

On the Reaction Pathway for the Hydrogenation of Acetylene and Vinylidene on Pd(111)[†]

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The pathways for the hydrogenation of adsorbed acetylene and vinylidene on Pd(111) are investigated using temperature-programmed desorption and infrared reflection–absorption spectroscopies. The chemistry of the vinyl intermediate formed by the hydrogenation of both species is investigated by adsorbing vinyl iodide on Pd(111) where it is found that vinyl species hydrogenate more rapidly than adsorbed acetylene, indicating that the rate-limiting step in acetylene hydrogenation is the addition of the first hydrogen to acetylene to form a vinyl species. Infrared spectroscopy also reveals that vinyl species convert to ethylidyne as Pd(111) is heated above ~160 K. The hydrogenation of vinylidene by up to ~0.2 Torr of hydrogen involves intermediate ethylidyne species in accord with this observation. Surprisingly, the rate constant for the conversion of vinylidene into ethylidyne is identical to that for the titration of ethylidyne from the surface by hydrogen, an effect that may be explained in terms of the different saturation coverages of the two species.

Introduction

Palladium is an active catalyst for the selective hydrogenation of acetylene and ethylene.^{1–12} Two acetylene-derived species have been identified on Pd(111). The first is an adsorbed acetylenic species which is considerably rehybridized to $\sim\text{sp}^2$ and forms following acetylene adsorption at low temperatures (~ 100 K) on Pd(111).^{13,14} This is the reactive precursor to the formation of both hydrogenation products as well as benzene on clean Pd(111) in ultrahigh vacuum.^{16–19} As palladium is heated to ~ 300 K, this converts to a thermodynamically more stable vinylidene species.²⁰ While this is not reactive under ultrahigh vacuum conditions and merely thermally decomposes on heating to evolve hydrogen and deposit carbon on the surface, it reacts at high pressures with acetylene to eventually form benzene.²¹ It has also been found that the addition of hydrogen to acetylene, as well as yielding hydrogenation products, also accelerates the rate of benzene formation.²² This may be due to the removal of these vinylidene species under catalytic conditions. Certainly this is feasible since analogous strongly bound ethylidyne species on Pd(111) have been demonstrated to react with hydrogen at high pressures.^{23,24} This paper therefore addresses the hydrogenation of adsorbed acetylene ($\text{C}_2\text{H}_{2(\text{ads})}$), vinylidene ($\text{CH}_2=\text{C}_{(\text{ads})}$), and ethylidyne ($\text{CH}_3-\text{C}_{(\text{ads})}$). Assuming that dissociatively adsorbed atomic hydrogen initially reacts with both acetylene and vinylidene on Pd(111),²⁵ they must both form intermediate vinyl species. The chemistry of this intermediate is therefore followed by grafting it onto the surface by exposing Pd(111) to vinyl iodide ($\text{CH}_2=\text{CHI}$). This strategy has been used extensively to graft hydrocarbon moieties onto metal surfaces where the relatively weak C–I bond cleaves to adsorb the hydrocarbon fragment and iodine.²⁶

As noted above, adsorbed vinylidene is unreactive in ultrahigh vacuum. As is shown below, however, it can react with high external pressures of hydrogen where the reaction is followed

in situ using reflection/absorption infrared spectroscopy. It has recently been shown that coadsorbing hydrogen and acetylene on Pd(111) leads to the formation of ethylidyne species²⁷ in complete contrast to the behavior in the absence of any surface hydrogen where acetylene converts exclusively into vinylidene.²⁰ Infrared spectroscopy results described below reveal that adsorbed vinyl species can react to form ethylidyne so that this reaction presumably also proceeds via a vinyl intermediate. Consistent with this observation, it is also found that pressurizing a vinylidene-covered surface with hydrogen results in the formation of intermediate ethylidyne species which are also removed by reaction with hydrogen. To understand this process in greater detail, we have also examined the kinetics of ethylidyne removal by high pressures of hydrogen using reflection/absorption infrared spectroscopy (RAIRS).

Experimental Section

These experiments were carried out in two stainless steel ultrahigh vacuum chambers operating at a base pressure of $\sim 1 \times 10^{-10}$ Torr following bakeout and which have been described in detail elsewhere.^{28,29} Infrared data were collected from a palladium single crystal mounted in a modified $2\frac{3}{4}$ " six-way cross equipped with KBr infrared-transparent windows. The sample could be resistively heated to ~ 1200 K or cooled to 80 K using liquid nitrogen. Light from a Midac infrared spectrometer is polarized and focused onto the sample at an incident angle of $\sim 80^\circ$ and the reflected light steered onto a liquid nitrogen cooled, mercury–cadmium–telluride detector. The light path is enclosed and purged with dry, CO_2 -free air. The spectrometer is controlled using SpectraCalc software and was typically operated at 4 cm^{-1} resolution; data were collected for 1000 scans.²⁹

In the second chamber, the sample was mounted to a carousel-geometry manipulator and could be similarly heated to ~ 1200 K and cooled to 80 K by thermal contact with a liquid nitrogen filled reservoir.²⁸ Temperature-programmed desorption data were collected using a heating rate of 7.5 K/s and desorbing species detected using a Dychor quadrupole mass spectrometer

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interfaced to a PC allowing five masses to be monitored sequentially during the desorption sweep. To minimize spurious signals, the mass spectrometer was enclosed in a shroud with a 1 cm diameter hole in the front. In this case, the sample was dosed via a tube which minimized background contamination and dosing of the supports. This also allowed adsorption kinetics to be measured using the so-called King and Wells³⁰ method, and comparison of the acetylene uptake kinetics in this chamber with previous measurements¹⁷ showed that the dosing source provided a pressure enhancement of 58 ± 2 compared with the background pressure. This enhancement factor was used to provide exposures that are quoted in Langmuirs (1 Langmuir (L) = 1×10^{-6} Torr s). Pressures are not corrected for ionization gauge sensitivities.

The sample was cleaned using a standard procedure which consisted of heating to ~ 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing in vacuo to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, a more sensitive gauge of the presence of carbon was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of carbon is manifested by the desorption of CO. As the sample becomes depleted of carbon, the CO desorption yield decreases and the oxygen desorption yield increases correspondingly. The complete absence of carbon is indicated by the desorption of only O₂.

Vinyl iodide (Lancaster Synthesis, Technical grade) and acetylene (Linde, Purified grade) were transferred to glass bottles and further purified by repeated bulb-to-bulb distillations and their cleanliness monitored mass spectroscopically. The hydrogen (Gas Tech, CP Grade) was transferred directly to a glass bottle and used without further purification. Deuterium (Linde, CP Grade) was also transferred from the cylinder to a glass bottle and used without further purification.

