Thermal Evolution of Acetylene Overlayers on Pd(111)

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The thermal evolution of acetylene adsorbed on the (111) surface of palladium has been studied by high resolution electron energy loss spectroscopy (HREELS). This study encompasses the temperature range 120−800 K for acetylene exposures of 0.25−3.5 langmuirs and includes HREELS data for both specular and off-specular scattering. The spectra are interpreted in terms of acetylene evolution to ethylidyne via a vinylidene intermediate, with the additional hydrogen supplied by the residual gas. Evidence for benzene formation is also seen in the appearance of the benzene ν_4 (720 cm^{-1}) band. Subsequent heating to 400 K results in dehydrogenation of ethylidyne to CCH species. A spectral normalization method is employed to compare intensities of vibrational bands as a function of temperature and proves useful in analysis of the temperature dependence of the surface species. We find that 0.25-langmuir exposure results in an essentially pure ethylidyne layer whereas higher coverages eventually result in lower ethylidyne production, likely due to steric hindrances on the vinylidene intermediate and the competing channel of benzene production.

1. Introduction

Seventeen years have passed from the first announcement of acetylene cyclotrimerization on palladium at low temperatures.[1−3] Since then the interplay of the palladium surface and acetylene has maintained the attention of scientists. A variety of techniques have been used to establish the formation of benzene on the palladium surface following acetylene adsorption. Thermal programmed reaction (TPR) experiments showed that after C_2H_2 adsorption at low temperatures, reactively formed benzene desorbs with two desorption maxima, the first maximum near 230 K, the second broader one near 500 K.[4] Isotopic labeling experiments proved that no CC bond breaking takes place during this reaction. TPR studies showed that along with benzene the desorption of C_4H_x species also takes place. This observation led Tysoe *et al.*[2] to the suggestion that C_4H_4 is a possible intermediate of the reaction. The formation of C_4H_4S on a sulfur precovered Pd surface from the adsorbed acetylene was interpreted as further evidence for the stepwise mechanism of the reaction.[5]

Although substantial work has been done since then to better understand the mechanism and kinetics of acetylene cyclotrimerization to benzene on palladium surfaces, relatively little is known about the transformation of the acetylenic species with temperature. Near-edge X-ray absorption fine structure (NEX-AFS) data of acetylene adsorption at 300 K suggested vinylidene formation[6] on Pd(111), whereas high resolution electron energy loss spectroscopy (HREELS) data by Nascente *et al.* argued for ethylidyne.[7] Early data by our group[8] (low temperature C_2H_2 adsorption and subsequent heating to temperatures of 250, 300, 400, and 500 K) were interpreted in terms of a mixture of ethylidyne and vinylidene up to 300 K. At 400 K, the appearance of a CCH species was observed as a result of ethylidyne and vinylidene decompositions. This is in agreement with TPR experiments where the hydrogen desorption peak maximum was

found at 460 K.[2,3] Recently, theoretical work[9] has indicated that the barrier for acetylene−vinylidene conversion on palladium clusters is significantly lower than estimated for the gas phase conversion ($\approx$2 eV) and that vinylidene is $\approx$0.3−0.4 eV lower in energy than adsorbed acetylene on Pd(111). A recent study by Azad *et al.*[10] suggests that vinylidene is a stable species under high vacuum and that high hydrogen pressure (0.1 Torr) or preadsorbed hydrogen is necessary for the conversion to ethylidyne and ethylene.

In this paper we present a detailed study of the acetylene transformation on Pd(111) with temperature. The investigated temperature interval is between 120 and 800 K. A range of acetylene coverages was examined. For coverages below 0.3 monolayer or, in other words, exposures smaller than 0.4 langmuir (1 langmuir = 1×10^{-6} Torr·s) no mutual reaction of acetylene molecules takes place.[11,12] Therefore we expect to obtain spectra where only C_2H_x species are present for these low coverages of acetylene. For higher exposures, more complex spectra were anticipated, which might indicate an associative reaction of adsorbed acetylenic species. Here we focus on the thermal evolution to C_2H_x species and their eventual dehydrogenation. New spectral evidence for benzene formation will be presented elsewhere.[13]

2. Experimental Section

The LK2000 HREELS spectrometer was housed in an ultra-high-vacuum chamber (base pressure 5×10^{-11} Torr). The spectrometer was operated with a resolution of (fwhm) 6−7 meV (48−56 cm^{-1}) and the typical elastic beam rate was 10^6 cps (counts per second). The chamber was also equipped for ion-sputtering, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and quadrupole mass spectrometry.

Prior to each C_2H_2 adsorption, the Pd(111) sample was cleaned by several cycles of Ar$^+$ bombardment (1 kV/300 K) and annealed at 1100 K. Residual carbon was removed by oxidation treatment ($p_{O_2} = 10^{-7}$ Torr at 770 K), followed by flash desorption to 1100 K. Sample cleanliness was monitored

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by AES (sulfur, oxygen) and by dosing O_2 followed by thermal desorption while monitoring the CO and CO_2 (carbon).

An acetone stabilizer was removed from the acetylene by passing the mixture through a dry ice/acetone-cooled trap. Purity was checked with the mass spectrometer. The surface was exposed to acetylene by backfilling the chamber. Note that after closing the leak valve the partial pressure of C_2H_2 fell at a much slower rate at low temperatures than at room temperature. The effect is presumably caused by condensation of acetylene on liquid nitrogen supply lines and subsequent slow liberation of C_2H_2 molecules to the residual atmosphere. The resulting exposure was measured and accounted for to determine the total exposures. Pressure readings were also corrected for the ion gauge sensitivity; according to Varian ionization gauge sensitivity tables we used a factor 2.

