

An Investigation of the Reaction Pathway for Ethylene Hydrogenation on Pd(111)

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The hydrogenation of ethylene on Pd(111) is probed using a combination of temperature-programmed desorption (TPD) and reflection–absorption infrared spectroscopy (RAIRS). Ethylene adsorbs on clean Pd(111) in a di- σ configuration but converts to π -bonded species when the surface is presaturated by hydrogen. Ethane is formed with an activation energy of 3.0 ± 0.3 kcal/mol only when Pd(111) is pre-covered by hydrogen and not when ethylene and hydrogen are co-dosed, indicating that ethylene blocks hydrogen adsorption. Experiments performed by grafting ethyl species onto the surface by reaction with ethyl iodide indicate that ethyl species hydrogenate much more rapidly than the overall rate of ethylene hydrogenation, demonstrating that the addition of the first hydrogen atom to adsorbed ethylene to form an ethyl species is the rate-limiting step in the hydrogenation reaction. The adsorption geometry of ethyl iodide is found to depend on dosing conditions. When adsorbed at low exposures at 80 K, the mirror symmetry plane of ethyl iodide is oriented close to parallel to the surface. At higher exposures, it adopts a geometry in which the symmetry plane is closer to perpendicular to the surface.

Introduction

It is now well established that transition-metal-catalyzed double- and triple-bond hydrogenation reactions proceed in a stepwise fashion via the so-called Horiuti-Polanyi model.¹ In the case of acetylene hydrogenation to ethylene catalyzed by Pd(111), it was shown, by grafting vinyl intermediates onto the surface using vinyl iodide, that the addition of the first hydrogen to acetylene to form the vinyl intermediate was rate-limiting in the overall reaction pathway and that the second hydrogenation step was fast.² This result was in accord with the observation that the rate of acetylene hydrogenation to ethylene monitored using temperature-programmed desorption on Pd(111) was proportional to the coverage of hydrogen atoms on the surface.³ This methodology is extended in this work to examining Pd(111)-catalyzed ethylene hydrogenation. Here, stepwise addition of hydrogen to ethylene proceeds via an ethyl intermediate which would then react with a second hydrogen to form ethane. The rate-limiting step is probed by forming ethyl species on the surface by exposing it to ethyl iodide. The surface species are characterized using reflection–absorption infrared spectroscopy (RAIRS) and the surface reaction kinetics monitored using temperature-programmed desorption (TPD).

Experimental Section

Experiments were carried out in three stainless steel ultrahigh vacuum chambers operating at base pressures of less than 1×10^{-10} Torr following bakeout, and which have been described in detail elsewhere.^{4–6}

Infrared data were collected from a palladium single crystal sample mounted in a modified 2 ³/₄-in. six-way cross equipped with infrared-transparent KBr windows. The sample could be

resistively heated to 1200 K or cooled to 80 K using liquid nitrogen. Infrared spectra were collected using a Bruker Equinox infrared spectrometer and a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO₂-free air. Data were typically collected for 1000 scans at 4 cm⁻¹ resolution.

Molecular beam experiments were carried out in a second system comprising an 8-in.-diameter, stainless-steel vacuum chamber pumped by means of a 6-in.-diameter, liquid-nitrogen-trapped diffusion pump (pumping speed 850 L/s). This configuration was selected to maximize the pumping speed compared to the chamber volume to minimize the background pressure when the beam is operating. A diffusion pump also provides the throughput necessary for a molecular beam apparatus where gas is continually leaked into the system. The Pd(111) sample is mounted to a carousel geometry manipulator which allows the sample to be moved in and out of the beam. The sample can also be resistively heated to 1200 K and cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir. The chamber also houses a quadrupole mass spectrometer which is mounted on a flange on a nipple attached to the side of the chamber so that the mass spectrometer is not in line of sight of the sample. The quadrupole mass spectrometer is under computer control and can sequentially monitor the intensity of up to five masses. This is used for temperature-programmed desorption experiments and for measuring the background pressure during a molecular beam experiment. Background pressures are also monitored by a nude ionization gauge located in the chamber and all pressures are uncorrected for ionization gauge sensitivity.

Temperature-programmed desorption spectra were collected in a third chamber operating at base pressure of 5×10^{-11} Torr following bakeout which is pumped by a combination of ion and sublimation pumps. The sample is also mounted to a carousel geometry manipulator and can be placed close to, and in line of site of, the ionizer of a Dichor quadrupole mass

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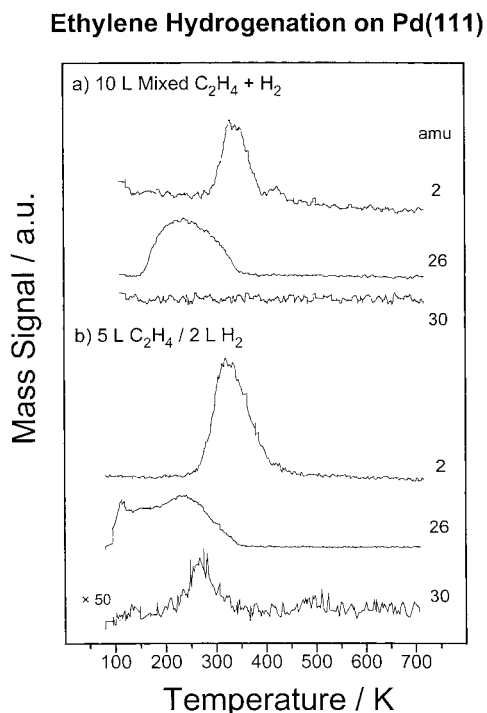


Figure 1. Temperature-programmed desorption spectra collected at 2 amu (H_2), 26 amu (ethylene), and 30 amu (ethane) of (a) 10 L exposure of an equimolar mixture of ethylene and hydrogen, and (b) 2 L of H_2 followed by 5 L of ethylene, on Pd(111).

spectrometer, also interfaced to a computer and capable of collecting five masses sequentially during the desorption sweep.

