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Carbon−Carbon Bond Activation in Cyclopropane by Energetic Forms of Hydrogen on the Ni(100) Surface

Kyung-Ah Son and John L. Gland*

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109

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Carbon−carbon bond activation is observed at a low temperature (<180 K) during reactions of adsorbed cyclopropane with both gas phase atomic hydrogen and bulk hydrogen in the presence of surface hydrogen on the Ni(100) surface. Propane is by far the dominant reaction product observed, in contrast to the reactions performed over Ni catalysts under high-pressure conditions. This high selectivity to propane formation may be a direct result of the low-temperature ring-opening process initiated by highly reactive hydrogen species, where thermal activation by the surface should not cause C−C bond activation. No significant C−C bond activation is observed in cyclopropane coadsorbed with only surface hydrogen. The high potential energy of gas phase atomic hydrogen and bulk hydrogen may influence the high reactivity and selectivity observed. To the best of our knowledge, this is the first time that carbon−carbon bond activation has been observed as the result of reactions with energetic forms of hydrogen.

Carbon−carbon bond activation is important in catalytic processes such as hydrogenolysis during catalytic reforming for octane enhancement and hydrogen removal of carbonaceous poison precursors in a wide range of hydrogenation and dehydrogenation reactions. A detailed understanding of C−C bond activation would be a valuable addition to our understanding of several important catalytic processes. Mechanistic studies of C−C bond activation have been attempted using adsorbed bibenzyl on a Pt(111) surface.[1] Even though the C−C bond between two benzyl groups is quite weak and bibenzyl remains adsorbed up to fairly high temperatures, simple dehydrogenation was the dominant surface process observed.

Cyclopropane is a promising molecule for studying C−C bond activation because the C−C bonds are relatively weak and the molecule is simple. Using typical catalytic pressures and temperatures, C−C bond cleavage in cyclopropane has been demonstrated on Co, Ni, Mo, Ru, Rh, Pd, Os, Ir, and Pt catalysts.[2−9] No C−C bond activation for adsorbed cyclopropane has been previously observed in the absence of gas phase cyclopropane and hydrogen during reaction. Rapid dehydrogenation or molecular desorption (<180 K) is dominant for cyclopropane adsorbed on the Ir(110) surface, depending on coverage.[10] Cyclopropane desorbs intact at 150 K from the Ru(001) surface.[11] Low-temperature desorption of cyclopropane limits the thermal energy available for C−C bond activation in cyclopropane to the point that thermal activation by the surface is not an efficient way to induce C−C bond activation.

Energetic forms of hydrogen are of considerable interest as reactants in their own right and offer a new method for inducing C−C bond activation under conditions where detailed mechanistic studies can be performed. Gas phase atomic hydrogen has an additional 52.1 kcal/mol of potential energy compared to a hydrogen atom in a hydrogen molecule (H_2) and is much more reactive than molecular hydrogen. Gas phase atomic hydrogen has been shown to cause cyclohexene hydrogenation on Ni surfaces,[12] ethylene and benzene hydrogenation on the Cu(111) surface,[13] hydrogen abstraction from cyclohexane on the Cu(111) surface,[14] and hydrogenation of carbon monoxide on the Ru(001) surface.[15] Hydrogen diffusion through and desorption from a range of transition metals is well known, clearly establishing the existence of bulk hydrogen.[16] Recently, formation of bulk hydrogen at low pressure and temperature has been observed in both Ni(111) and Cu(110) samples based on absorption of hydrogen ions[17,18] and atoms.[19,20] Bulk hydrogen in Ni has a 15 kcal/mol higher potential energy than adsorbed surface hydrogen[16] and desorbs with considerable excess translational energy, as evidenced by its strongly forward-peaked angular distribution.[17] Hydrogenation of adsorbed methyl,[21] ethylene,[22] and cyclohexene[12] by bulk hydrogen on Ni surfaces has been recently demonstrated.