In the case of low temperature spectra, the acetylene was dosed at low sample temperature (120 K). We increased the temperature to the indicated value for a period of 5 min. The sample was then allowed to cool to 120 K, at which point the spectra were recorded. The spectra for temperatures over 350 K were recorded at room temperature.

3. Spectra Normalization

A normalization method described in detail in ref 14 was used to compare spectra presented in this work. Briefly, we obtained a spectrum of a clean palladium, divided it by its elastic peak count rate and multiplied by 10^6, i.e., the elastic peak count rate for clean palladium was set to 10^6 cps. Each spectrum for adsorbed acetylene was then multiplied by a constant to normalize the background to the clean palladium spectrum value. The normalization constants were obtained from intervals where no peaks are present; these intervals were always found between 1950 and 2700 cm^{-1}. This normalization is based on an assumption that the background of spectra is due to multiple and recombination losses which are enhanced in the impact regime, i.e., the intensity of background is proportional to the incident electron beam current.

We caution that a normalization procedure based on matching the intensities of elastic peaks of different spectra cannot be used for the adsorption experiment. It is known from theory that the intensity of losses is proportional to elastic peak intensity only for losses which are scattered via the dipole mechanism, while the intensity due to the impact mechanism is proportional to the incident electron beam current.[15] For smooth surfaces, the elastic peak intensity is roughly proportional to the incident beam, and the normalization method based on the elastic peak might be appropriate. This assumption, however, fails utterly for the adsorbed overlayer since the adsorbate introduces an additional roughness, i.e., more electrons are inelastically scattered and the elastic peak intensity decreases. In our experiment, this effect was strongest for intermediate temperatures (190–250 K) where different species coexist on the surface after acetylene adsorption (for details see the next two sections).

4. Results

At low acetylene exposures (<0.5 langmuir), ordered, (2 × 2), acetylene domains form.[16,17] At these exposures no mutual chemical reactions of adsorbed species were detected.[12,16] We expected that only transformations of adsorbed species themselves will be observed with increasing temperature resulting in formation of the C_2H_x class of species. On the other hand, at larger exposures (>0.5 langmuir) the (2 × 2) domains are gradually replaced with the ($\sqrt{3}$ x $\sqrt{3}$) $R30°$ domains and,

eventually, a saturated overlayer of acetylenic species forms at exposures ≈3 langmuir. Along domain boundaries the cyclotrimerization reaction was observed.[16] Hence, we expect to obtain more complex spectra following exposures of 0.5 langmuir and larger.

During our study different concentrations of acetylene were adsorbed on the Pd(111) surface (exposures ranged from 0.25 langmuir to 3.5 langmuirs) at the low temperature (120 K), and temperature dependent HREEL spectra were taken for each acetylene exposure. Acetylene was adsorbed at room temperature as well and these high-temperature spectra (not shown here) have the same overall character as those for which acetylene was adsorbed at low temperature and subsequently heated to room temperature and above room temperature. The only difference between low-temperature and room-temperature exposure data at high temperatures is that the latter have smaller intensities of losses, which we explain as a consequence of a lower sticking probability of acetylene on palladium at room temperature than at 120 K.

Most of the experimental data presented here were recorded for 0.5 langmuir and 3.5 langmuir exposures of C_2H_2 on a clean Pd(111) surface. In the temperature regimes showing the most dramatic effects we compare the 0.5 and 3.5 langmuir spectra with additional data taken at 0.25 langmuir exposure. Both specular and off-specular directions were investigated. The HREEL spectra for 0.5 langmuir and 3.5 langmuir exposures are presented in Figures 1 and 2, respectively. Intensity profiles vs temperature of selected peaks are plotted in Figures 3 and 4.

A brief inspection of Figures 1 and 2 suggests that three basic temperature intervals can be distinguished. (i) 120–213 K: Mostly acetylenic species are present, the most intense loss is the $\rho(CH)_{sym}$, i.e., symmetric CH bend, at 675 cm^{-1}. (ii) 233–350 K: Within this temperature interval the two most pronounced losses are attributed to ethylidyne (1327 cm^{-1} is assigned to the symmetric methyl deformation $\delta(CH_3)_{sym}$ and 1095 cm^{-1} assigned to the CC stretch $\nu(CC)$). (iii) Above 400 K: The main feature is a broad peak at 750 cm^{-1}. It is attributed to the CH bending mode of CCH species, which is a product of C_2H_x dehydrogenation. Heating above 450 K resulted in a decrease of the 750 cm^{-1} loss, which is related to further CCH decomposition, leading to the surface covered with carbon. Spectra taken at temperatures above 500 K are not presented since no new features were observed.