The Pd(111) sample is cleaned using a standard procedure which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly in intensity. The complete absence of carbon is indicated by the desorption of only O_2 .

Ethylene (Matheson) and hydrogen (Gas Tech, CP Grade) were transferred to glass bottles and attached to the gas-handling system of the vacuum chambers. Ethylene was further purified by several freeze-pump-thaw cycles. Ethyl iodide (Acros, 98% purity) was transferred to a glass vial and cleaned using several freeze-pump-thaw cycles. The deuterium (Linde, CP Grade) was used as received. The cleanliness of all reactants was monitored mass spectroscopically.

Results

Shown in Figure 1 is a series of temperature-programmed desorption spectra obtained either by co-dosing ethylene and hydrogen (Figure 1a) or by sequentially dosing hydrogen and then ethylene (Figure 1b). When equimolar amounts of ethylene and hydrogen are co-dosed on the surface, no ethane desorption is detected and hydrogen desorbs at ~ 360 K due to the recombination of hydrogen atoms on the Pd(111) surface.⁷ Ethylene desorbs molecularly in a broad feature centered at

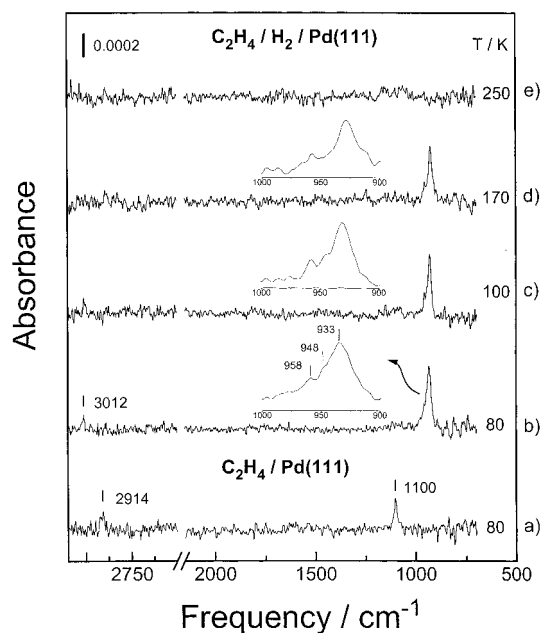


Figure 2. Reflection-absorption infrared spectra of (a) 5 L of ethylene adsorbed on clean Pd(111) at 80 K and (b–e) 5 L of ethylene adsorbed on a surface pre-dosed with 2 L H_2 and annealed to various temperatures. The annealing temperatures are displayed adjacent to the corresponding spectrum.

~ 230 K in a profile that is essentially identical to that found in the absence of hydrogen.⁸ In contrast, when the surface is first dosed with 2 L of hydrogen (1 L (Langmuir) = 1×10^{-6} Torr s), and then dosed with 5 L of ethylene, a small amount of ethane desorption is detected at ~ 270 K. Note that the amount of ethane formed by ethylene hydrogenation is significantly less than the corresponding temperature-programmed desorption yield of ethylene from the hydrogenation of acetylene on Pd(111).³ Hydrogen desorbs at ~ 330 K, again due to the recombination of hydrogen atoms on the surface. However, despite the lower hydrogen exposure in the spectra of Figure 1b compared to that in Figure 1a (2 L compared to 5 L), the desorption yield of hydrogen is lower when ethylene and hydrogen are co-dosed. This indicates that ethylene blocks hydrogen adsorption on Pd(111). A similar effect has been found on Pt(111)⁹ and Pd/ Al_2O_3 /NiAl(110).¹⁰ In addition, the ethylene desorption profile has been substantially modified by the presence of a hydrogen overlayer so that, in addition to consisting of a broad feature centered at ~ 230 K, it also exhibits a small feature at ~ 120 K. Temperature-programmed desorption spectra were also collected for ethylene adsorbed on deuterium-precovered Pd(111) (not shown). These spectra revealed the formation of ethane at ~ 270 K with the maximum mass at 32 amu (corresponding to $\text{C}_2\text{H}_4\text{D}_2$) indicating that two adsorbed deuterium atoms add to the ethylene double bond in accord with the Horiuti-Polanyi pathway,¹ and that the extent of exchange between adsorbed hydrogen and ethylene is negligible.

Surface science studies have shown that more open crystal faces are generally more active for hydrogenation than close-packed surfaces.¹¹ Sekitani et al.¹² found that a Pd(110) surface formed ethane by self-hydrogenation of ethylene and that the ethane production increased with addition of hydrogen to the surface. In accord with this view, we found only ethane when the surface was first saturated with hydrogen on the close-packed (111) face of palladium.

Figure 2 shows the reflection-absorption infrared spectra for ethylene (5 L) adsorbed on clean Pd(111) at 80 K (Figure 2a).