Results

Figure 1 displays a series of 29 amu temperature-programmed desorption spectra for acetylene adsorbed onto a deuterium-saturated Pd(111) surface formed by exposing it to 5 L of deuterium at a sample temperature of 80 K. This results in a single ethylene desorption state centered at ~ 245 K due to acetylene hydrogenation, and these spectra are in reasonable agreement with previous results.¹⁵ Since only adsorbed, rehybridized acetylene is present on the surface when dosing at 80 K,^{13,14} this confirms that this species is the reactive precursor to ethylene formation. This conclusion is corroborated by other experiments which reveal that coadsorption of hydrogen and vinylidene on Pd(111) in ultrahigh vacuum yields no hydrogenation products.¹⁵

To probe the rate-limiting step in the hydrogenation of acetylene, vinyl species were grafted onto a clean Pd(111) surface by exposure to vinyl iodide. Figure 2 displays a series of temperature-programmed desorption data collected at 27 amu following the adsorption of vinyl iodide on Pd(111) at 80 K. The vinyl iodide exposures are marked adjacent to the corresponding spectrum. Note that this mass corresponds to the desorption of both vinyl iodide and ethylene. At low coverages, the spectrum consists of a single feature at ~ 235 K which grows in intensity with increasing exposure. A sharp feature appears at 145 K at an exposure of 1.7 L of vinyl iodide which does not saturate with increasing exposure and is assigned to the desorption of vinyl iodide multilayers (see below). An additional feature appears at ~ 330 K for vinyl iodide exposures of 0.6 L and greater, which increases in intensity with the addition of

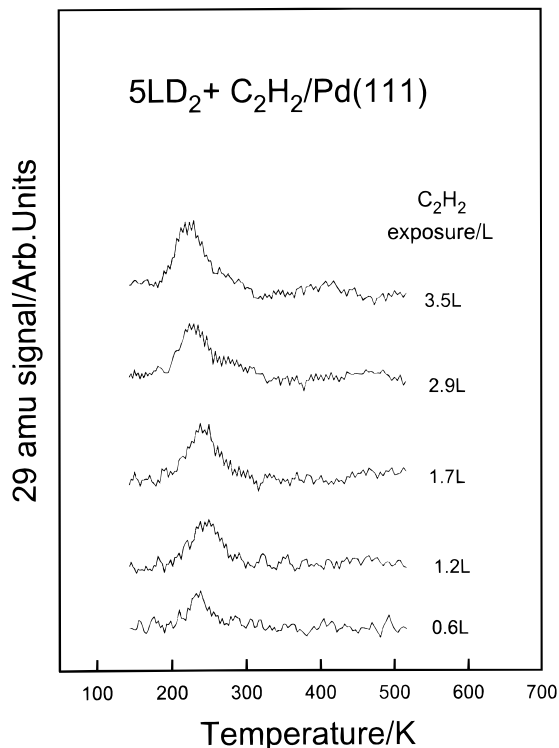


Figure 1. The 29 amu temperature-programmed desorption spectra for acetylene adsorbed onto a deuterium precovered surface (5 L exposure) at 80 K as a function of acetylene exposure, where the acetylene exposures are marked adjacent to the corresponding desorption spectra.

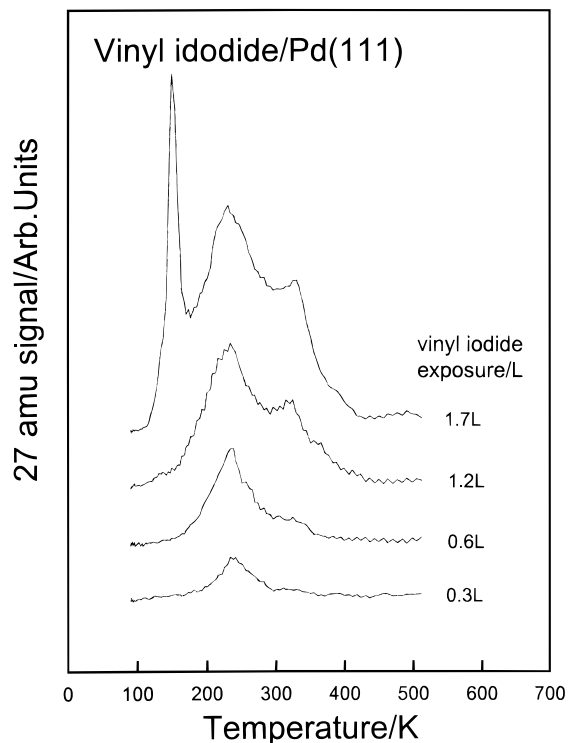


Figure 2. The 27 amu temperature-programmed desorption spectra following adsorption of vinyl iodide on Pd(111) at 80 K as a function of exposure. The vinyl iodide exposures are indicated adjacent to each spectrum.

vinyl iodide. The corresponding temperature-programmed desorption spectra monitored at 26, 27, 28, and 127 amu are displayed for a 1.2 L vinyl iodide exposure in Figure 3a and

