

Direct Observation of Surface Reactions of Acetylene on Pd(111) with Scanning Tunneling Microscopy

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Received: March 5, 1998; In Final Form: June 18, 1998

The cyclotrimerization of acetylene to benzene on a Pd(111) surface has been studied by scanning tunneling microscopy (STM). The formation of benzene becomes visible upon increasing the acetylene coverage at 140 K. Initially, the acetylene molecules adsorb in a (2×2) ordered layer, which is compressed into an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure when more acetylene is added. The cyclotrimerization reaction is observed just before saturation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and stops when the saturation coverage is reached. Further exposure to acetylene does not result in a reaction, indicating that the cyclotrimerization reaction involves a transient adsorption state, different from that in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer itself is stable up to 230 K, even when a background pressure of acetylene is present. At 230 K, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer decays, a process which is related to the isomerization and further decomposition of acetylene. The results are consistent with the available spectroscopic data and indicate that the limited conversion of acetylene to benzene is determined by the relative rates of $(\sqrt{3} \times \sqrt{3})R30^\circ$ domain formation and cyclotrimerization.

1. Introduction

Surface reactions of hydrocarbons on transition-metal surfaces play an important role in many catalytic processes applied in chemical industry. However, studies of the basic mechanisms are hampered by the fact that reactions involving C–C bond formation or breaking are only rarely observed in the single-crystal model systems under ultrahigh-vacuum (UHV) conditions.¹ The cyclotrimerization of acetylene to benzene on Pd(111), which was independently and almost simultaneously discovered by three groups,^{2–4} is one of the few reactions involving C–C bond formation that is known to occur in UHV.^{5–9} This reaction occurs on a few other metal surfaces as well, e.g., Sn/Pd(111),¹⁰ Sn/Pt(111),¹¹ Cu(110);¹² but on most other surfaces, such as Fe¹³ or Pt,^{14,15} the acetylene decomposes to hydrogen and surface carbon instead. For this reason the acetylene/Pd(111) system has already been studied with a variety of surface scientific methods, including temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), metastable deexcitation spectroscopy (MDS), high-resolution electron energy loss spectroscopy (HREELS), low-energy electron diffraction (LEED), and near-edge X-ray absorption fine structure (NEXAFS).^{3,4,6–9,16–20}

It has been found so far that acetylene forms an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern at 175 K.⁸ The triple C≡C bond rehybridizes to an ethylene-like C=C bond, and the molecules assume a di- σ configuration, i.e., each carbon atom is attached to a Pd atom in the surface; the HCCH plane is tilted by about 20° with respect to the surface normal.^{6,17,21} A recent scanning tunneling microscopy (STM) study confirmed this geometry.²² The cyclotrimerization of acetylene to benzene occurs only at coverages above about 0.3, where the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern is observed, with estimated maximum conversions of about 20–35%.^{6,8,9} The remaining acetylene follows the same reaction

pathway as observed at lower acetylene coverages: It predominantly isomerizes to vinylidene at approximately 250 K, after which it decomposes.^{8,18} The cyclotrimerization to benzene at coverages above 0.3, however, takes place at temperatures as low as 140 K, and the benzene formed desorbs in two stages at approximately 230 and 500 K.^{3,4,8} The desorption of benzene at 230 K is associated with desorption of molecules having a tilted configuration on the surface, while that at 500 K comes from flat-lying molecules.²³ The most straightforward mechanism to form benzene from acetylene is a two-step process: First, two acetylene molecules are coupled to form an adsorbed C₄ dimer, and then a third acetylene molecule is inserted into this dimer. Support for this mechanism comes from TPD experiments with *cis*-3,4-dichlorocyclobutene (DCB)—a convenient precursor to selectively produce the C₄H₄ fragments on the surface—and coadsorbed C₂D₂, which revealed that a C₂D₂ molecule can be directly inserted into a C₄ fragment without C–C-bond rupture.²⁴