For completeness we also note here that the spectra also contain evidence for benzene formation. The benzene ν_4 mode (720 cm^{-1}) is most clearly visible in Figure 2 (233, 253K traces) and is shifted from the acetylene mode at 682 cm^{-1}. However, due to the complexity of these spectra, the clear extraction of benzene requires more detailed analysis.[13]

A strong feature at approximately 1800 cm^{-1} is due to carbon monoxide impurity. It appears at a frequency of 1750 cm^{-1} in the spectrum taken at 120 K. Since collecting the spectra for one temperature in specular and off-specular directions takes several hours, the exposure of CO from the residual atmosphere is not negligible. The CO peak gains in intensity and shifts toward higher frequencies for spectra at subsequent temperatures.[18] At temperatures above 400 K, CO desorbs (see, for example, ref 19) and the CO mode almost disappears. This CO peak behavior repeats in each temperature cycle. This explains why in the off-specular direction, which is always taken after the specular one, the CO stretching mode is more pronounced even though this mode is dipole in nature.

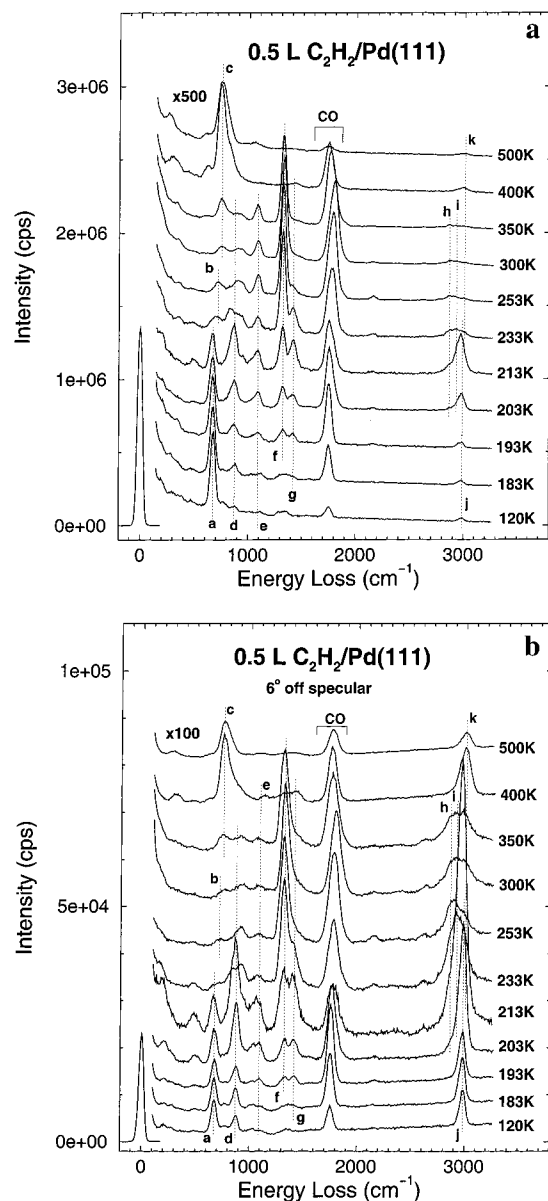Besides the main peaks, other weaker peaks are resolved. Below we summarize their frequencies and assignments and

Figure 1. Vibrational spectra obtained after 0.5 langmuir exposure of C_2H_2 on Pd(111) at 120 K. (a) specular direction; (b) 6° off-specular direction. Dotted lines mark the frequencies at 675 (a), 725 (b), 750 (c), 875 (d), 1095 (e), 1327 (f), 1415 (g), 2864 (h), 2930 (i), 2985 (j), and 3010 cm^{-1} (k).

Figure 2. Vibrational spectra obtained after 3.5 langmuir exposure of C_2H_2 on Pd(111) at 120 K. (a) specular direction; (b) 6° off-specular direction. Dotted lines mark the frequencies at 682 (a), 725 (b), 750 (c), 880 (d), 1100 (e), 1327 (f), 1420 (g), 2864 (h), 2930 (i), 2995 (j), and 3010 (k).

point out cases where the temperature evolution of a peak can directly be interpreted in terms of the transformation of acetylene to ethylidyne and CCH species. More complicated transformations will be analyzed in detail in the Discussion.

4.1. 120−213 K. Peak frequencies and assignments for 0.25, 0.5, and 3.5 langmuir exposures at 120 K are listed in Table 1. Note that a broad peak near 1400 cm^{-1}, previously assigned in the literature to $\nu(CC)$, was separated into two peaks. For all three exposures one of the two peaks lies near the frequency 1355 cm^{-1}. We assign this peak to the $\nu(CC)$ mode. The second peak frequency varies with exposure and is left unassigned. The CO peak is not listed in Table 1 as it is not relevant to our study.