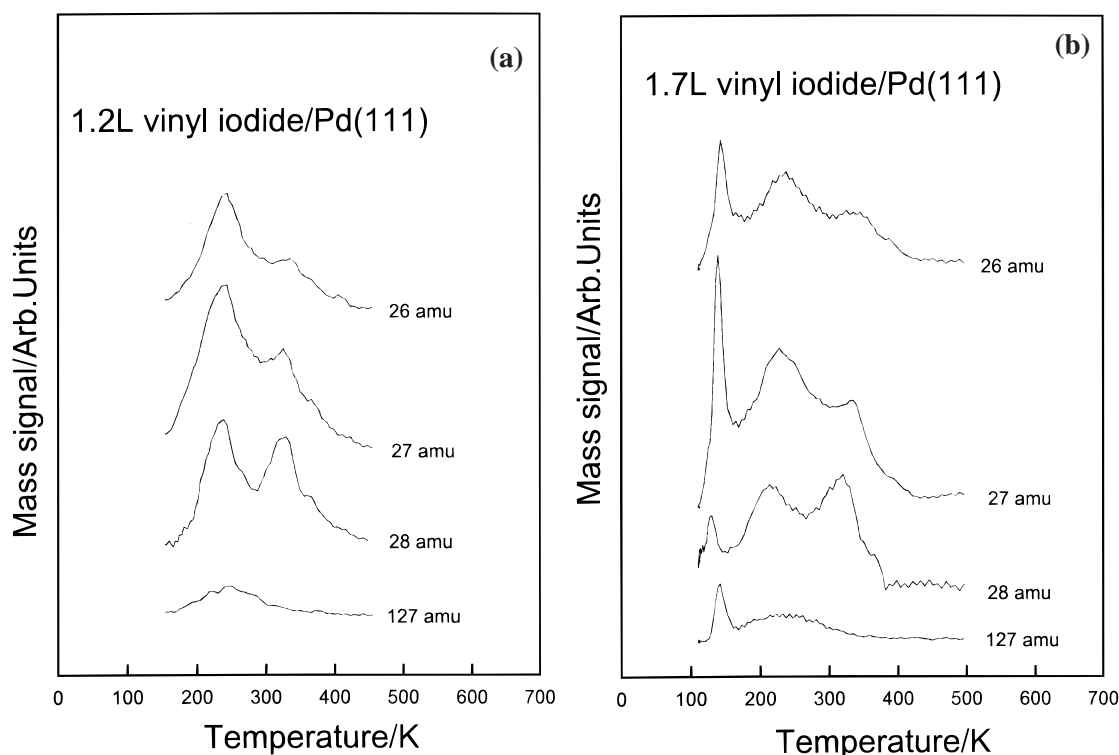


Figure 3. Temperature-programmed desorption spectra for vinyl iodide adsorbed onto Pd(111) monitoring 26, 27, 28, and 127 amu following (a) 1.2 L and (b) 1.7 L exposures of vinyl iodide.

for a 1.7 L vinyl iodide exposure in Figure 3b. The 330 K feature in both spectra has the largest intensity at 28 amu with less intense contributions at 27 and 26 amu. The relative intensities at each of these masses agrees well with the mass spectrometer fragmentation pattern due to ethylene. There is no intensity in this temperature range at 127 amu (iodine) so that the 330 K peak is ascribed to the formation of ethylene. As noted above, the 145 K feature (Figure 3b) grows continually with increasing vinyl iodide exposure and is thus assigned to the desorption of condensed vinyl iodide. This conclusion is corroborated by the observation that the integrated areas under the desorption peaks agree with the mass spectrometer ionizer fragmentation pattern for vinyl iodide. Note that, while the 235 K feature has a significant intensity at 127 amu showing that vinyl iodide desorbs at this temperature, the intensities of the 26, 27, and 28 amu features do not correspond exactly to vinyl iodide. Subtracting out the vinyl iodide contribution from these desorption states at 26, 27, and 28 amu using the 127 amu desorption peak intensity (which derives exclusively from vinyl iodide) reveals that the remaining signal is due to ethylene desorption which correspond to $70 \pm 10\%$ of the ethylene desorbing at 330 K. A simple Redhead analysis assuming a pre-exponential factor of $1 \times 10^{13} \text{ s}^{-1}$ yields a first-order desorption activation energy for adsorbed vinyl iodide of $\sim 59 \text{ kJ/mol}$. Hydrogen desorption (not shown) is also detected due to the thermal decomposition of adsorbed vinyl species. No other desorbing species, particularly acetylene or benzene, were found.

The corresponding infrared spectra following adsorption of 5 L of vinyl iodide on Pd(111) at 80 K are displayed in Figure 4. The spectrum displays intense features at 1581, 1362, 1226, 948, and 912 cm^{-1} with weaker features at 1053 and 985 cm^{-1} . The majority of these features are due to vinyl iodide adsorbed on Pd(111), and their assignments are given in Table 1.³¹ The 1053 cm^{-1} peak will be discussed in greater detail below. These peak intensities decrease as the sample temperature increases, and all features due to vinyl iodide are essentially absent on

TABLE 1: Frequencies and Assignments of the RAIRS Spectrum Collected by Dosing Pd(111) with Vinyl Iodide at 85 K (see Figure 4)

frequency/ cm^{-1}	symmetry	assignment ^a
912	a''	$\rho_{\text{out}}(\text{CH}_2)$
948	a''	$\delta_{\text{out}}(\text{CH})$
985	a'	$\delta_{\text{in}}(\text{CH}_2)$
1053		
1226	a'	$\delta_{\text{in}}(\text{CH})$
1362	a'	$\gamma(\text{CH}_2)$
1581	a'	$\nu(\text{C}=\text{C})$

^a Assignments made by comparison with gas-phase vinyl iodide.³¹

warming the sample to $\sim 130 \text{ K}$ due to the desorption of the vinyl iodide multilayer. After heating to 140 K, the only features evident are at 965, 1053, and 1235 cm^{-1} and, on heating to 160 K, the 1053 and 965 cm^{-1} peaks disappear and a feature becomes evident at 1326 cm^{-1} . Further annealing causes the 1326 cm^{-1} mode to increase in intensity, reaching a maximum at an annealing temperature of $\sim 300 \text{ K}$. Heating the vinyl iodide covered surface to 600 K removes all adsorbate-induced features. The 1326 cm^{-1} feature is characteristic of the formation of ethylidyne on Pd(111),²⁹ indicating the conversion of adsorbed vinyl species into ethylidyne. This feature has a peak absorbance of $\sim 1.4 \times 10^{-4}$ on heating to 300 K (Figure 4). The infrared spectrum of a saturated ethylidyne overlayer ($\Theta_{\text{sat}} = 0.25$),³² collected using the same apparatus and an identical protocol, has an absorbance of $\sim 8.3 \times 10^{-4}$ ²⁹ so that, assuming the absorbance scales linearly with coverage, it yields an ethylidyne coverage from vinyl iodide at $\sim 300 \text{ K}$ of 0.05 ML.

The effect on vinyl iodide of precovering Pd(111) by deuterium is shown in Figure 5, which displays the 29 amu desorption spectra of a deuterium-saturated Pd(111) (5 L exposure) surface exposed to vinyl iodide. The vinyl iodide exposures are indicated adjacent to each spectrum. For vinyl iodide exposures below 0.3 L, the spectra show an asymmetric