The striking features of the low-temperature cyclotrimerization of acetylene on Pd(111) are the coverage dependence of the reaction and the limited yield of benzene, which indicate that a certain bonding type or geometry of acetylene is required for the reaction. On the one hand, the special bonding geometry of the acetylene molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase is believed to be responsible for the reaction, because the abrupt increase in benzene yield at an acetylene coverage of about 0.3 coincides with the development of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. This conclusion represents the basis of the present understanding of this reaction and is the main ingredient for the discussion of the exceptionally high efficiency of benzene formation on the (111) face of Pd, as compared to the (100) and (110) faces. The close packing of the acetylene molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase should be favorable for a coupling reaction, as only local bond shifts could be sufficient. This is further supported by coadsorption experiments of acetylene with NO,²⁵ in which benzene formation occurred at significantly

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lower acetylene coverages. Since acetylene and NO form separate domains, this result shows that the essential parameter for the benzene formation to occur is a minimum local density of acetylene molecules.

On the other hand, the limited conversion to benzene of 20–35% at most, which means that only a small portion of the acetylene participates in the cyclotrimerization reaction, conflicts with a uniformly reactive $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase. Because at a coverage close to 1/3, corresponding to the ideal $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, the surface must be almost completely covered with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase, it is not clear why the cyclotrimerization does not go to completion. One group of authors proposed that “active sites” are involved, which are used up as the reaction proceeds.^{26,27} Such a mechanism implies that only distinct acetylene molecules react, in contrast to the above scheme that assumes a reaction between the equivalent molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase.

The most straightforward way to access this question on the active phases and local geometries involved in the cyclotrimerization reaction is to study the acetylene/Pd(111) system with STM. Basically, two kinds of STM experiments were performed. The first experiment is focused on the surface structures formed as a function of acetylene coverage at 140 K, to get insight into the nature of the critical coverage needed for the cyclotrimerization reaction and the reason for the limited yield of benzene. The second experiment deals with the thermal behavior of a saturated layer of acetylene on Pd(111) between 140 and 230 K. Our data demonstrate that the reaction occurs only in a narrow coverage range, parallel to the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase, while the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase itself is not reactive. The reaction to benzene involves at least one, transient, adsorption state of acetylene that is different from that in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase. These findings may resolve the mentioned contradictions derived from the coverage dependence and limited conversion of the cyclotrimerization reaction.

2. Experimental Section

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 5×10^{-11} Torr, equipped with optics for low-energy electron diffraction (LEED), a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a mass spectrometer, an Ar^+ -sputtering gun, and a variable-temperature scanning tunneling microscope (STM) with an etched tungsten tip. The sample holder of the STM was connected to a liquid He cryostat by a copper braid, which allowed to cool the sample to 60 K. Higher temperatures could be achieved by simultaneous irradiative heating of the sample from the back. Surface temperatures were measured with a chromel–alumel thermocouple spot-welded to the back of the crystal.

The Pd(111) sample was routinely cleaned by cycles of Ar^+ -sputtering at room temperature (1 kV, $\sim 2 \mu\text{A}$ sample current), annealing at 1030 K, oxidation in 10^{-7} Torr of oxygen at 700 K, and flash desorption of excess oxygen at 1000 K. After this procedure large areas without contamination were found with STM. The acetylene (99.6%, dissolved in acetone) was purchased from Messer Griesheim. To remove the acetone contamination in the acetylene, the gas coming out of the bottle was frozen to liquid nitrogen temperature in a glass bulb and then allowed to evaporate into vacuum. The vapor coming off in the initial phase of evaporation was trapped. The mass spectrum of the trapped gas showed no detectable contamination.