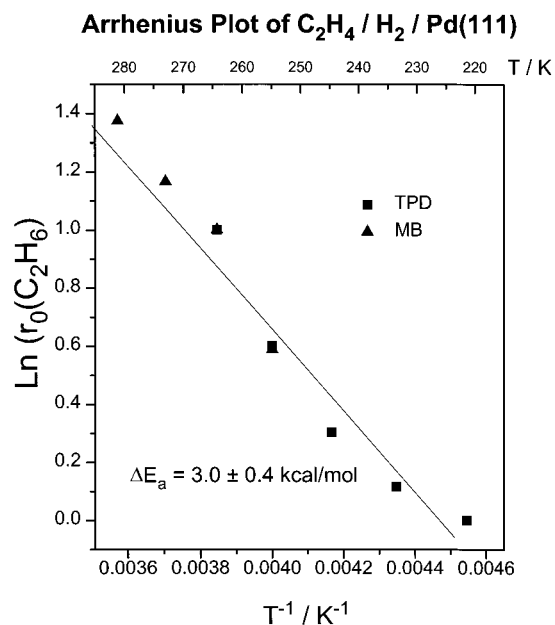


Figure 3. An Arrhenius plot of the leading edge region of the temperature-programmed desorption data shown in Figure 1 (■) compared with results obtained using molecular beams (▲) for scattering of ethylene from hydrogen-covered Pd(111).

Also shown are a series of spectra for ethylene (5 L) adsorbed on hydrogen precovered (2 L H₂ exposure) Pd(111) at 80 K, and annealed to various temperatures. The annealing temperatures are indicated adjacent to the corresponding spectrum. The spectra for ethylene on clean and hydrogen-covered Pd(111) are significantly different, indicating that the presence of preadsorbed hydrogen substantially affects the adsorption of ethylene. Ethylene adsorbed on clean Pd(111) exhibits two features at 1100 and 2914 cm⁻¹, while pre-covering the surface with hydrogen causes the 1100-cm⁻¹ feature to shift to 933 cm⁻¹ and the 2914-cm⁻¹ feature to move to 3012 cm⁻¹. The 933-cm⁻¹ peak for ethylene on H/Pd(111) is relatively broad (Figure 2b–d) and expanded depictions of this feature are displayed above the corresponding spectrum. This reveals that the 933-cm⁻¹ feature comprises a manifold of peaks at 933, 948, and 958 cm⁻¹ (Figure 2b). Heating to 100 K causes the 948-cm⁻¹ peak to decrease slightly in intensity while the 933- and 958-cm⁻¹ peaks are unaffected. Both the 948- and 3012-cm⁻¹ peaks disappear completely on heating to 170 K, while the 958- and 933-cm⁻¹ features are only minimally attenuated by heating to this temperature. This suggests the presence of two ethylene-derived species on H/Pd(111), one with frequencies at 3012 and 948 cm⁻¹ and the other with peaks at 933 and 958 cm⁻¹. All features disappear completely on heating to 250 K.

A reaction activation energy for ethylene hydrogenation can be estimated from the leading-edge region of the ethane (30 amu) desorption profile in the spectrum of Figure 1. The advantage of this method is that it does not rely on any assumptions regarding the reaction order or the value of the preexponential factor. The value of $\ln(r_0(\text{C}_2\text{H}_6))$ measured in this way is plotted versus $1/T$ in Figure 3 (■). The hydrogenation of ethylene was also measured using a dc molecular beam from the initial rate of ethane formation when a hydrogen-covered Pd(111) surface is exposed to a beam of ethylene at various temperatures. An activation energy can also be estimated for this reaction and $\ln(r_0(\text{C}_2\text{H}_6))$ is also shown plotted versus $1/T$ in Figure 3 (▲). Note that the two sets of data have been normalized for reaction at 265 K where the ordinate was arbitrarily set to unity. The slopes of both sets of data are in

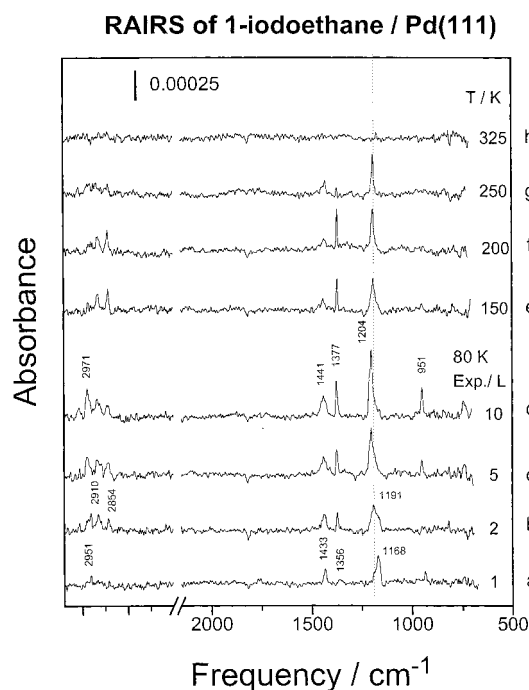


Figure 4. Infrared spectrum of ethyl iodide adsorbed on Pd(111) as a function of exposure at 80 K (a–d) and subsequently heated to various temperatures (e–h). The exposures and annealing temperatures are displayed adjacent to the corresponding spectrum.