Intensities of losses for 0.25 langmuir exposure were approximately half as intense as those following 0.5 langmuir exposure. The losses for 0.5 and 3.5 langmuir exposures were comparable except for the $\delta(CH)_{sym}$ and $\nu(CH)$ modes, which were more pronounced in the 3.5 langmuir case. In the following
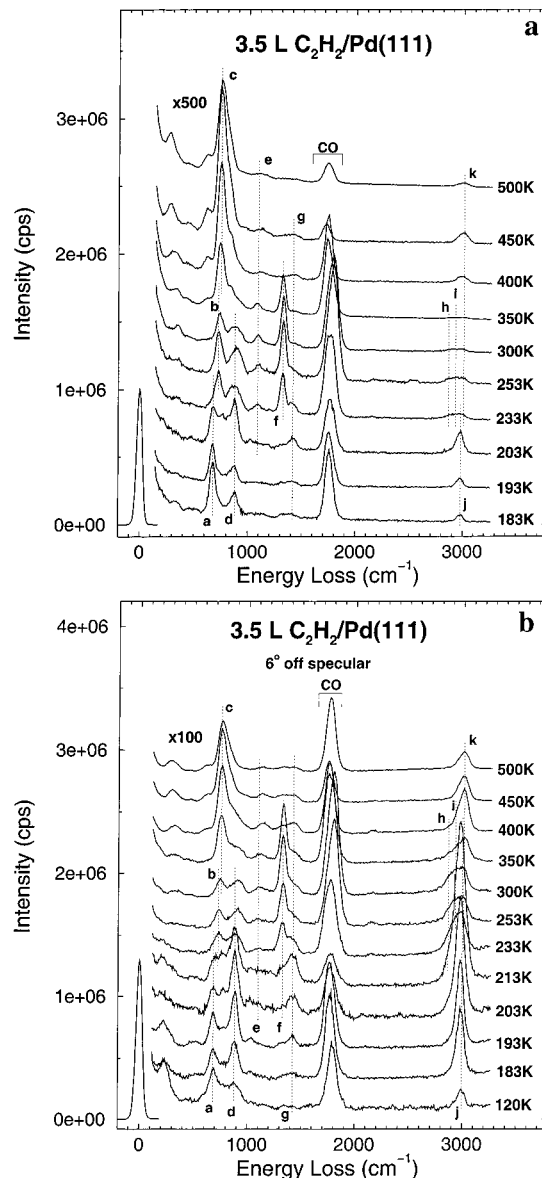
paragraphs we discuss the temperature evolution of selected peaks.

As the temperature was increased to 183 K, no significant changes in peak positions were observed. Similarly, the intensities remained nearly constant except for the loss at 872 (880) cm^{-1} (if not specified, the listed frequencies are for 0.5 langmuir exposure, and in brackets we give the values for 3.5 langmuir exposure) whose intensity increased for both 0.5 langmuir and 3.5 langmuir exposures. An increase in intensity was also observed for losses assigned to the CH stretch (2995 cm^{-1}) and for the loss at 1420 cm^{-1}, but only for the 3.5 langmuir exposure.

Upon heating to 193 K the increase of intensity for the above mentioned losses continued. Furthermore, for 0.5 langmuir adsorption new peaks appeared at 1095 and 1327 cm^{-1}, indicating ethylidyne formation, and a new loss at 1415 cm^{-1} also appeared. Note that for 3.5 langmuir exposure, the loss at nearly identical frequency 1420 cm^{-1} was already present at
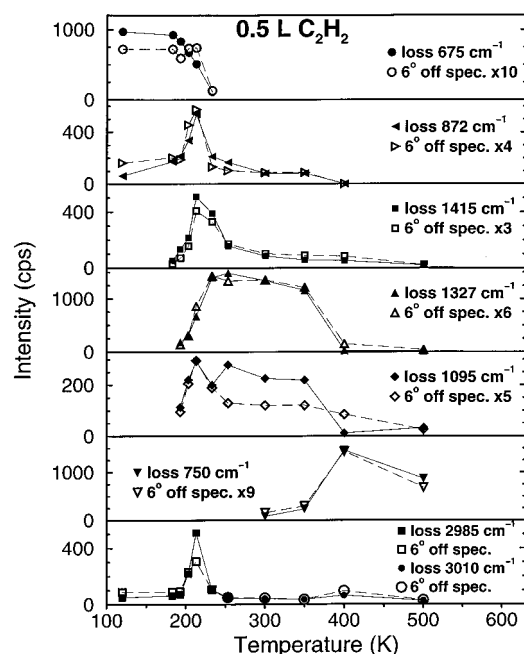
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Figure 3. Intensity of selected peaks vs temperature following 0.5 langmuir exposure of C_2H_2 on Pd(111). Intensities of energy loss peaks are shown for specular scattering by darkened symbols and for off-specular by open symbols. The lines serve as a guide to the eye.

Figure 4. Intensity of selected peaks vs temperature following 3.5 langmuir exposure of C_2H_2 on Pd(111). Intensities of energy loss peaks are shown for specular scattering by darkened symbols and for off-specular by open symbols. The lines serve as a guide to the eye.
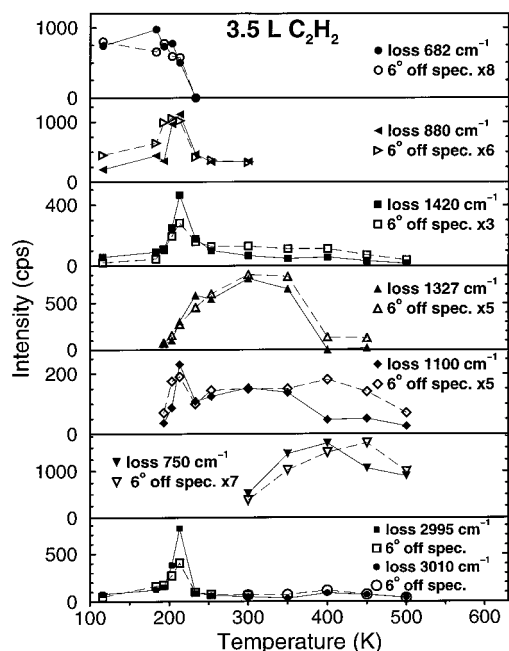
120 K and as the temperature increased this loss gained in intensity.