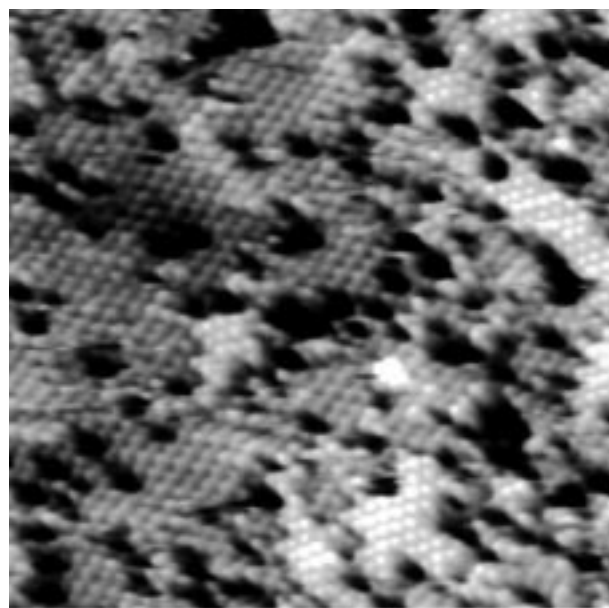


Figure 1. STM image obtained after adsorption of 2 langmuirs of acetylene on Pd(111) at 140 K ($180 \times 180 \text{ \AA}$, 0.8 nA, 91 mV). Ordered domains with a (2×2) (gray) and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ (brighter) structure can be observed. Black areas are assigned to uncovered areas.

3. Results

As already mentioned, it is known that the cyclotrimerization of acetylene to benzene on a Pd(111) surface can take place at quite low temperatures (140–150 K) at acetylene coverages of about 0.3 monolayers. To obtain more information on this reaction, a series of STM pictures for different coverages of acetylene on Pd(111) at 140 K were recorded. This temperature was chosen, because spectroscopic data indicate that benzene formation takes place,^{3,8} and multilayers of acetylene, which would complicate the STM results, are not stable.⁴ The starting point of this series is shown in the STM picture in Figure 1, which was obtained after adsorption of 2.0 langmuirs of acetylene at 140 K. At this stage, the larger part of the surface is covered by a (2×2) ordered overlayer, appearing gray in the picture in Figure 1; this structure has been found recently for acetylene on Pd(111)²⁸ and could also be clearly detected with LEED in the present study. The brighter areas in the picture have the close-packed rows rotated by 30° with respect to those in the (2×2) patches and correspond to small domains with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Disordered structures and uncovered areas (black patches) can be distinguished as well. Because the previous spectroscopic data on this system indicate that formation of benzene and decomposition or isomerization of acetylene do not yet occur at these coverages and temperature,^{3,8,9} all observed structures are assigned to adsorbed acetylene. The fact that the molecules appear round and structureless despite their geometry and asymmetric adsorption site may be explained, apart from the limited resolution of the STM, by the rapid rotation of the molecules about their 3-fold adsorption site that was shown to set in at 44 K.²²

Figure 2 shows three consecutive STM frames of acetylene on Pd(111) at approximately the same position on the surface, taken while exposing the surface shown in Figure 1 to 5×10^{-9} Torr of acetylene at 140 K; in each frame 0.5 langmuir of acetylene is added. The top frame shows the coexisting (2×2) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ phases, similar to those in Figure 1. When more acetylene is added, the (2×2) phase is gradually replaced by the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase, indicating a compression of the chemisorbed acetylene. In the bottom frame, the $(\sqrt{3} \times$