good agreement and yield a value of the reaction activation energy of 3.0 ± 0.3 kcal/mol. Note that this value is lower than that found for catalytic ethylene hydrogenation on supported palladium between 6.5 and 10.7 kcal/mol.¹³ These values are in good agreement with activation energy measurements for ethylene hydrogenation catalyzed by a palladium foil at high pressures, of ~ 8.3 kcal/mol.¹⁴ A similar effect has been noted for acetylene hydrogenation where the activation energy measured on the clean single crystal in temperature-programmed desorption is much lower than that for catalytic acetylene hydrogenation,¹⁵ and also for Pt(111)-catalyzed ethylene hydrogenation where the activation energy is 10.8 kcal/mol at high pressures¹⁶ but ~ 6 kcal/mol when measured using molecular beams in ultrahigh vacuum.⁹

According to the Horiuti-Polanyi model,¹ the formation of ethane by reaction with hydrogen must necessarily proceed via an intermediate ethyl species. The observations that C₂H₆ is formed by reaction of C₂H₄ with adsorbed atomic hydrogen (Figure 1) and that C₂H₄D₂ is formed on a deuterium-precovered surface are in accord with this view. To probe the addition of hydrogen with an adsorbed ethyl species, and to follow the reaction pathway of this intermediate, we have followed a common strategy of grafting intermediates onto the surface using an iodine-containing precursor, in this case, ethyl iodide.¹⁷ The infrared spectra of ethyl iodide adsorbed on Pd(111) are displayed in Figure 4 as a function of exposure, and then after annealing the sample to various temperatures, where the annealing temperatures and exposures are marked adjacent to the corresponding spectra. Both the peak positions and relative intensities of the features change as a function of exposure, an effect that has been noted previously for ethyl iodide adsorption on Pt(111).¹⁷ Since the frequencies change only slightly from those of the multilayer, they can be assigned by comparison with the pure compound.^{18,19} The assignments for the multilayer (after 10 L exposure at 80 K) are made in Table 1, where the agreement with the spectrum of the liquid is good.

TABLE 1: Comparison of the Vibrational Frequencies (cm^{-1}) for a Condensed Layer of Methyl Iodide on Pd(111) with the Infrared Spectrum of the Liquid

mode ^a	liquid frequency ^{18,19}	multilayer frequency/Pd(111)
$\nu_a(\text{CH}_2); A''$	3014	3018
$\nu_a(\text{CH}_2), \nu_a(\text{CH}_3); A', A''$	2972	2971
$\nu_s(\text{CH}_3); A'$	2918	2910
$2 \delta_a(\text{CH}_3); A'$	2862	2854
$\delta_a(\text{CH}_3), \delta(\text{CH}_2); A', A''$	1452, 1437	1441
$\delta_s(\text{CH}_3) + \nu(\text{C}-\text{C}); A'$	1377	1377
$\omega(\text{CH}_2) + \rho(\text{CH}_3); A'$	1203	1204
$\rho(\text{CH}_3) + \nu(\text{C}-\text{C}); A'$	952	951

^a ω , wag; ν , stretch; ρ , rock; δ , scissor.

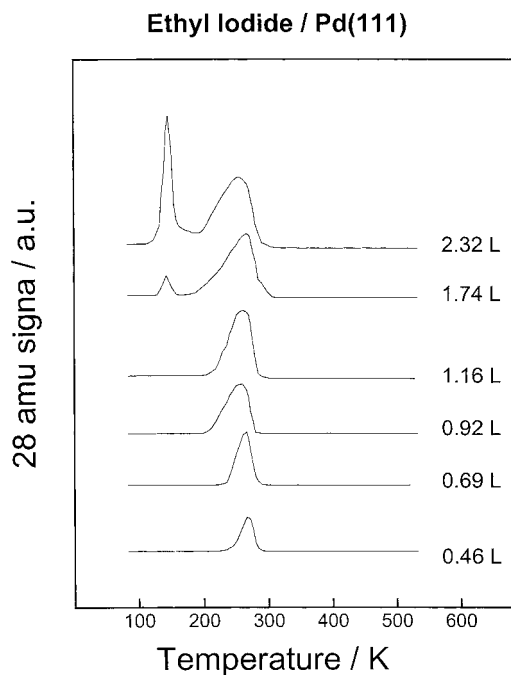
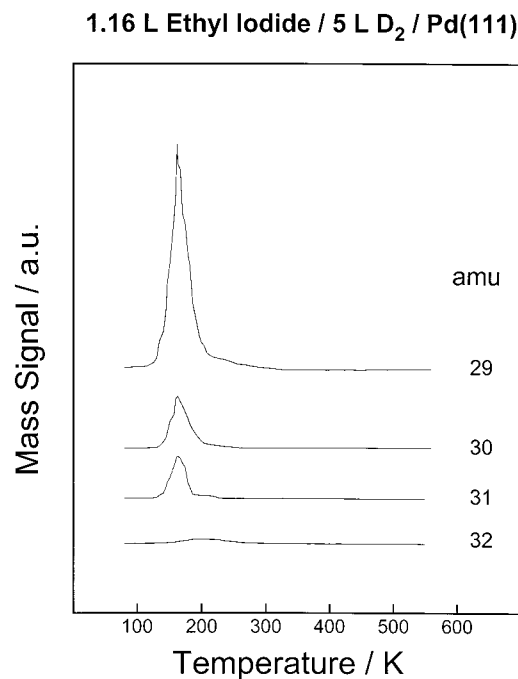
TABLE 2: Frequencies (cm^{-1}) and Relative Intensities for Ethyl Iodide Adsorbed on Pd(111) at Low Exposures (1 L) and after Annealing a Multilayer-Covered Surface to 150 K