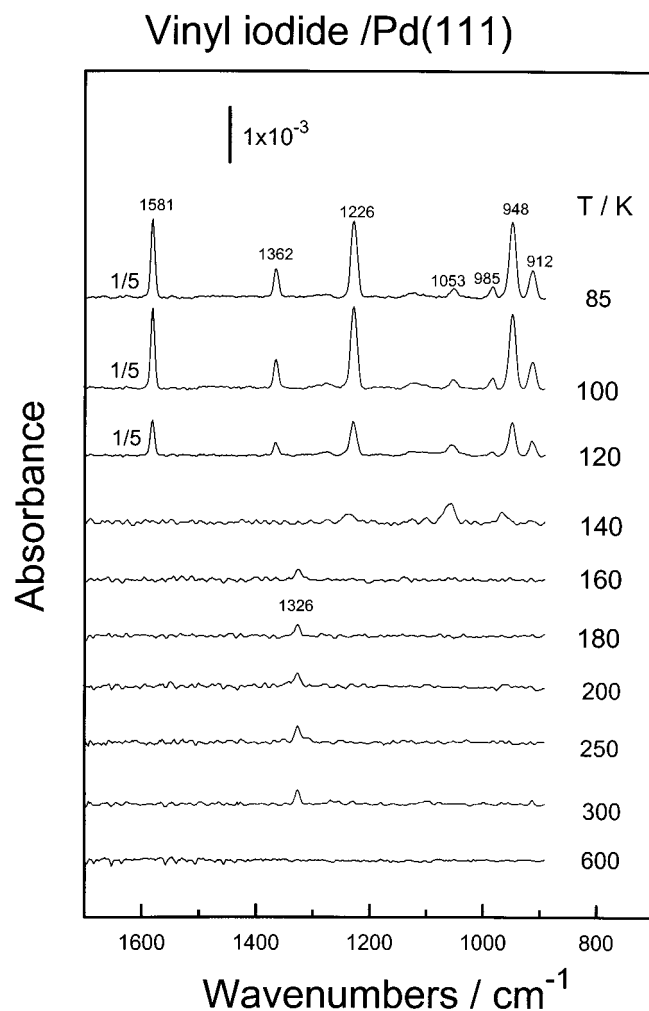


Figure 4. Infrared spectra of a monolayer of vinyl iodide adsorbed onto Pd(111) at 85 K collected as a function of annealing temperature, where the annealing temperatures are marked adjacent to the corresponding spectra. The vertical bar on the figure indicates 1×10^{-3} au. The spectra were collected at 4 cm^{-1} resolution for 1000 scans.

peak centered at $\sim 240 \text{ K}$. However, when the vinyl iodide exposure exceeds 0.6 L, a broad feature appears with a peak temperature centered at $\sim 170 \text{ K}$. This increases in intensity as the vinyl iodide exposure increases to 1.2 L but shows no further increase for a 2.6 L exposure. This is in accord with the temperature-programmed desorption data of Figure 2 which shows that the overlayer saturates at a vinyl iodide exposure between 1.2 and 1.7 L. In addition, a small feature is noted centered at $\sim 330 \text{ K}$.

The desorption spectra collected at various masses for vinyl iodide adsorbed on a deuterium-saturated Pd(111) surface are displayed in Figure 6 where signals at 28, 29, 30, and 127 amu are monitored. In this case, Pd(111) was saturated with deuterium at 80 K (5 L exposure) and then exposed to 1.2 L (Figure 6a) and 2.6 L (Figure 6b) of vinyl iodide, and the desorbing species were monitored at various masses. The masses are marked adjacent to each spectrum. In the data displayed in Figure 6a, the broad 175 K feature has its major intensity at 29 amu with a fragment at 28 amu but with no intensity at 30 amu. No signal was detected in this temperature range at higher masses. This corresponds to the formation of d_1 -ethylene in accord with the addition of a deuterium atom to an adsorbed vinyl species. In contrast, the 330 K feature, which has only a small contribution at 29 amu, has its major feature at 28 amu and also some intensity at 30 amu. Note that this peak is also

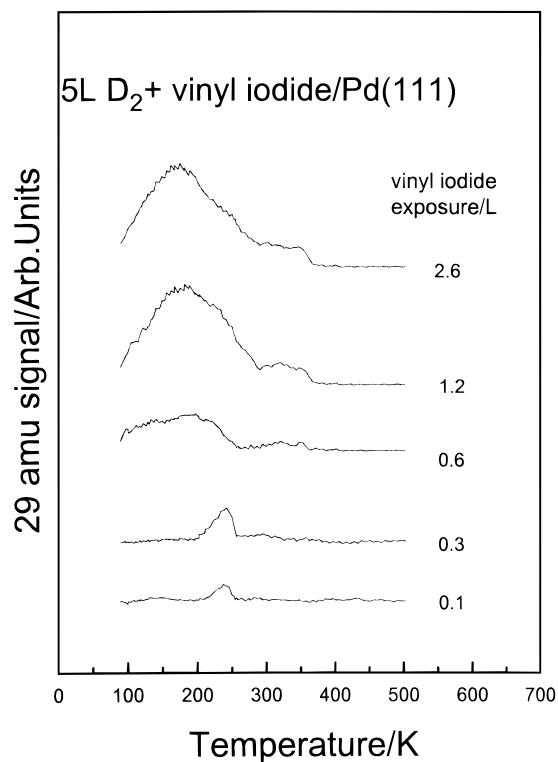


Figure 5. A series of temperature-programmed desorption spectra collected at 29 amu after saturating a Pd(111) surface with deuterium (5 L exposure) and exposing to vinyl iodide. The vinyl iodide exposure is indicated adjacent to each spectrum.

present in the data shown in Figures 2 and 3. Similar conclusions are arrived at from the data of Figure 6b for higher vinyl iodide exposures, except that the 127 amu intensity increases drastically due to the desorption of vinyl iodide multilayers. The sharp peak at $\sim 145 \text{ K}$ on the broad background of the 28 amu spectrum in this figure is due to the mass spectrometer ionization of desorbing vinyl iodide.

The infrared spectra of vinyl iodide on Pd(111) (Figure 4) show the growth of a feature at 1326 cm^{-1} on heating to 160 K and above. This peak is characteristic of ethylidyne on Pd(111),²⁹ and it has recently been demonstrated that coadsorption of hydrogen and acetylene on Pd(111) leads to the formation of ethylidyne.²⁷ The infrared data are consistent with this observation and suggest that ethylidyne is formed via a vinyl intermediate produced by the addition of atomic hydrogen to acetylene. This further implies that, if vinylidene species hydrogenate via a similar vinyl intermediate, they might therefore also form ethylidyne. Note that vinylidene species do not react with hydrogen in ultrahigh vacuum.¹⁵ To establish whether they can react with high pressures of hydrogen, a saturated vinylidene overlayer was prepared by adsorbing acetylene on Pd(111) at 300 K. The small-volume infrared cell was then pressurized with hydrogen and RAIRS spectra collected as a function of time for 50 scans at 4 cm^{-1} resolution. The formation of ethylidyne was noted from the appearance of a feature at 1326 cm^{-1} in accord with the above conjecture. A typical time course of the intensity of the 1326 cm^{-1} feature (due to ethylidyne) of a surface initially saturated with vinylidene and pressurized with 100 mTorr of hydrogen is displayed in Figure 7. Note that no infrared radiation is absorbed by gas-phase hydrogen. The ethylidyne coverage is estimated by comparing the signal intensity at each time with that of a saturated surface,²⁹ where the ethylidyne coverage is 0.25 monolayers (where the coverage is referenced to the palladium atom density of the (111) face).