At the temperature of 203 K a decay of the strongest acetylene peak at 675(682) cm^{-1} has begun and this peak has vanished at 253 K; all acetylenic species have either changed to other species or desorbed by 253 K. Remarkably, the intensity of losses at frequencies 872(880), 1415(1420), and 2985(2995) cm^{-1} do not decrease uniformly with temperature unlike the acetylene symmetric CH bend. Instead, a maximum occurs at 213 K before the peaks nearly disappear at 253 K. This indicates that some intermediate species were present on the surface

TABLE 1: Comparison of Observed Losses following 0.25, 0.5, and 3.5 Langmuir Acetylene Exposures on Pd(111) at 120 K

mode assignment	exposure, langmuir		
	0.25	0.5	3.5
PdC stretch (ν(PdC))	487w	490w	
CH out-of-plane bend sym (ρ(CH)$_{sym}$)	670s	675s	682s
CH out-of-plane bend asym (ρ(CH)$_{asym}$)	755m	768m	765m
CH in-plane bend sym. (δ(CH)$_{sym}$)	868m	872m	880m
CH in-plane bend asym (δ(CH)$_{asym}$)	1042w	1030w	1025w
not assigned	1114w	1113w	1144w
not assigned	1291w	1292w	
CC stretch(ν(CC))	1353w	1355w	1355w
not assigned			1420w
CH stretch (ν(CH))	2980w	2985w	2995m

^{a} Frequencies are in cm^{-1}. Intensities of losses in specular direction: w = weak, m = medium, s = strong.
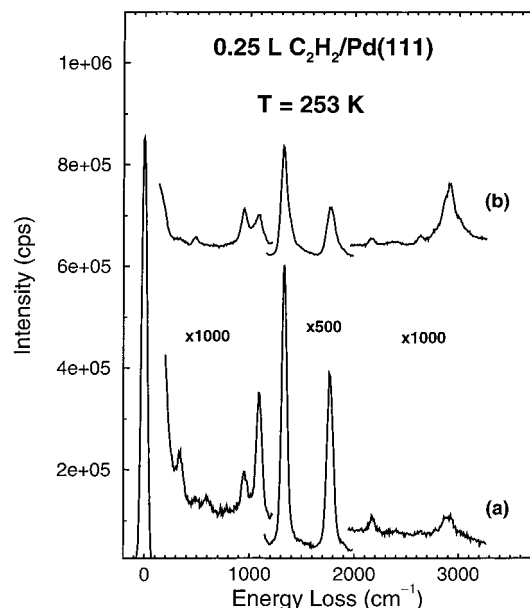

Figure 5. Ethylidyne spectrum resulting from 0.25 langmuir adsorption of C_2H_2 at 120 K and subsequent heating to 253 K. (a) Specular direction, (b) 6° off-specular direction.

during the acetylene transformation to ethylidyne. This issue will be discussed in more detail in section 5.

4.2. 233−350 K. Above 233 K the character of the spectra significantly changes. We observe that for a very low acetylene exposure (0.25 langmuir) on palladium the entire amount of acetylenic species converts to ethylidyne by the temperature 253 K, as shown in Figure 5. Very narrow and well-resolved peaks are found at frequencies listed in Table 2 together with corresponding assignments. We note the observation of several overtone and combination bands not previously reported.

For 0.5−3.5 langmuir exposures the ethylidyne losses coexist with other features, which assignment will be discussed in section 5. For 0.5 langmuir exposure the strongest ethylidyne peak at 1327 cm^{-1} is fully developed at 233 K and remains constant up to 350 K. On the other hand, for the saturation coverage, the strongest ethylidyne peak at 1327 cm^{-1} reaches at the temperature 233 K only about two-thirds of its maximum value. The maximum is reached at 300 K and the intensity remains constant up to 350 K. Another interesting difference between the 0.5 and 3.5 langmuir exposures is that the absolute value of maximal intensity of the 1327 cm^{-1} peak for 3.5 langmuir is about one-third smaller than the intensity of the same peak developed after 0.5 langmuir exposure. Hence, for

TABLE 2: Comparison of Modes Assigned to CCH₃ Formed from 0.25 langmuir Acetylene Exposure on Pd(111) with Corresponding Modes in the Cluster Compound CH₃CCo₃(CO)₉[20]

	CH₃CCo₃(CO)₉	surf species
mode assignment	ref 20	$T = 253$ K
CH₃bend (ρ(CH₃))	1004s	953w
CC stretch (ν(CC))	1163m	1095m
sym methyl deformation (δ(CH₃)$_{sym}$)	1356m	1327s
asym methyl deformation (δ(CH₃)$_{asym}$)	1420m	
overtone ($2 \times \nu$(CC))		2172w
combination band (ν(CC) + δ(CH₃))		≈2400w
overtone ($2 \times \delta$(CH₃)$_{sym}$)		2635w
sym CH stretch (ν(CH₃)$_{sym}$)	2888m	2864w
asym CH stretch (ν(CH₃)$_{asym}$)	2930m	2930w

[a] Frequencies are in cm⁻¹. Intensity of losses (our results are given for the specular direction): w = weak, m = medium, s = strong).

the saturation coverage, the C₂H₃ production is suppressed compared to the 0.5 langmuir exposure. We surmise that for small coverages the dominant reaction is hydrogenation of C₂H₂ species, where the extra hydrogen for the reaction was available from the residual atmosphere in the chamber. (Note that the vacuum chamber is pumped by an ion pump, leaving mostly hydrogen in the residual atmosphere.) The influence of the exposure upon ethylidyne formation will also be discussed in more detail in section 5.