mode ^a	$\text{C}_2\text{H}_5\text{I}/\text{Pd}(111)$		$I(1)/I(2)^b$
	1 L exposure	10L exposure, annealed to 150 K	
$\nu_a(\text{CH}_2); A''$			
$\nu_a(\text{CH}_2), \nu_a(\text{CH}_3); A', A''$	2951		
$\nu_s(\text{CH}_3); A'$		2910	0
$2 \delta_a(\text{CH}_3); A'$		2854	0
$\delta_a(\text{CH}_3), \delta(\text{CH}_2); A', A''$	1433	1441	1.2
$\delta_s(\text{CH}_3) + \nu(\text{C}-\text{C}); A'$	1356	1377	0.125
$\omega(\text{CH}_2) + \rho(\text{CH}_3); A'$	1168	1204	0.84

^a ω , wag; ν , stretch; ρ , rock; δ , scissor. ^b $I(1)/I(2)$ is the intensity ratio of the features for 1 L of ethyl iodide to that for a multilayer annealed to 150 K.

It is striking that the spectrum of ethyl iodide adsorbed on Pd(111) at low exposures is different to that after the sample has been heated to 150 K to remove the multilayer (Figure 4). The frequencies are slightly shifted from each other. However, the major differences are the very different relative intensities. The frequencies and intensities are summarized in Table 2 and will be discussed in greater detail below. The spectrum formed by annealing the multilayer-covered sample persists as the sample is heated to 200 K but changes substantially as the sample is heated to 250 K where the 1377-cm^{-1} feature disappears almost completely, and the C–H stretching modes are significantly attenuated. Heating to 325 K causes all of the surface features to disappear completely, connoting complete thermal decomposition of surface molecular species.

The 28-amu temperature-programmed desorption spectra are displayed in Figure 5 following ethyl iodide adsorption at 80 K. Ethyl iodide exposures are displayed adjacent to the corresponding spectrum. A 28-amu feature is detected at low exposures (0.46 L) centered at 270 K. This feature grows and shifts slightly to lower temperatures (255 K) as the exposure increases. Desorption spectra were also collected at 26 and 27 amu following an ethyl iodide exposure of 0.46 L and their desorption profiles exactly mirror the 28-amu signal. In addition, their relative intensities agree with the mass spectrometer ionizer fragmentation pattern of ethylene measured using the same mass spectrometer by back-filling the chamber with ethylene. From the ethylene desorption temperature of 270 K, and using the experimental heating rate of 7 K/s, and assuming a preexponential factor of $1 \times 10^{13} \text{ s}^{-1}$, yields a reaction activation energy of 16.2 kcal/mol.²⁰ At higher exposures, this feature is due to the desorption of both ethylene and some unreacted ethyl iodide.¹⁷ For ethyl iodide exposures of 1.74 L and greater, a sharp feature appears at ~ 145 K. This corresponds to the exposure at which condensed layers are detected by infrared

**Figure 5.** Temperature-programmed desorption spectra of ethyl iodide adsorbed on Pd(111) collected at 28 amu as a function of ethyl iodide exposure where the ethyl iodide exposures are marked adjacent to the corresponding spectra.**Figure 6.** Temperature-programmed desorption spectrum of ethyl iodide (1.16 L) adsorbed on a deuterium precovered surface (using a deuterium exposure of 5 L) collected at various masses. The mass is displayed adjacent to the corresponding spectrum.

spectroscopy (Figure 4, Table 2) and also with the annealing temperature at which it is removed (Figure 4). The other major desorption product is hydrogen which desorbs at ~ 320 K.

The desorption spectrum of ethyl iodide adsorbed on a deuterium precovered surface monitored at 29, 30, 31, and 32 amu is shown in Figure 6 for a deuterium-saturated surface (5 L exposure) and an ethyl iodide exposure of 1.16 L. This displays a reasonably symmetric peak centered at 160 K. Note that this temperature is significantly lower than that for the addition of hydrogen to ethylene (Figure 1).

TABLE 3: Infrared Frequencies (cm⁻¹) of Ethylene Adsorbed on Clean Pd(111) Compared with the Gas-Phase Values and di-σ-Bonded Ethylene on Pt(111)^{26,27}

mode ^b	gas-phase frequency ²¹	C ₂ H ₄ /Pd(111) (this work)	di-σ C ₂ H ₄ /Pt(111)
B _{1u} , ω-CH ₂	949	1100	993
A _g , ν(C=C)	1343	1100	1047
A _g , δ-CH ₂	1623		1414
A _g , ν _s -CH ₂	3019	2914	2903, 2910

^a Gas-phase *D*_{2h} symmetry. ^b ω, wag; ν, stretch; ρ, rock; δ, scissor.