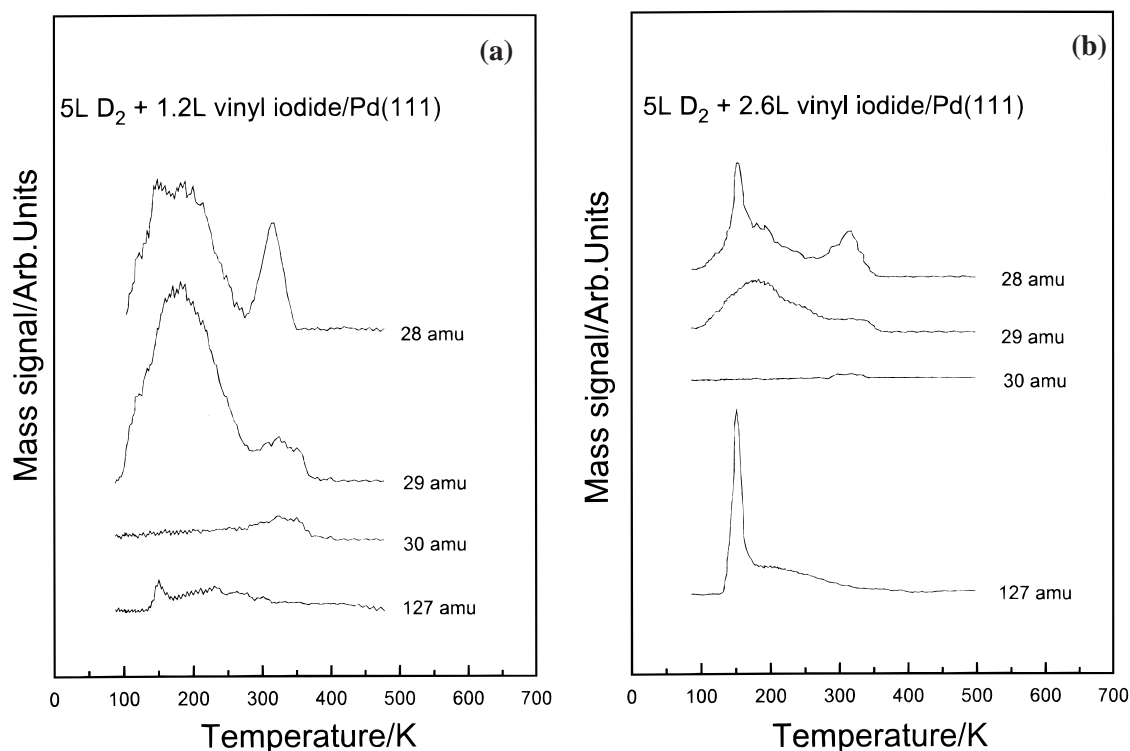


Figure 6. A series of temperature-programmed desorption spectra collected at 28, 29, 30, and 127 amu after saturating a Pd(111) surface with deuterium (5 L exposure) and exposing to (a) 1.2 L and (b) 2.6 L of vinyl iodide.

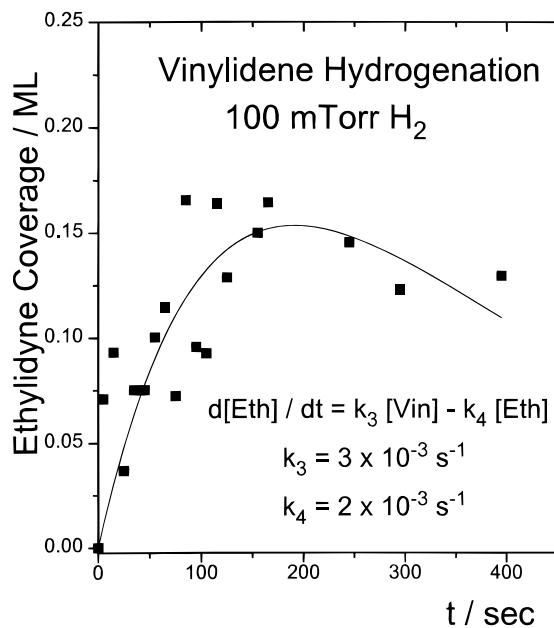


Figure 7. Plot of the time course of ethylidyne coverage after pressurizing a vinylidene-covered Pd(111) surface to 0.1 Torr of hydrogen where the ethylidyne coverage is monitored using infrared spectroscopy.

The ethylidyne coverage initially increases for the first ~ 150 s but then starts to decrease after reaching a maximum of 0.15 monolayers. It was not possible to measure the corresponding vinylidene signal intensity during this kinetic experiment because of its small absorbance.²¹ These results, however, confirm that vinylidene species can react with relatively high pressures of hydrogen. For times greater than ~ 200 s, the ethylidyne signal once again decreases, which indicates that the ethylidyne that is formed on the surface is also being removed by gas-phase hydrogen. The kinetics of ethylidyne removal by

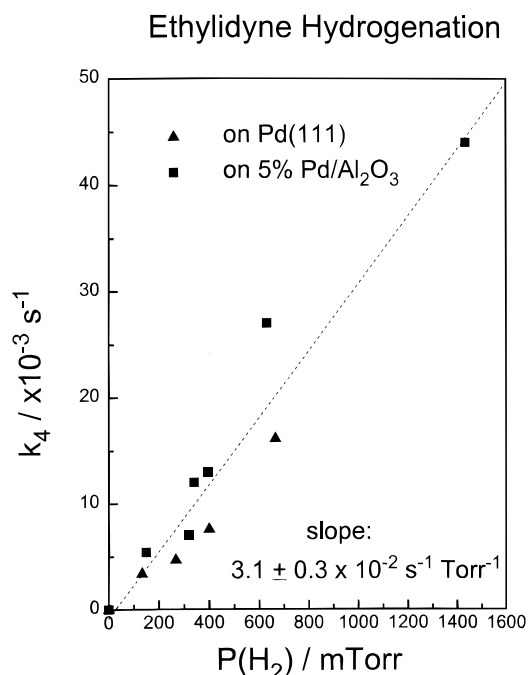


Figure 8. Plot of the rate of ethylidyne hydrogenation versus hydrogen pressure on Pd(111) measured using infrared spectroscopy.

hydrogen were therefore also measured. In this experiment, an ethylidyne-saturated surface was prepared by exposing a Pd(111) sample to ethylene at 300 K. Note that it has been shown previously that ethylidyne species on Pd/Al₂O₃ also react with hydrogen but the hydrogen pressure dependence of this reaction rate was not explicitly measured.^{23,24} The results of this experiment are displayed in Figure 8 which plots the rate constant for ethylidyne removal measured from the intensity of the ethylidyne signal (at 1326 cm⁻¹) as a function of time,