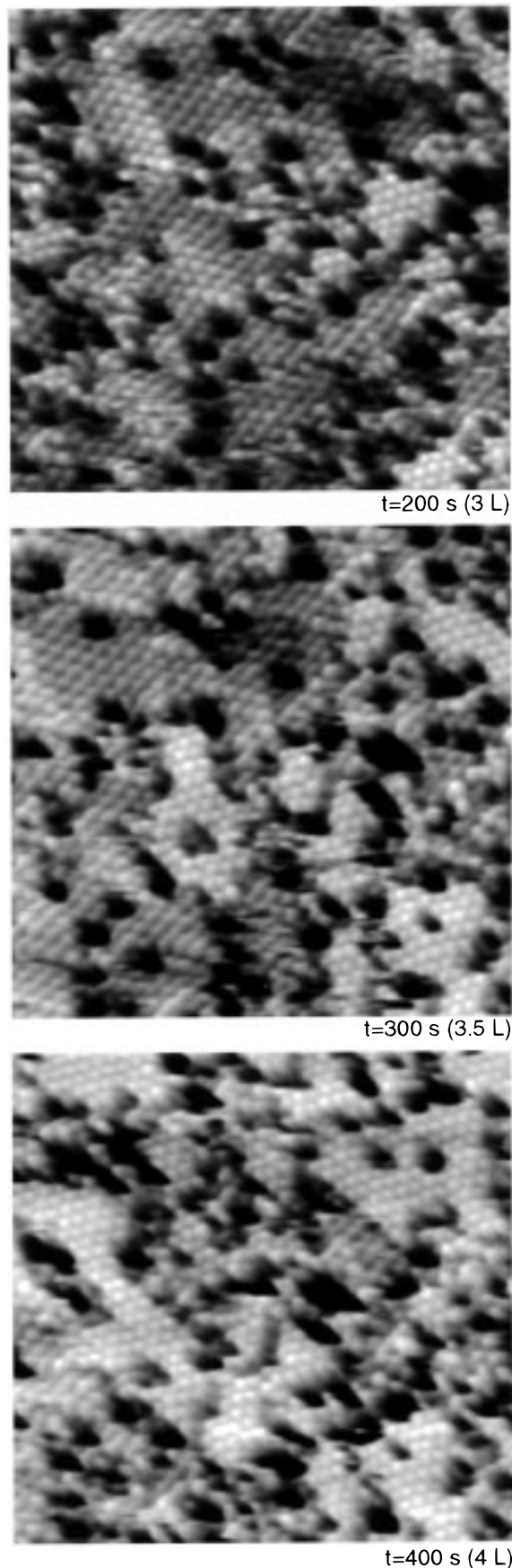


Figure 2. Sequence of STM frames of acetylene on Pd(111) at 140 K, taken with 5×10^{-9} Torr of acetylene in situ (150×150 Å, 0.8 nA, 91 mV). Scanning rate: 100 s/frame. Exposure times and approximate doses as indicated. The sequence displays the compression of the (2×2) to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer.

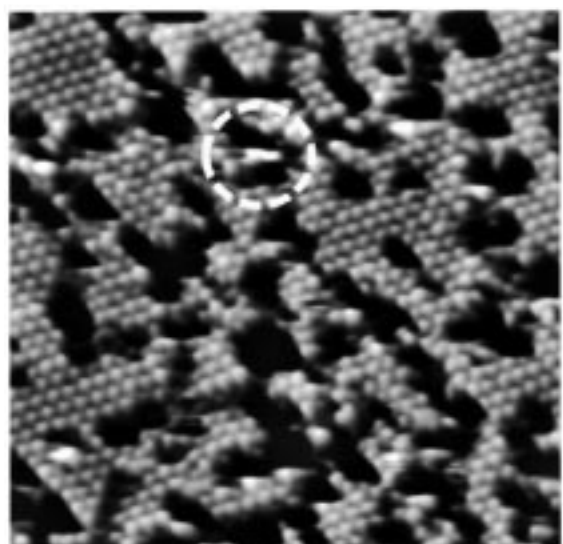
$\sqrt{3}R30^\circ$ phase does not cover the whole surface yet but consists of quite small patches with rather disordered areas in between. Because all features in the STM pictures look similar, it is concluded that in the bottom frame the critical coverage for benzene formation has not yet been reached.

Upon further increasing the acetylene coverage, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ patches develop further and bright features appear in the STM pictures, indicative of a second surface species. This is displayed in Figure 3, which shows the next three frames of the same sequence as in Figure 2, also in an atmosphere of 5×10^{-9} Torr of acetylene. These bright features are assigned to benzene, because similar features appear in an STM picture of a small amount of acetylene with coadsorbed benzene (Figure 4). A complication is that the adsorbed benzene molecules lie flat on the surface, whereas the reactively formed molecules probably have a tilted configuration on the surface, as was determined by NEXAFS,⁶ which is expected to lead to different appearances in STM. Since good reference data are lacking, a definite conclusion about the orientation of the benzene molecules cannot be drawn from our STM data.