Discussion

Ethylene adsorbs on clean Pd(111) and exhibits vibrational frequencies at 1100 and 2914 cm⁻¹ (Figure 2). Gas-phase ethylene has *D*_{2d} symmetry.²¹ Assuming that it adsorbs with its molecular plane parallel to the Pd(111) surface,^{22,23} the symmetry is lowered to *C*_{2v}. Note that this symmetry is maintained even if the carbons rehybridize from sp² to sp³ as long as the carbon-carbon bonds remains parallel to the surface. In this case, the gas-phase A_g and B_{1u} irreducible representations in *D*_{2d} correlate with A₁ in *C*_{2v} symmetry.²⁴ The gas-phase frequencies for these modes are at 949.2, 1342.4, 1623.3, and 3019.3 cm⁻¹.²¹ The B_{2g} and B_{3u} representations correlate with B₁, and the corresponding gas-phase frequencies are at 943, 1443.5 and 2989.5 cm⁻¹. Finally, B_{2u} correlates with B₂ with gas-phase frequencies at 955 and 3105.5 cm⁻¹. Only modes of A₁ symmetry are active in RAIRS²⁵ so that, in principle, ethylene adsorbed with *C*_{2v} symmetry should exhibit four peaks. These are detected on Pt(111) and the assignments are displayed in Table 3 for di-σ-bonded ethylene.^{26,27} The infrared spectrum for ethylene on Pd(111) (Figure 2) exhibits two features at 1100 and 2914 cm⁻¹. The ν_s-CH₂ mode at 2914 cm⁻¹ (shifted from 3019 cm⁻¹ in the gas phase) is in reasonable agreement with the value for di-σ-bonded ethylene on Pt(111) (Table 3). However, rather than detecting two features for the ν(C=C) and ω-CH₂ modes (at 1047 and 993 cm⁻¹ on Pt(111)), only a single feature is detected. The 1414-cm⁻¹ feature for Pt(111) is extremely weak.²⁷ It is, however, worthy of note that, for π-bonded ethylene on silver adsorbed with the molecular plane parallel to the surface, only the ω-CH₂ mode is detected in this region in HREELS^{28,29} and RAIRS.^{30,31} Note that this mode is also detected only on hydrogen-covered Pd(111) (Figure 2b-d). This may imply that the 1100-cm⁻¹ peak is due to the ω-CH₂ mode or that the ν(C=C) and ω-CH₂ vibrations are accidentally degenerate. In either case, these results indicate that ethylene is substantially rehybridized on adsorption on clean Pd(111).

This conclusion appears to contradict previous HREELS,³² photoelectron spectroscopic,²² and near-edge X-ray absorption fine structure (NEXAFS) data²³ which indicate that ethylene adsorbed on clean Pd(111) is not substantially distorted from the gas-phase geometry. These results have also been questioned recently as a result of theoretical studies³³ which suggest a combination of π- and di-σ-adsorbed ethylene as the most stable surface composition.

The results of Figure 2 indicate that the ethylene structure is strongly affected by the presence of hydrogen on the surface since features are detected at 933 and 3012 cm⁻¹ on hydrogen-covered Pd(111) (Figure 2). These values are close to those found for π-bonded ethylene on Pt(111)^{26,34} and silver.²⁸⁻³¹ The data of Figure 2, however, show that the 933-cm⁻¹ peak comprises several features. The features at 948 and 3012 cm⁻¹ disappear on heating to 170 K. This temperature coincides with the sharp desorption state seen in temperature-programmed desorption of C₂H₄/H/Pd(111) at ~120 K (Figure 1). These

TABLE 4: Infrared Frequencies (cm⁻¹) of Ethylene Adsorbed on Hydrogen-Covered Pd(111) Compared with the Gas-Phase Values and π-Bonded Ethylene on Pt(111)^{26,34}

mode ^b	gas-phase frequency ²¹	C ₂ H ₄ /H/Pd(111) (this work)	π-bonded C ₂ H ₄ /Pt(111)
B _{1u} , ω-CH ₂	949	933, 948, 958	954
A _g , ν(C=C)	1343		
A _g , δ-CH ₂	1623		
A _g , ν _s -CH ₂	3019	3012	2995

^a Gas-phase *D*_{2h} symmetry. ^b ω, wag; ν, stretch; ρ, rock; δ, scissor.

vibrational frequencies are very close to those of gas-phase ethylene (Table 4) and are assigned to undistorted, very weakly bound ethylene. From the peak desorption temperature of 114 K, a Redhead analysis²⁰ yields a desorption activation energy of 28 kJ/mol. This is reasonably close to the value of 40 ± 10 kJ/mol for π-bonded ethylene on Pt(111).³⁵

The spectrum formed by heating to 170 K reveals two features at 933 and 958 cm⁻¹. These disappear on heating to 250 K coincident with the broad ~230 K ethylene desorption peak (Figure 1). Ethane is also formed in the same temperature range, indicating that the second ethylenic species hydrogenates by reaction with adsorbed hydrogen. The most intense 933-cm⁻¹ peak is assigned to the ω-CH₂ mode. A similar structure in this feature has been detected for ethylene on silver³¹ and ascribed to the appearance of the gas-phase B_{2g} mode (943 cm⁻¹).²¹ This correlates with a B₁ mode as the symmetry is reduced to *C*_{2v}²⁴ and transforms as *x* (which is oriented along the C-C axis²¹). This implies that the π-bonded ethylene might be slightly tilted so that one carbon is somewhat farther away from the surface than the other. It is clear, however, that preadsorption of hydrogen on Pd(111) leads to the formation of relatively undistorted ethylenic species. A similar effect has been noted for Fe(100)³⁶ and Pd/Al₂O₃/NiAl(110).¹⁰ These observations suggest that the photoelectron spectroscopic and NEXAFS data may have been collected for ethylene adsorbed on a hydrogen-contaminated surface. It should be noted that palladium, because of its ability to absorb large quantities of hydrogen, is particularly susceptible to hydrogen contamination and great care must be taken to ensure that the background pressure is sufficiently low, and the sample sufficiently carefully cleaned, to exclude all hydrogen.