In our experiments, the Ni(100) surface was exposed to gas phase atomic hydrogen at 130 K, and a new H_2 thermal desorption peak was observed at 188 K in addition to the usual adsorbed surface hydrogen peak in the 227−430 K temperature range.[12] The peak at 188 K has never been observed during desorption of adsorbed surface hydrogen formed by dissociative adsorption of gas phase molecular hydrogen on the Ni(100) surface. The size of this low-temperature hydrogen peak can be increased with increasing exposure to atomic hydrogen to well over 10 monolayer equivalents, indicating that the bulk of the sample must be involved. Bulk hydrogen desorbs from a Ni(111) sample at the same temperature (~180−250 K).[17−19] Taken together, these observations clearly indicate that the hydrogen desorption peak at 188 K from the Ni(100) sample is caused by desorption of bulk hydrogen. A mixture containing <30% atomic hydrogen was formed by dissociation of molecular hydrogen on a 2000 K tungsten filament at 9.3×10^{-7} Torr in these experiments.[23,24]

Cyclopropane adsorbed on a clean Ni(100) surface at 100 K desorbs intact without reaction at 127 K. No carbon−carbon bond activation was observed during temperature programmed reaction (TPR) experiments following cyclopropane adsorption on the clean Ni surface (data not shown). In a similar manner, carbon−carbon bond activation was not significant during TPR experiments following cyclopropane coadsorption with surface hydrogen (Figure 1). Cyclopropane desorbs at 122 K without significant reaction in the presence of coadsorbed surface hydrogen. The small methane peak at 122 K (<0.02% of desorbing cyclopropane) and the propane peak at 127 K (<0.03% of desorbing cyclopropane) may be caused by reac-

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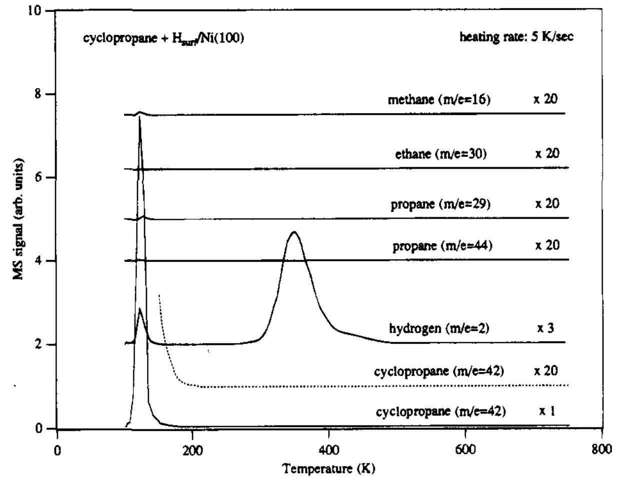

Figure 1. Thermal desorption spectra taken after a 0.074 langmuir exposure of cyclopropane to 0.25 ML of surface hydrogen preadsorbed on the Ni(100) surface.[25]

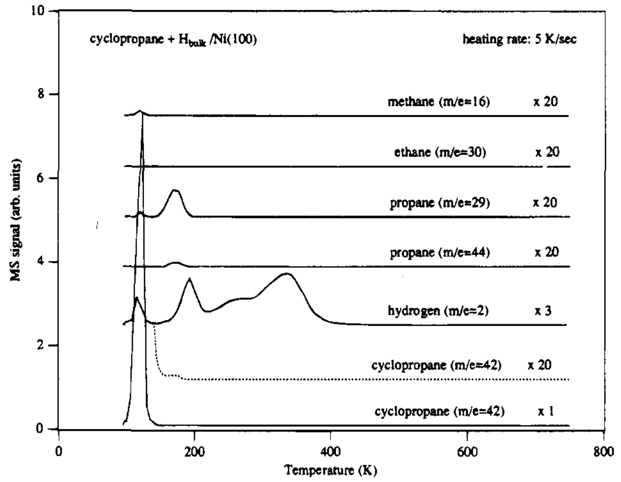

Figure 2. Thermal desorption spectra following a 0.043 langmuir exposure of cyclopropane to the Ni(100) crystal containing 0.3 equivalent ML of bulk hydrogen and 1 ML of surface hydrogen.[25]

tions on surface defects or on the Ta support wires since no simultaneous ethane is observed and the amount of methane is basically independent of surface coverages. The 2 amu desorption peak below 200 K is caused by fragmentation of cyclopropane in the ionizer since the intensity decreases dramatically as the ionization energy is decreased.