4.3. Above 400 K. The next dramatic change in the overlayer occurred at 400 K. The symmetric methyl deformation peak of ethylidyne at 1327 cm⁻¹ disappeared. The loss at 750 cm⁻¹, which appeared at 350 K, significantly gained in intensity. We interpret this behavior as a temperature activated dehydrogenation. Our observation is consistent with TPR studies where a hydrogen desorption peak was observed between 400 and 500 K.[2]

4.4. CH Stretch Region. The CH stretch (ν(CH)) peak found near 3000 cm⁻¹, not discussed so far, is present over the whole temperature range; however, its exact position and intensity show a complex temperature dependence. Since the CH stretching mode is predominantly impact excited, its relative intensity is more pronounced in the off-specular direction. Hence, the temperature evolution of this loss is more conveniently studied in the off-specular direction. For the lowest temperature (120 K) the acetylene CH stretch mode was found at 2985 cm⁻¹ for 0.5 langmuir exposure and at 2995 cm⁻¹ for 3.5 langmuir exposure. As the temperature was increased the CH stretch loss strongly gained in intensity for both exposures. It reached a maximum intensity at 213 K, similar to losses at 872(880) and 1415(1420) cm⁻¹.

After heating to 233 K, the intensity of the ν(CH) mode declined and the peak broadened toward lower frequencies as the surface species changed to mostly ethylidyne for 0.5 and 3.5 langmuir exposures. Three peaks of the shape of the elastic peak provided the best fit[21] to our broad ν(CH) peak, indicating the coexistence of species with different carbon–carbon bond order. For all spectra following 0.5 and 3.5 langmuir exposures in the temperature interval 233−350 K, we obtained the CH stretch at 3000 cm⁻¹, which indicates the presence of hydrocarbon species with the same or similar carbon hybridization as adsorbed acetylene. The two other peaks lie at 2930 and 2864 cm⁻¹ within ±5 cm⁻¹ accuracy. For spectra resulting from 0.25 langmuir exposure at 253 K, the high frequency part in the ν-(CH) region is missing, and only two peaks at frequencies 2930 and 2864 cm⁻¹ were resolved. Since other ethylidyne losses occurred in this temperature range, as mentioned above, we associate the 2930 and 2864 cm⁻¹ peaks with asymmetric and

symmetric CH stretching modes of the ethylidyne methyl group (see Table 2). This observation is in agreement with previous HREELS data[8] where the maximum of a broad ethylidyne CH stretch peak was found at 2900 cm⁻¹ and with previous infrared spectroscopy assignment of ethylidyne tricobalt nonacarbonyl (see also Table 2).[20] Furthermore, the relative intensity of the acetylene-like CH stretch loss at 3000 cm⁻¹ and the methyl CH stretch at 2930 cm⁻¹ is qualitatively different for 0.5 and 3.5 langmuir exposures, as seen from Figures 1b and 2b. For 0.5 langmuir exposure and temperatures 233 and 253 K, the 2930 cm⁻¹ peak has about 30% higher intensity than the 3000 cm⁻¹ peak. The situation for 3.5 langmuir adsorption is just opposite. At the same temperatures the peak at 3000 cm⁻¹ remains dominant and is about 20% higher than the 2930 cm⁻¹ peak. This indicates that the majority of the species formed from the saturated overlayer have a similar carbon hybridization as acetylene, while for the lower initial coverages of acetylene, the majority of the species transform with temperature to a species with lower carbon−carbon bond order. For the reasons described above this latter species is ethylidyne. Finally, for very low coverages (exposure 0.25 langmuir) no species with acetylene-like carbon hybridization were observed at 253 K; the only species detected on the Pd surface was ethylidyne.

After the temperature is increased to 400 K and ethylidyne transforms to CCH species, the character of the ν(CH) peak also changes. The peak narrows and becomes more pronounced, and the maximum shifts to higher frequency (~3010 cm⁻¹).

5. Discussion

5.1. Origin of Reaction Intermediate at 213 K. As seen from Figures 3 and 4, the temperature dependence of several peaks (872(880), 1415(1420), and 2985(2995) cm⁻¹) is inconsistent with the dependence of either the strongest acetylene peak at 675 cm⁻¹ or the ethylidyne peak at 1327 cm⁻¹. The peaks develop in a narrow temperature interval between 203 and 233 K. The lower limit is the temperature at which the decay of acetylenic species begins, the upper one corresponds to a full development of the ethylidyne overlayer in the case of 0.5 langmuir exposure.

