9). Since no deuterium exchange occurs between cyclopropane and coadsorbed deuterium, and molecular cyclopropane desorbs at 130 K in these experiments, the 170 K peak must be a new cyclopropane reaction channel that involves deuterium incorporation. In experiments with gas-phase atomic hydrogen, cyclopropyl hydrogenation is the cause of the high-temperature shoulder on the cyclopropane ( $m/e = 42$ ) peak. Since propene also appears at 42 amu, the possibility of propene formation by  $\beta$  hydrogen elimination from a surface propyl was also investigated. No evidence for propene desorption was found after careful analysis of mass spectroscopic fragmentation patterns. The increased availability of surface hydrogen may

be responsible for the inhibition of alkene formation via  $\beta$  hydrogen elimination. Therefore, the 170 K cyclopropane peak appears to be associated with hydrogenation of a cyclopropyl species at 170 K.

We propose that the 220 K propane peak (Figures 4 and 5) is associated with direct hydrogen addition to cyclopropane, resulting in C—C bond breaking and formation of a propyl intermediate as observed previously on Ni(100).<sup>3</sup> This intermediate is subsequently hydrogenated by coadsorbed hydrogen to form propane at 220 K on this Pt(111) surface. This propane formation temperature is consistent with ethane formation at 255 K from the reaction of ethyl and coadsorbed hydrogen on the Pt(111) surface observed by Zaera et al.<sup>23</sup>

As seen in Figure 5, the 220 K propane peak from propyl hydrogenation dominates at low hydrogen atom exposures but decreases as exposure increases. The largest 220 K propane peak occurs for exposures of approximately 150 langmuirs of gas-phase atomic hydrogen with peak intensity falling rapidly for larger exposures of gas-phase atomic hydrogen. With exposures greater than 150 langmuirs of gas-phase atomic hydrogen, new propane and cyclopropane desorption features at 170 K become increasingly dominant. We believe that the growth of the new 170 K propane peak and the decrease of the 220 K peak are associated with increasing amounts of strongly adsorbed intermediates. As the surface becomes more crowded, interactions between the higher concentrations of adsorbed propyl, cyclopropyl, and hydrogen become increasingly important, favoring the low-temperature reaction channel at 170 K.

From this information, the mechanism shown in Figure 10 is proposed. In the presence of coadsorbed hydrogen, no propane formation occurs and cyclopropane desorbs at 130 K. With low exposures of gas-phase atomic hydrogen, a surface propyl species is formed. After the desorption of the unreacted cyclopropane at 130 K, the propyl is hydrogenated by surface hydrogen and forms propane, which desorbs at 220 K. Large exposures of gas-phase atomic hydrogen induce the formation of a high concentration of surface propyl and cyclopropyl species. After the molecular cyclopropane desorbs at 130 K, the cyclopropyl and propyl species become hydrogenated and desorb at 170 K. Gas-phase atomic hydrogen can also populate a previously unobserved  $\beta_3$  hydrogen state which causes propane formation at 190 K. These mechanistic pathways are consistent with all of the TPRS data presented here and with previous work on Ni(100).<sup>3</sup>

Future experiments will focus on obtaining spectroscopic data to confirm the structure and bonding of the propyl and cyclopropyl species generated by the exposure of cyclopropane to gas-phase atomic hydrogen on the Pt(111) surface.

## Conclusions

Gas-phase atomic hydrogen induces carbon—carbon bond activation in cyclopropane on the Pt(111) surface, resulting in

propane formation. Propane formation occurs through hydrogenation of a propyl intermediate. This intermediate is generated by direct reaction of cyclopropane with gas-phase atomic hydrogen or by reaction with the new  $\beta_3$  Pt(111) hydrogen state. Formation of a cyclopropyl intermediate at high hydrogen atoms exposures causes a new reaction-limited cyclopropane peak at 170 K. High hydrogen atom exposure also causes the primary propane peak to decrease from 220 to 170 K. Coadsorbed surface hydrogen does not induce C—C bond breaking.

**Acknowledgment.** This work was supported by D.O.E. Grant DE-FG02-91ER1490 and is greatly appreciated. We would also like to thank Kim Firestone for his aid in the development of our hydrogen atom source.

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