The C−C bond in cyclopropane can be activated by desorbing bulk hydrogen in the presence of surface hydrogen at 170 K, in the trailing edge of the cyclopropane peak and in the leading edge of the bulk hydrogen peak (Figure 2). The substantial amount of propane formed (>1% of the desorbing cyclopropane) desorbs at 170 K and appears to be reaction limited. Comparison between experiments done with and without bulk hydrogen (compare Figures 1 and 2) clearly indicates that (1) bulk hydrogen is necessary for C−C bond activation and (2) a substantial fraction of the cyclopropane remaining adsorbed on the surface above 145 K reacts with bulk hydrogen and decreases the trailing edge of the cyclopropane peak. No ethane formation was observed, indicating that multiple C−C bond activation is not significant. The small methane peak at 117 K (<0.02% of desorbing cyclopropane) and the small propane peak at 120 K (<0.04% of desorbing cyclopropane) are believed to be the

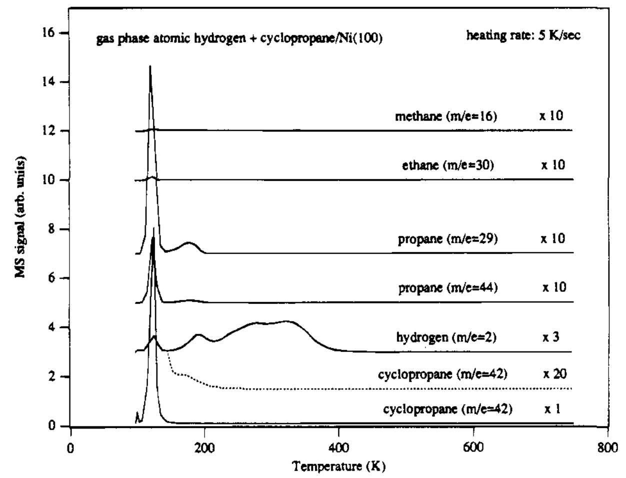

Figure 3. Thermal desorption spectra taken after a 112 langmuir exposure of gas phase atomic hydrogen to the Ni(100) surface preexposed to 0.22 langmuir of cyclopropane.[25]

result of reactions with surface defects or with the Ta support wires since they do not depend on surface coverages, as discussed previously. As discussed earlier, the 2 amu peak below 200 K is caused by cyclopropane fragmentation in the ionizer.

The C−C bond in adsorbed cyclopropane can also be activated by gas phase atomic hydrogen in the presence of surface hydrogen even at 100 K (Figure 3). The propane formed (>10% of desorbing cyclopropane) desorbs in the 105−140 K temperature range. Propane produced from the reaction with incident gas phase atomic hydrogen desorbs 50 K below the desorption temperature of bulk hydrogen. Therefore, the propane peak at 122 K is not caused by bulk hydrogen-induced hydrogenation. The small contribution of bulk hydrogen to the hydrogenation appears at 170 K, where a propane peak is observed as the result of reaction between adsorbed cyclopropane and the small amount of bulk hydrogen formed during exposure to gas phase atomic hydrogen. The small 30 amu peak at 122 K matches the 29 amu peak and is consistent with the natural abundance of ^{13}C in the propane product (<4% of desorbing 29 amu). The small methane peak at 122 K (<0.08%) may be due to reactions with surface defects or the Ta support wires, as discussed earlier.

Ethane and methane formation by multiple C−C bond activation is not significant during reaction of cyclopropane with either gas phase atomic hydrogen or bulk hydrogen in the presence of surface hydrogen on the low-temperature Ni surface. In contrast, both single and multiple C−C bond activation processes are observed during more classical cyclopropane hydrogenation studies on both supported Ni catalysts and Ni single crystal surfaces.[4,7] Previous authors proposed that a propyl surface intermediate formed during initial ring-opening experiences thermal C−C bond activation to form methyl and ethyl adsorbates on the surface prior to hydrogen addition. However, in the TPR experiments discussed here, adsorbed cyclopropane is in contact with a Ni surface only below 170 K, so thermal C−C bond activation by the surface is not feasible. The large energies possessed by gas phase atomic hydrogen and bulk hydrogen may allow substantial activation barriers to be overcome in the absence of thermal energy. Therefore, we propose that ring-opening may be initiated by reaction with energetic forms of hydrogen to produce propyl at a low temperature on the surface. These propyl intermediates may be hydrogenated selectively to propane at this low temperature, where thermal activation of the C−C bond is not feasible.

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(25) All exposures were performed in front of directed doser assemblies which minimize system contamination. The exposure units are arbitrary and included primarily as a basis for internal comparisons. Exposures are presented in langmuirs (1 langmuir = 1×10^{-6} Torr s) on the basis of the background pressure reading from the ion gauge and have not been corrected for large preferential dosing fluxes and ion gauge sensitivity factors. ML, monolayer.