The data of Figure 1 indicate that ethylene can hydrogenate to ethane on Pd(111) when the surface has been precovered by hydrogen (Figure 1b) but not when ethylene and hydrogen are co-dosed (Figure 1a). The Arrhenius plot for the hydrogenation rate as a function of temperature (Figure 3) shows that the activation energy for ethylene hydrogenation is 3.0 ± 0.3 kcal/mol, a value that is substantially lower than the catalytic hydrogenation activation energy found at higher pressures.^{13,14} A similar effect has been found for acetylene hydrogenation to ethylene on Pd(111).¹⁵ Part of the origin of this discrepancy is likely to be the fact that catalytic hydrogenation does not take place on a clean surface but on an ethynylidyne-covered catalyst in the case of ethylene hydrogenation,⁶ and a surface comprising a mixed ethynylidyne + vinylidene layer for acetylene hydrogenation.³⁷ The leading edge of the ethane desorption state depends on the activation energy and preexponential factor for the reaction of atomic hydrogen with adsorbed ethylene. The trailing edge of the ethane (30 amu, Figure 1) desorption state is coincident with the trailing edge of the ethylene (26 amu, Figure 1) desorption profile. Hydrogen continues to desorb at significantly higher temperatures (where the onset of desorption is at ~280 K), suggesting that the trailing edge of the ethane desorption state is due to the loss of ethylene from the surface.

A similar effect has been observed previously for the hydrogenation of acetylene to ethylene in temperature-programmed desorption³ where, in this case, the trailing edge of the ethylene desorption state was due to the loss of adsorbed acetylene which converts into unreactive vinylidene species.³⁸ In the case of ethylene adsorbed on Pd(111), the corresponding conversion of adsorbed ethylene into ethylidyne species is much slower than the rate of ethylene desorption and the infrared spectra of ethylene adsorbed both on hydrogen-precovered and clean Pd(111) show no evidence for ethylene-to-ethylidyne conversion since the presence of ethylidyne would be clearly indicated by an intense infrared feature at 1329 cm⁻¹.⁶ This behavior is in contrast to that found on Pt(111) where ethylidyne is detected,³⁹ indicating that the rate of ethylidyne formation on palladium is much slower than that on platinum. Since π -bonded ethylene is exclusively detected by infrared spectroscopy on hydrogen-precovered Pd(111) (Figure 2), this suggests that a π -bonded ethylene species hydrogenates to form ethane. It has been shown previously that, on Pt(111), π -bonded ethylene hydrogenates to ethane while the di- σ species is inactive.²⁶ The results presented here are in accord with this observation.

To probe the rate-limiting step in the hydrogenation of ethylene to ethane, we have investigated the adsorption of ethyl iodide on Pd(111). The data of Figure 6 indicate that adsorbing ethyl iodide onto a deuterium pre-covered Pd(111) surface yields a maximum mass at 31 amu corresponding to the formation of d₁-ethane, suggesting that a single adsorbed deuterium reacts with an adsorbed ethyl group to form ethane, where this reaction occurs at 160 K. If this reaction indeed takes place, this suggests that the rate of ethyl hydrogenation is faster than the rate of formation of ethane by the hydrogenation of ethylene (Figure 1), so that the rate at which adsorbed ethylene reacts to form an ethyl species is the rate-limiting step in the stepwise addition of hydrogen. This conclusion is in accord with theoretical work on Pt(111).⁴⁰

The surface properties of adsorbed ethyl iodide on Pd(111) are summarized in Figures 4 and 5. The infrared data of Figure 4 indicate that a condensed layer of ethyl iodide forms after an exposure of 10 L and the assignments for the multilayer are displayed in Table 1, showing good agreement with the spectrum of liquid ethyl iodide.^{18,19} The infrared spectrum of ethyl iodide adsorbed on clean Pd(111) at 80 K with an exposure of 1 L (Figure 4a), and that formed by heating a condensed layer to 150 K to remove the multilayer (Figure 4e), have similar vibrational frequencies, but very different relative intensities. This is shown in the data summarized in Table 2 where the intensity ratio designated $I(1)/I(2)$ for the $\delta_a(\text{CH}_3)$ mode (at 1433 cm⁻¹ for a 1 L exposure at 80 K and at 1441 cm⁻¹ after desorbing the multilayer) is 1.2, but is ~ 0.13 for the $\delta_s(\text{CH}_3)$ mode (at 1356 cm⁻¹ for the low-exposure surface, and at 1377 cm⁻¹ after desorbing the multilayer). This implies that ethyl iodide adopts different adsorption geometries when adsorbed under these different conditions. A similar conclusion has been arrived at for ethyl iodide adsorbed on Pt(111).¹⁷ The gas-phase point group of ethyl iodide is C_s where the x - y plane is the symmetry plane of the molecule.²⁴ In this case, modes of A' symmetry transform as x and y , vectors oriented in the symmetry plane of ethyl iodide, and modes of A'' symmetry transform as z , oriented perpendicularly to this plane.²⁴ The surface selection rule for RAIRS indicates that only modes that transform as a vector oriented perpendicularly to the surface are infrared active²⁵ and can be used to indicate adsorbate orientations. In the case of ethyl iodide adsorbed at low exposures at 80 K, the methyl bending mode of A'' symmetry is the most intense while