Since the species with the above characteristic losses is intermediate between acetylene and ethylidyne, it must keep the CC bond intact and only a rearrangement of hydrogen atoms occurs. Three possible candidates (and their combinations) come into play: CCH, CCH₂, and CHCH₂. The spectrum of the proposed CCH species (see data for temperatures higher than 400 K in Figures 1 and 2) is completely different from the spectra taken at 213 K. Hence, we can rule out the CCH species as an intermediate. Furthermore, the CCH species is very stable. Even several days after the formation of a CCH overlayer, by heating the adsorbed acetylene to 400 K for 5 minutes and then leaving it at the room temperature, the spectrum has remained unchanged. There is no evidence that the CCH species reacts with adsorbed hydrogen from residual atmosphere. We can also exclude the CHCH₂ species as a possible intermediate using the same argument as Mate *et al.*[22] in a study of acetylene transformation at Rh(111). An IR study of organometallic cluster complexes containing CCH₂ and CHCH₂ moieties[23] showed that the main difference between these vibrationally similar ligands is the δ(CH) mode for CHCH₂ at about 1250 cm⁻¹, which is absent in CCH₂. No loss near this frequency is observed in our spectra. Azad *et al.*[10] proposed that a hydrogenation of CCH₂ to ethylidyne proceeds via a CHCH₂ intermediate but the (1,2) hydrogen shift is very fast compared to a hydrogen attachment to CCH₂ and therefore in our experimental setup is not

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TABLE 3: Comparison of Modes Assigned to Vinylidene Formed from Acetylene Adsorbed on Pd(111) with Corresponding Modes in the Cluster Compound Os$_3$(CO)$_9$ (μ-H)$_2$(μ_3-η^2CCH$_2$),[23] with Theoretically Calculated Modes,[9] and with Modes of Vinylidene Formed from Acetylene on Rh(111)[22] ^{a}

mode	Os$_3$(CO)$_9$(μ-H)$_2$ (μ_3-η^2CCH$_2$) ref 23	theory ref 9	CCH$_2$/Rh(111) T = 320 K ref 22	CCH$_2$/Pd(111) T = 213 K
ρ_τ	811m	—	—	~770w
ρ_w	961s	790–800s	990w	875–880s
ρ_r	1051s	600–640s	—	~1100m
ν(CC)	1331m	1481–1491s	1145m	—
δ(HCH)	1470m	mixed with ν(CC)	1405m	1415–1420m
ν(CH$_2$)$_{sym}$	2986w	2955–2960w	2950s	2995s
ν(CH$_2$)$_{asym}$	3047w	—	—	—

^{a} Frequencies are in cm^{-1}. Intensities of losses (our results are given for the specular direction): w = weak, m = medium, s = strong.

detectable. Hence, we conclude that CCH$_2$ (vinylidene) is the predominant stable intermediate.

In addition to losses at ~770, 872(880), 1415(1420), and 2995 cm^{-1} which have similar temperature dependence we add the loss near 1100 cm^{-1} to the class of modes belonging to vinylidene. As seen from Figures 3 and 4, the peak at ~1100 cm^{-1} cannot be ascribed exclusively to either ethylidyne or vinylidene. Above 233 K the loss corresponds to the ethylidyne CC stretch; however, below 233 K ethylidyne is not yet formed and the ~1100 cm^{-1} belongs to the intermediate species. Consistently, the temperature dependence of the 1100 cm^{-1} loss intensity behaves as a superposition of temperature dependencies of the vinylidene loss at, e.g., 1415 cm^{-1}, and ethylidyne peak at 1327 cm^{-1}. Another difference in behavior of the 1100 cm^{-1} peak below and above 233 K indicates that this loss belongs to two species in the case of 0.5 langmuir exposure. Below 233 K the intensity in 6° off specular direction is 5 times smaller than in specular direction. Above 233 K the scattering mechanism of the loss near 1100 cm^{-1} is more dipole pronounced; the intensity in the off-specular direction is ~10 times smaller than the intensity in the specular direction. For 3.5 langmuir exposure the temperature dependence of modes near 1100 cm^{-1} is more complicated, which is likely caused by benzene formation at higher coverage. The benzene ν_{10} mode was found at 1100 cm^{-1} and the mode is impact excited.[24] A more detailed study of benzene formation will be presented elsewhere.[13] As explained in the following paragraph we surmise that the 1100 cm^{-1} loss below 233 K is associated with a vinylidene in-plane CH$_2$ bend (or rocking mode).

Comparing our spectra to previous assignments (see Table 3), the 1100 cm^{-1} loss at temperatures below 233 K could either be the CC stretch (ν(CC)) or an in-plane bend (ρ_r). The following observation rules against the CC stretch assignment. The CH stretch for vinylidene and acetylene are identical within the experimental resolution. Therefore the CC bond order should also be similar for vinylidene and acetylene, i.e., the vinylidene CC stretch should be closer to the acetylene CC stretch (1355 cm^{-1}) than to the ethylidyne one (1095 cm^{-1}). For these reasons we associate the 1100 cm^{-1} loss below 233 K with the CH$_2$ rocking mode.

A weak loss at ~770 cm^{-1} is associated with the vinylidene CH$_2$ torsion mode (ρ_τ) and a strong loss at 872(880) cm^{-1} with the CH$_2$ out-of-plane bend, or wagging mode (ρ_w), because of their proximity to cluster compound vinylidene moiety IR modes. The loss at 1415(1420) cm^{-1} is assigned to the HCH in-plane bend, or scissors mode (δ(HCH)), and not to the CC stretch. We would expect the CC stretch to exhibit more pronounced dipole activity in an adsorption geometry where the CC axis is not parallel with the surface, such as in the case of vinylidene (angle from the plane-normal was experimentally estimated to ~50° [6] and theoretically to 16°–26° [9]). The
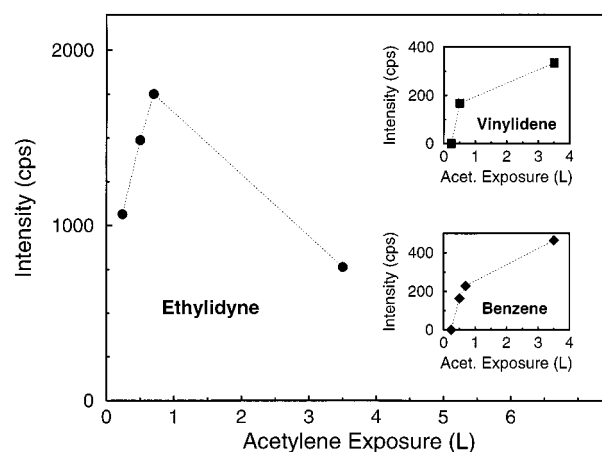