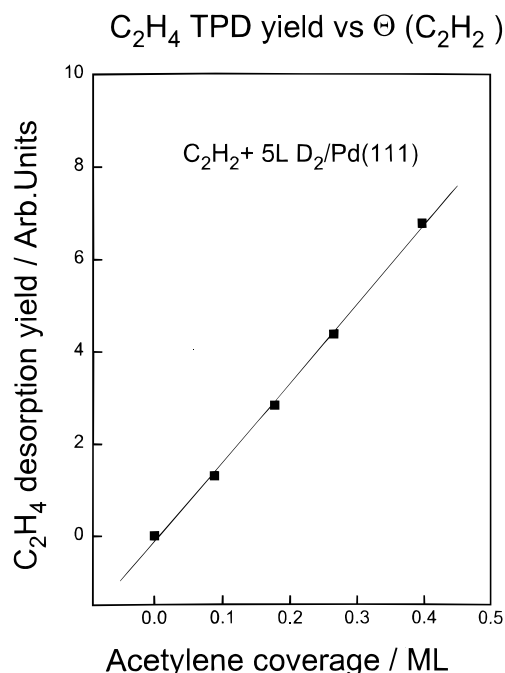


Figure 9. Plot of the ethylene desorption yield versus acetylene coverage for the temperature-programmed desorption data shown in Figure 1 where various coverages of acetylene were adsorbed on a surface saturated with deuterium (5 L deuterium exposure).

for various hydrogen pressures. Data were collected for a Pd(111) single crystal (\blacktriangle), where the ethylidyne-saturated surface was made by exposing it to ethylene (100 L, 300 K), and for Pd/Al₂O₃ (\blacksquare), where a pellet of alumina-supported palladium (5% Pd/Al₂O₃) was pressuring with ethylene (5 Torr, 300 s). The ethylidyne infrared spectral features were the same for both samples.²¹ The ethylidyne hydrogenation kinetics at 300 K are identical on both samples and are first-order in hydrogen pressure. The resulting ethylidyne removal rate constant is $3.1 \pm 0.3 \times 10^{-2} \text{ Torr}^{-1} \text{ s}^{-1}$. It should be noted that these data were measured for the initial rate of ethylidyne removal. It was found that not all of the ethylidyne could be removed from the surface even after a prolonged exposure to hydrogen and the limiting final ethylidyne coverage corresponded (from the intensity of the 1326 cm⁻¹ feature) to a coverage of ~ 0.08 monolayers. A similar effect has been noted for ethylidyne hydrogenation on Pt(111) (which is much slower than on Pd(111)) where an initial fast removal rate is followed by a much slower rate as the coverage decreases.³²

Discussion

Adsorbed acetylene reacts with adsorbed atomic hydrogen to yield ethylene (Figure 1) where the desorption state exhibits a maximum at ~ 245 K, in reasonable agreement with previous data.¹⁵ It has also been shown that the acetylene hydrogenation rate was first order in hydrogen coverage,¹⁵ suggesting that ethylene is formed by the sequential addition of hydrogen to adsorbed acetylene. The data of Figure 1 also show that the ethylene yield increases with acetylene coverage. This is displayed more explicitly in Figure 9, which plots the integrated ethylene desorption yield measured from the area of the desorption features shown in Figure 1 versus the initial acetylene coverage. This yields a good straight line, implying that the reaction rate is first order in acetylene coverage in accord with the above model in which ethylene is formed by the sequential addition of hydrogen to adsorbed acetylene.

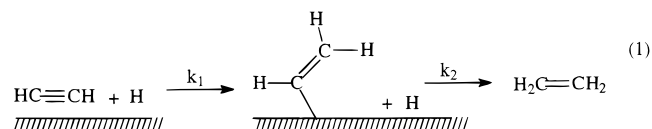
The reaction of acetylene to form ethylene therefore proceeds in a stepwise fashion forming an intermediate vinyl species which subsequently reacts forming ethylene. The first-order dependence in hydrogen coverage implies that one of these steps is slower than the other and limits the overall hydrogenation rate. To establish which is the rate-limiting step, the vinyl intermediate was grafted onto the surface by vinyl iodide adsorption. This has now become a relatively common strategy for forming hydrocarbon moieties on surfaces since the C–I bond is substantially weaker than the corresponding surface bond so that the removal of the iodine to form I_(ads) and a hydrocarbon fragment is thermodynamically allowed. Furthermore, the C–I bond is weaker than the C–H bond, so the reaction is kinetically favored.²⁶ The 27 amu temperature-programmed desorption spectra for vinyl iodide adsorbed on Pd(111) are shown in Figure 2. Vinyl iodide and ethylene desorb at ~ 235 K where the first-order vinyl iodide desorption activation energy is ~ 59 kJ/mol and multilayers desorb at ~ 145 K (see parts a and b of Figure 3). Ethylene also desorbs at ~ 330 K. This is ascribed to the hydrogenation of vinyl species formed on the surface. These results are similar to those found for vinyl iodide adsorbed on Pt(111).^{33,34} In this case, overlayer desorption was found at ~ 160 K and multilayer desorption at ~ 140 K. Ethylene formation was found on Pt(111) at ~ 300 K compared to ~ 330 K on Pd(111). The chemistry of vinyl species on silver is completely different where they dimerize yielding C₄ products.³⁵ Approximately 30% of the vinyl iodide adsorbed on Pt(111) was shown to dissociate at ~ 105 K although X-ray photoelectron spectroscopy data indicated that dissociation takes place above ~ 165 K.³³ It was also suggested that, in the presence of large iodine coverages, some vinyl species are stable up to ~ 450 K.³³ The RAIRS data (Figure 4) reveal the formation of a condensed molecular vinyl iodide layer at 85 K which persists up to 140 K. A significant diminution in intensity is noted at ~ 120 K, and by 140 K the multilayer features have completely disappeared consistent with the temperature-programmed desorption data of Figures 2 and 3. The spectrum formed on heating to ~ 140 K exhibits weaker features at 1053 and 965 cm⁻¹ with perhaps a very weak peak at ~ 1235 cm⁻¹. Only modes with a'' symmetry would be allowed by the infrared surface selection rules for vinyl iodide bonded with its C=C axis parallel to the surface.³⁶ The absence of features with a' symmetry following heating to above 140 K (see Table 1) and the presence of a peak at ~ 965 cm⁻¹ (assigned to the out-of-plane CH bending mode of a'' symmetry) suggests that desorption of the multilayer leaves adsorbed vinyl iodide bonded with its C=C axis parallel to the surface. The 912 cm⁻¹ mode should also be symmetry allowed in this geometry, but its lower absorbance compared to the 965 cm⁻¹ mode (present at 948 cm⁻¹ in condensed vinyl iodide) suggests that it is not detectable. The remaining intensity at ~ 1235 cm⁻¹ may be due to the persistence of a small amount of residual second-layer vinyl iodide or may suggest that the molecular plane does not lie exactly parallel to the Pd(111) surface. This would not be inconsistent with the presence of a relatively large iodine atom on the vinyl iodide preventing it from laying completely flat. The origin of the feature at ~ 1053 cm⁻¹ is not clear. Note that this feature also appears to be present immediately following vinyl iodide adsorption at 85 K and remains up to an annealing temperature of ~ 160 K. A peak at 1071 cm⁻¹ has been noted on Pt(111) following adsorption of vinyl iodide and after annealing to between 130 and 160 K and is assigned to the methylene rocking mode of a vinylidene species.³⁴ The infrared spectrum of vinylidene, however, has