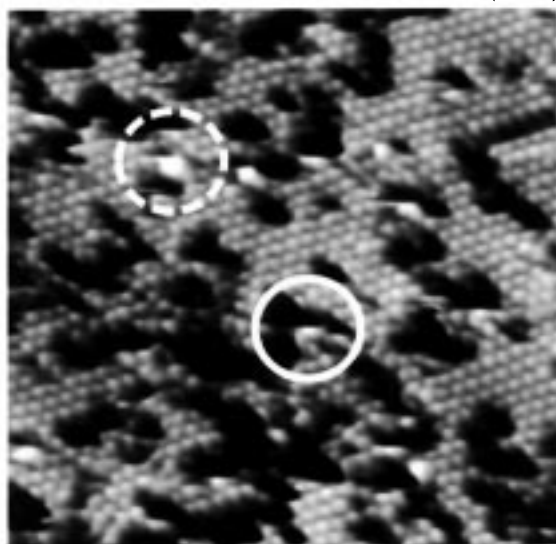
Further support for the assignment of the bright features to benzene is provided by the previous spectroscopic data. First, the amount of benzene that is formed in a TPD experiment after adsorption of acetylene on Pd(111) rapidly increases when a clear $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is observed,⁸ in full agreement with the situation observed in the STM pictures. Second, benzene can be identified in UP spectra after higher doses of acetylene on Pd(111) at 140 and 175 K.^{3,8} The HREELS data of acetylene on Pd(111) are also consistent with the formation of a certain amount of benzene under those circumstances, although some controversy exists about the interpretation of these data.^{18–20, 29}

The top frame in Figure 3 shows the initial phase of the benzene formation. It can be seen that the reaction does not take place within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands, but in the disordered areas in between. The number of benzene molecules gradually increases (middle and bottom frames in Figure 3), until the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase occupies practically the whole surface. In our experiment this situation was reached after an exposure of about 7 langmuirs, and further dosing of acetylene does not result in a discernible reaction, even when the background pressure of acetylene is increased to 5×10^{-7} Torr for about 400 s. Since the temperature of 140 K is well below that of benzene desorption, the formation of additional benzene would be visible in the STM pictures. A typical STM picture of the saturated surface is displayed in Figure 5, which was taken after a total dose of 12 langmuirs; the diameter of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains is on the order of 100–150 Å.

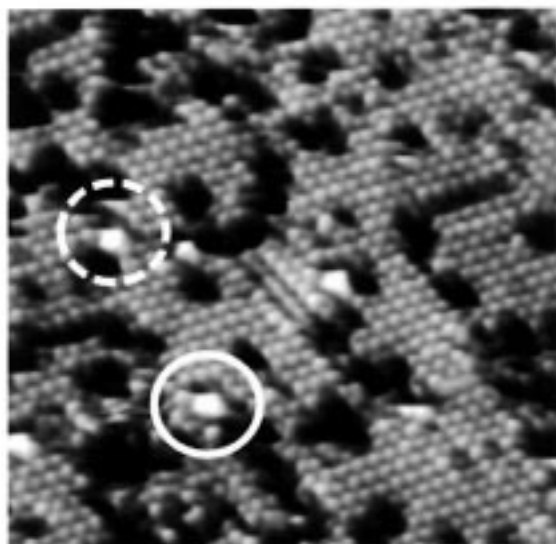
To investigate the thermal behavior of the adsorbed acetylene, STM sequences of saturated layers of acetylene were recorded as a function of time at several temperatures between 150 and 230 K. The saturated surface was prepared by adsorption of 5 langmuirs of acetylene at 150 K; typical STM images of these surfaces are shown in Figure 6. We carefully looked for thermal reactions between 150 and 200 K on the saturated surface but did not detect any significant changes in the STM images over extended periods of time (up to 1000 s). Moreover, further exposure of a saturated surface to acetylene at 190 K did not result in a visible reaction either. This is explicitly shown in Figure 6: the top part displays a saturated surface before adsorption of the additional acetylene, and the bottom part shows the same area on the surface after an additional acetylene dose of 12 langmuirs. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains and the reactively formed benzene, which is predominantly located at



t=500 s (4.5 L)



t=600 s (5 L)



t=700 s (5.5 L)

Figure 3. Sequence of STM frames of acetylene on Pd(111) at 140 K, taken immediately after those in Figure 2 ($150 \times 150 \text{ \AA}$, 0.8 nA, 91 mV). Scanning rate: 100 s/frame. Exposure times and approximate doses as indicated. The sequence shows the formation of benzene and the further saturation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer. The circles mark the appearance of bright features attributed to benzene molecules.