Figure 6. Intensity of 1327 cm^{-1} loss (ethylidyne δ(CH$_3$) mode) vs acetylene exposure at temperature 253 K. Upper inset: Intensity of 880 cm^{-1} loss (vinylidene ρ_w mode) vs acetylene exposure at temperature 253 K. Bottom inset: intensity of 725 cm^{-1} loss (benzene ρ(CH) mode) vs acetylene exposure at temperature 253 K.

vinylidene CC stretch is probably masked by the strong ethylidyne vibration at 1327 cm^{-1}. Frequencies and assignments of CCH$_2$ are listed in Table 3. Note that the frequencies associated in this paper with vinylidene are almost identical to "converted acetylene" losses, which were observed after heating adsorbed C$_2$H$_2$ on Pt(111) to 350 K (775, 900, 1100, 1420, and 2970 cm^{-1}).[25]

5.2. Ethylidyne Formation: Dependence on Exposure. In section 4.2 we mentioned that the extra hydrogen needed for acetylene to convert into ethylidyne comes from the residual atmosphere in the vacuum chamber. Since it takes approximately a day from adsorption at low temperature to collect all the spectra below 253 K, the adsorption from residual atmosphere is not negligible. The nominal pressure during the experiment is ~5 × 10^{-11} Torr; if we assume that roughly half of it is due to hydrogen, then the H$_2$ exposure over 24 h is roughly 2.6 langmuir. This value readily accounts for the conversion of a small amount (0.25 langmuir) of acetylene into ethylidyne.

We also mentioned in section 4.2 that ethylidyne production is lower for saturation coverage than for 0.5 langmuir exposure. The dependence of the ethylidyne production is more complicated when observed over a wider exposure interval. As the acetylene concentration increases the ethylidyne peaks at 253 K gain in intensity up to 0.7 langmuir exposure, as shown in Figure 6. After 3.5 langmuir exposure the main ethylidyne losses, δ(CH$_3$)$_{sym}$ and ν(CC), are approximately half the intensity of the same peaks resulting from 0.7 langmuir exposure. On the other hand, from the vinylidene concentration at 253 K one finds an increasing dependence of vinylidene with acetylene exposure (see upper inset in Figure 6). After 0.25 langmuir exposure, no vinylidene peaks are observed in the spectra

measured at 253 and 300 K. In the case of 0.5 and 0.7 langmuir adsorption the peak at 880 cm^{-1} is half as intense as the same loss at 3.5 langmuir adsorption. Note that we cannot use other vinylidene peaks to confirm this concentration relation. The loss at 1095 cm^{-1} consists also of the ethylidyne CC stretch and the benzene CH bend.[24] The loss at 1415 cm^{-1} is a superposition of the vinylidene scissor mode (see Table 3), the ethylidyne asymmetric methyl deformation (see Table 2), and the benzene CC stretch mode.[24] The vinylidene and benzene CH stretch modes around 3000 cm^{-1} are indistinguishable within our resolution. Finally, the loss at 770 cm^{-1} is very weak.

Our understanding of the above observations can be summarized in the following points. (i) Provided that the hydrogenation proceeds via the Langmuir–Hinshelwood mechanism, there is a lack of free adsorption sites for gaseous hydrogen because of the saturation overlayer of acetylenic species and/or vinylidene. (ii) Vinylidene saturation coverage relative to the number of Pd atoms is $\theta = 1$, while for ethylidyne $\theta = 0.25$.[10] Hence, vinylidene does not have sufficient space for its conversion to ethylidyne when formed from a saturated overlayer. (iii) Finally, with increasing acetylene coverage the production of ethylidyne via vinylidene is partly replaced with benzene formation, as seen from the bottom inset in Figure 6, and discussed in detail elsewhere.[13]

6. Summary

HREELS data for acetylene adsorption and thermal evolution on Pd(111) can be consistently interpreted in terms of associative adsorption of acetylene at 120 K followed by the formation of ethylidyne beginning around 233 K. In the range 203–233 K the formation of the intermediate vinylidene is also observed. The presence of surface hydrogen from the residual gas phase is believed to provide the additional hydrogen needed to complete the actylene to ethylidyne reaction. We also note that lower acetylene coverages favor a higher percentage of acetylene to ethylidyne conversion. The spectra at 233 and 253 K also contain evidence for benzene formation for higher initial acetylene coverages (exposures > 0.5 langmuir).[13] Heating the adsorbed layer to 400 K results in dehydrogenation of all hydrocarbon species, and all observed spectral features are ascribed to CCH species. Heating above 500 K causes further dehydrogenation, leaving the surface covered with carbon above 800 K.

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