its most intense feature at $\sim 1267\text{ cm}^{-1}$,²¹ whereas no signal is noted at this frequency. As the sample is heated to $\sim 160\text{ K}$, a feature grows at $\sim 1326\text{ cm}^{-1}$, assigned to ethylidyne. Molecular vinyl iodide and some ethylene also desorb (Figures 2 and 3). A similar formation of ethylidyne is noted on Pt(111) from adsorbed vinyl intermediates.³⁵ The formation of ethylidyne implies that vinyl formation is underway by $\sim 150\text{ K}$. Note that there is no evidence for the formation of vinylidene species nor for the formation of acetylene. As the temperature increases further to $\sim 300\text{ K}$, the coverage of ethylidyne on the surface increases correspondingly. Comparing the intensity of the ethylidyne feature at 300 K in Figure 4 with that for a saturated monolayer formed by adsorbing ethylene on Pd(111) suggests that the ethylidyne coverage is ~ 0.05 monolayers.

Ethylene also forms at $\sim 330\text{ K}$. As noted above, similar ethylene desorption is found from Pt(111) at between 262 and 293 K which is ascribed to vinyl self-hydrogenation, and a similar assignment is made here.³⁵ Interestingly, vinyl species convert to ethylidyne at lower temperatures (Figure 4) but the desorption of ethylene at $\sim 330\text{ K}$ appears to imply the persistence of some vinyl species at this remarkably high temperature. Certainly, an ethylidyne-covered Pd(111) surface cannot be responsible for the formation of ethylene at this temperature. Any possible adsorbed acetylene hydrogenates to ethylene at $\sim 245\text{ K}$ (Figure 1) so that this reaction route can be excluded. The results suggest, then, that vinyl iodide adsorbs with its C=C axis parallel to the surface following multilayer desorption at $\sim 145\text{ K}$ with the adsorbed monolayer either desorbing with an activation energy of $\sim 59\text{ kJ/mol}$ or converting to ethylidyne in a competitive reaction. Some adsorbed vinyl species appear to persist to relatively high temperatures although there is no direct evidence from the infrared data that there are any vinyl species on the surface. In any case, the relative coverage of such intermediates is likely to be low. Note, however, that the persistence of vinyl species up to $\sim 450\text{ K}$ on Pt(111) has been suggested.³⁵

The effect of presaturating the surface with deuterium is shown in Figure 5 where ethylene desorbs in a broad feature centered at $\sim 170\text{ K}$ for exposures above 0.6 L with an additional desorption peak at $\sim 330\text{ K}$. This latter feature is identical to that found following vinyl iodide adsorption on clean Pd(111) (Figures 2 and 3). Hydrogenation products are also found for vinyl iodide exposures less than 0.6 L on a deuterium-precovered Pt(111) surface where the peak is at $\sim 230\text{ K}$ and shifts to lower temperatures as the deuterium coverage increases. There is also a substantial amount of H–D exchange in the high-temperature (330 K) ethylene desorption state (Figure 6), as evidenced by significant intensities for masses up to $\sim 30\text{ amu}$. The exchange between adsorbed deuterium and hydrogen in the low-temperature ($\sim 170\text{ K}$) ethylene desorption state is essentially negligible as demonstrated by the complete lack of intensity at 30 amu at between 200 and 300 K . The traces collected at higher masses (not shown) similarly show no intensity in this region. Thus, exclusively $\text{C}_2\text{H}_3\text{D}$ desorbs at 170 K with essentially no H–D exchange, at least at these low temperatures. The onset of d_1 -ethylene desorption in Figures 5 and 6 is at a relatively low temperature and may indicate that these reaction kinetics are limited by the formation of vinyl species from vinyl iodide. The position of the trailing edge of the broad feature ($\sim 250\text{ K}$) certainly coincides with the desorption of hydrogen.²⁵ It should finally also be pointed out that the deuteration of adsorbed vinyl iodide itself would be expected to lead to desorption products with masses larger than 29 amu . The results presented above

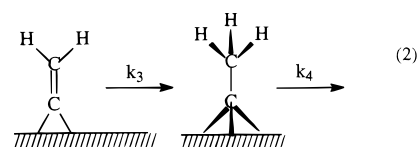
indicate that acetylene hydrogenates to ethylene in a stepwise fashion as



The individual reaction steps are probed by grafting vinyl species onto the surface by adsorbing vinyl iodide, which indicates that the addition of hydrogen to a vinyl species gives rise to a desorption feature at $\sim 175\text{ K}$ (corresponding to k_2). Adsorbed acetylene hydrogenates at $\sim 235\text{ K}$. This is higher than the temperature at which a vinyl species hydrogenates, suggesting that the rate-limiting step for the reaction shown in eq 1 corresponds to the addition of a hydrogen atom to adsorbed acetylene to yield a vinyl intermediate. This indicates that the desorption state at 235 K corresponds to k_1 so that $k_2 > k_1$. This result implies that the shape of the desorption spectrum shown in Figure 1 depends on k_1 , the rate of addition of the first hydrogen. The desorption data have been analyzed to yield an activation energy for this process of $23 \pm 1\text{ kJ/mol}$.¹⁵ Note that this value is much lower than the activation energy for palladium-catalyzed acetylene hydrogenation ($40 \pm 2\text{ kJ/mol}$).³⁷

The amount of vinyl iodide desorption appears to be only slightly affected by the presence of preadsorbed hydrogen since the 127 amu (iodine) desorption states in Figures 3 and 6 have approximately identical areas. The shapes of the desorption features are, however, modified substantially so that rather than consisting of a fairly broad feature on clean Pd(111) (Figure 3), a sharper feature is evident at 127 amu at $\sim 145\text{ K}$ after the exposure of 1.2 L of vinyl iodide (Figure 6a). This is accompanied by a slight enhancement in the 28 amu intensity at this temperature. The ethylene desorption state found at $\sim 330\text{ K}$, both in the presence of a saturated deuterium layer (Figure 6) and on clean Pd(111) (Figure 3), has its largest intensity at 28 amu , suggesting that it consists predominantly of C_2H_4 , although some intensity at 29 and 30 amu reveals that some H–D exchange has taken place, presumably in the vinyl precursor. The hydrogen required for the formation of this species probably derives from the decomposition of carbonaceous species present on the surface.