the mode of A' symmetry is relatively weak (Figure 4; Table 2). This implies that the normal to the mirror symmetry plane of ethyl iodide is oriented normal to the Pd(111) surface. That is, the symmetry plane is oriented substantially parallel to the surface. Note that there is some residual intensity for this species at 1356 cm⁻¹, suggesting that the mirror plane axis may be slightly tilted with respect to the surface. This adsorption geometry is confirmed by the methyl stretching modes also with A' symmetry (Figure 4; Table 2). In contrast, the relatively high intensity of the modes of A' symmetry for adsorbed ethyl iodide formed by desorbing the multilayer (Figure 4; Table 2) indicates that the ethyl iodide mirror plane is oriented more nearly perpendicularly to the surface. Again, the relative intensities of the methyl stretching modes are in accord with this proposal. These conclusions are in accord with the geometries found on Pt(111).¹⁷

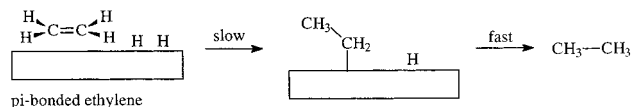
Further spectroscopic changes occur on heating the sample to 250 K where the 1377-cm⁻¹ feature diminishes significantly in intensity and the stretching modes at 2854 and 2910 cm⁻¹ also decrease. C-I bond scission was found using X-ray photoelectron spectroscopy and temperature-programmed desorption between 150 and 200 K.^{41,42} This conclusion is corroborated by the temperature-programmed desorption data of Figure 5 which show the appearance of a sharp 28-amu feature with a peak desorption temperature of 270 K. Measurement of the intensities at other masses for an ethyl iodide exposure of 0.46 L indicates that the peak is due to the desorption of ethylene. At higher exposures, a portion of the feature is due to the desorption of unreacted ethyl iodide which desorbs between 200 and 250 K at saturation. A trend has been proposed in the ethylene desorption temperature where it desorbs at 160 K on Ni(100), 180 K on Pd(100), 180 K on Pt(111), and 307 K on Au(111).⁴³ The desorption temperature of 270 K found here is consistent with this trend since ethylene forms more rapidly than on gold but slower than on more open palladium surfaces or close-packed platinum.

An additional feature is found at 145 K for ethyl iodide exposures of 1.74 L and larger. This peak continues to grow with increasing ethyl iodide exposure and its desorption temperature coincides with the loss of multilayer ethyl iodide in the infrared spectrum (Figure 4) and is therefore assigned to the desorption of multilayers of ethyl iodide (Table 1).

The formation of ethylene following ethyl iodide adsorption on Pt(111) has been interpreted as being due to a β -hydride elimination reaction from the adsorbed ethyl species.⁴³ The onset of ethylene desorption is at ~ 250 K, while the infrared data of Figure 4 show that the formation of surface ethyl species is complete by 250 K indicating that β -hydride elimination is the rate-limiting step in the formation of ethylene.

The effect of preadsorbing deuterium on the surface is shown in the data of Figure 6. It shows d₁-ethane formation in a peak centered at ~ 170 K. The incorporation of a single deuterium species into the product confirms that the ethane is formed by the addition of atomic deuterium to an ethyl species. The onset of ethane desorption, in this case, is very close to the temperature at which substantial amounts of ethyl species are formed on the surface (Figure 4). It is therefore not clear whether this desorption state is limited by the rate of hydrogen addition to the surface ethyl species or by the rate of ethyl formation on the surface. In either case, the rate of hydrogen (deuterium) addition to the ethyl species occurs at or below 170 K, a temperature that is much lower than the rate of ethylene hydrogenation on Pd(111) in temperature-programmed desorption (Figure 1). This indicates that the addition of the first

hydrogen to an adsorbed π -bonded ethylene to form an ethyl species is much slower than the rate of subsequent hydrogenation to form ethane. The surface reaction pathway on clean Pd(111) can be summarized as follows:



Conclusions

Ethylene rehybridizes following adsorption on clean Pd(111). The presence of preadsorbed hydrogen on the surface affects the ethylene adsorption geometry so that it becomes π -bonded. A small amount of ethane desorption is found in temperature-programmed desorption when the surface is precovered by hydrogen, but not when hydrogen and ethylene are co-dosed, indicating that ethylene blocks the adsorption of hydrogen on the surface. The amount of ethane formed during a temperature sweep is limited due to the loss of ethylene from the surface by desorption. Grafting ethyl species onto Pd(111) by reaction of ethyl iodide with the surface reveals that ethyl groups hydrogenate much more rapidly than the overall rate of ethylene hydrogenation, indicating that the addition of the first hydrogen to adsorbed ethylene is the rate-limiting step in ethylene hydrogenation. As part of this work, two ethyl iodide adsorption geometries were found. One forms at low exposures at 80 K in which the mirror symmetry plane of ethyl iodide is oriented close to parallel to the surface, and the other forms at high coverages where the mirror symmetry plane is oriented more closely to normal to the surface.

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