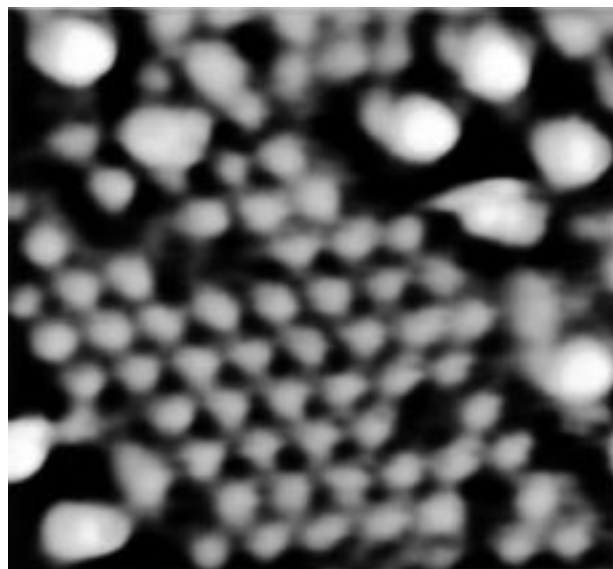


Figure 4. STM image of 1 langmuir of acetylene coadsorbed with 4 langmuirs of benzene on Pd(111) ($60 \times 55 \text{ \AA}$, 8 nA, 50 mV). The acetylene molecules (small spots) are arranged in a (2×2) structure; the benzene molecules appear as large, bright features.

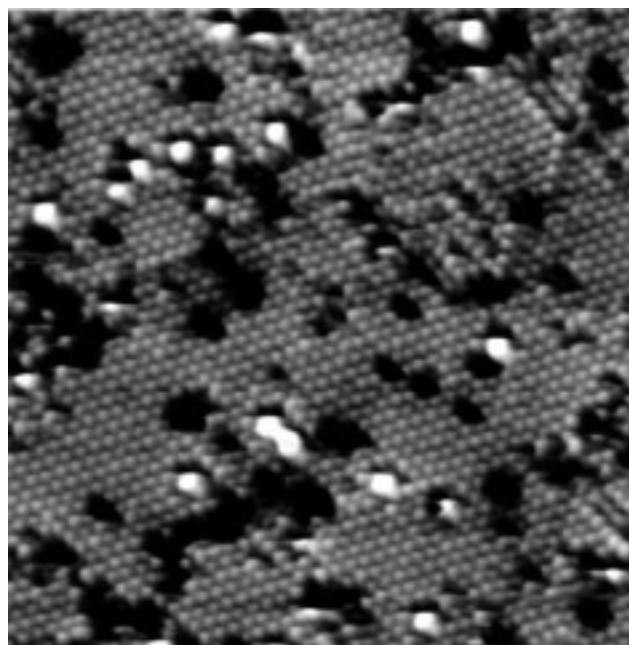
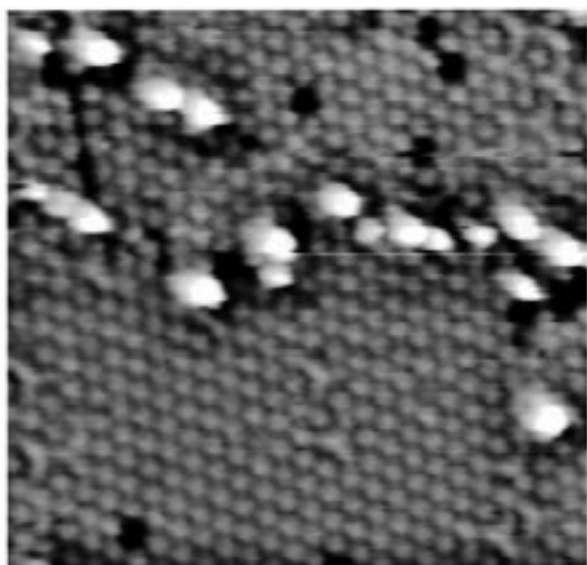
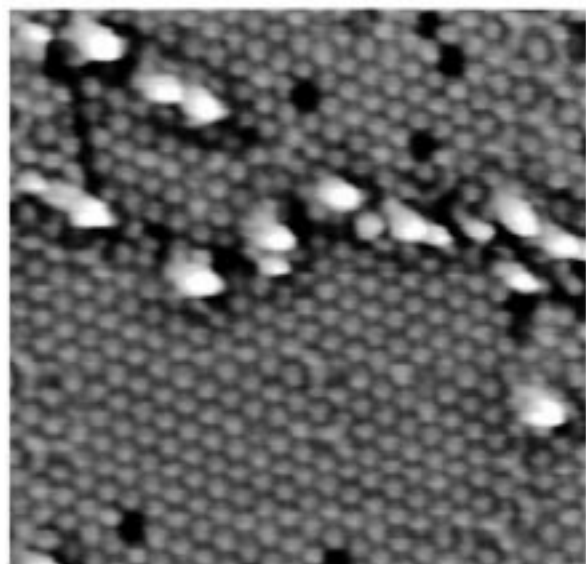