As noted above, hydrogenation of vinylidene species presumably also likely takes place via a vinyl intermediate. While vinylidenes do not hydrogenate in ultrahigh vacuum,²⁵ the data of Figure 7 demonstrate that vinylidene species react with high pressures ($\sim 0.1\text{ Torr}$) of hydrogen. This figure shows the time course of the reaction of a vinylidene-saturated Pd(111) surface with 0.1 Torr of hydrogen at 300 K where the ethylidyne coverage initially increases to a maximum of ~ 0.15 monolayers and subsequently decreases. Since hydrogenation of vinylidene is assumed to proceed via a vinyl intermediate and since this, according to the infrared data of Figure 4, reacts at 300 K to form ethylidyne, this behavior is ascribed to a stepwise process (eq 2).



The rate of ethylidyne hydrogenation (k_4 in eq 2) can be measured independently in a similar manner by monitoring the rate at which ethylidyne species are removed from the surface

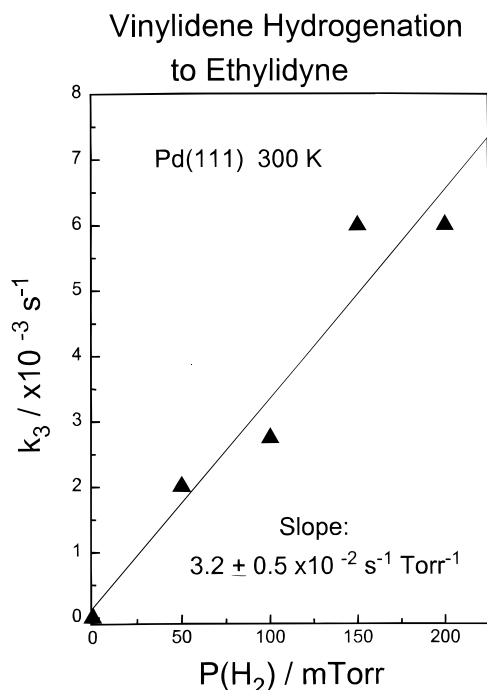
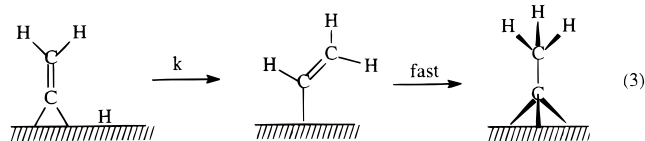


Figure 10. Plot of the rate of vinylidene to ethylidyne conversion on Pd(111) as a function of hydrogen pressure.

in an external pressure of hydrogen using infrared spectroscopy. Again, there is no interference from gas-phase species in this case. The results are displayed in Figure 8 for the initial rate of ethylidyne removal which is first order in hydrogen pressure on both Pd(111) and for a supported palladium sample (5% Pd/ Al_2O_3), with a rate constant of $3.1 \pm 0.3 \times 10^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$. The rate equations for the sequential reaction scheme shown in eq 2 can be solved analytically, and the solid line plotted with the data in Figure 7 is the solution to this equation fit using a single parameter, k_3 , since the rate constant k_4 has been measured independently from the data of Figure 8. Data similar to those shown in Figure 7 were collected as a function of hydrogen pressure for pressures up to 0.2 Torr. This allows the value of k_3 to be measured as a function of hydrogen pressure and the results are displayed in Figure 10. The rate constant again varies linearly with hydrogen pressure with a value of $3.2 \pm 0.5 \times 10^{-2} \text{ Torr}^{-1} \text{ s}^{-1}$. The conversion of vinylidene to ethylidyne is therefore proposed to take place via the following pathway:



since the addition of surface atomic hydrogen to vinylidene must form a vinyl species and this has been shown to react to form ethylidyne (Figure 4). However, assuming that hydrogen adsorbs dissociatively on Pd(111),²⁵ this suggests that the rate of the reaction depicted in eq 3 should be proportional to $\Theta(\text{H})$ and therefore to $\sqrt{P(\text{H}_2)}$, rather than the observed first-order dependence. It is striking, however, that the rate constants k_3 and k_4 are almost identical ($3.2 \pm 0.5 \times 10^{-3} \text{ Torr}^{-1} \text{ s}^{-1}$ (Figure 8) versus $3.1 \pm 0.3 \times 10^{-3} \text{ Torr}^{-1} \text{ s}^{-1}$ (Figure 10)). A possible explanation for this effect may lie in the different ethylidyne and vinylidene saturation coverages. Ethylidyne saturates at a coverage of 0.25³² (where coverages are again referenced to the palladium atom site density on Pd(111)), whereas the

saturation coverage of vinylidene is 1.0.¹⁷ This means that the conversion shown in eq 3 requires that vinylidene ($\Theta_{\text{sat}} = 1.0$) convert into ethylidyne where the saturation coverage is only 0.25. Clearly, there is insufficient space on the surface for this conversion to take place so that the transformation of vinylidene to ethylidyne requires that space be made to accommodate the ethylidyne that is formed. This is likely limited by the rate at which ethylidyne species are removed from the surface leading to the similarity between rate constants k_3 and k_4 and the similar first-order hydrogen pressure dependences of both of these rates. The nature of the gas-phase products formed during these reactions will be illustrative in further defining the reaction pathways for the titration of both ethylidyne and vinylidene species from Pd(111). However, since vinyl species on the surface hydrogenate to ethylene (Figures 5 and 6), gas-phase species are likely to consist primarily of ethylene.

Conclusions

Comparison of the rate of hydrogenation of acetylene coadsorbed with atomic hydrogen on Pd(111) with that of vinyl species formed by adsorbing vinyl iodide demonstrates that the rate-limiting step in the hydrogenation of acetylene to ethylene is the addition of the first hydrogen atom to acetylene to form a vinyl species. This result is in accord with the first-order dependence in hydrogen coverage for acetylene hydrogenation measured previously. Reflection/absorption infrared measurements also show that adsorbed vinyl species convert into ethylidyne moieties, an observation which rationalizes the observation that adsorbing acetylene onto a hydrogen precovered surface leads to the formation of ethylidyne rather than vinylidene. This reaction is proposed to proceed via an intermediate vinyl species. The hydrogenation of vinylidene in the presence of high pressures of hydrogen (up to 0.2 Torr) is followed at 300 K where the formation of ethylidyne intermediates is noted in accord with the reaction pathway found for vinyl species. In this case, vinylidene is found to convert into an ethylidyne species that is ultimately titrated from the surface by hydrogen. The rate constant for the conversion of vinylidene into ethylidyne is found to be identical to that for the removal of ethylidyne species from the surface, and both reactions are found to be first order in hydrogen pressure. This may be due to the different saturation coverages for each species where the saturation vinylidene coverage ($\Theta_{\text{sat}} = 1.0$) is much larger than that for ethylidyne ($\Theta_{\text{sat}} = 0.25$) so that the conversion of vinylidene into ethylidyne requires species to be removed from the surface to accommodate the ethylidyne that is formed.

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