Figure 5. STM image of a saturated layer of acetylene on Pd(111), taken after 2000 s with 5×10^{-9} Torr of acetylene in situ at 140 K ($190 \times 190 \text{ \AA}$, 0.8 nA, 91 mV). The hexagonal pattern corresponds to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer of acetylene; the bright spots are the benzene molecules, which are formed by the process displayed in Figure 3.

the domain boundaries, can be immediately recognized. The fact that the images in Figure 6 are practically identical provides evidence that no thermally activated reactions, and not even a rearrangement of the molecules, occur. (Starlike features with the tips rotated by 30° with respect to the close-packed rows are observed in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains. A positive assignment of these features cannot be made on the basis of our data, but it seems not very likely that these features are due to C_4H_4 dimers, the reaction intermediate in the cyclotrimerization, because they do not react with the additional acetylene.) All these results rule out thermally activated reactions of the chemisorbed acetylene between 150 and 200 K.



saturated surface at 190 K



400 s later, 12 L acetylene added

Figure 6. STM images of a saturated layer of acetylene at 190 K ($105 \times 105 \text{ \AA}$, 8 nA, 150 mV), before (top) and after (bottom) dosing of additional acetylene. The hexagonal pattern corresponds to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer of acetylene; the bright features are the reactively formed benzene molecules. The bottom frame was taken with an ambient pressure of 5×10^{-8} Torr of acetylene. The images are identical, indicating that the acetylene molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration are not reactive at 190 K.

The absence of any further reaction after the initial partial conversion of acetylene to benzene in this temperature range is consistent with the majority of the data in the literature. Several spectroscopic features obtained for the acetylene/Pd(111) system in this temperature range were assigned to chemisorbed acetylene,^{3,6,8,9,17,18,30} indicating that this is the majority species on the surface, in full agreement with our interpretation of the STM images. The desorption of benzene around 230 K can be accounted for by desorption of the initially formed benzene⁹ and does not indicate thermally activated benzene formation. However, in contrast to this picture, a thermal reaction between 150 and 200 K was detected in laser-induced desorption experiments,^{26,27} for which we have no satisfactory explanation so far.

The only thermal reaction we were able to detect occurred at 230 K; at this temperature definite changes between consecutive scans could be observed. This is illustrated in Figure 7, which shows four STM frames taken at different times after increasing the surface temperature to 230 K at approximately the same location on the surface. Initially, quite large areas are covered with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered overlayer, but a new disordered phase is observed as well (Figure 7a). In contrast to the situation at lower temperatures (see Figure 6), the holes within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands move and some new holes are created, pointing to a higher mobility of the acetylene molecules. During the reaction the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ area is gradually replaced by the disordered phase. A separate LEED experiment confirms these results: A $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern is observed after adsorption of 5 langmuirs of acetylene on the Pd(111) surface at 150 K, in agreement with previous findings.⁸ This pattern remains visible after heating to 220 K but disappears upon further heating to 240 K.

According to the available spectroscopic data, several processes occur around 230 K, which account for the decay of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase observed in the STM pictures.^{3,8,18} The chemisorbed acetylene is transformed to vinylidene ($\text{Pt}_2=\text{C}=\text{CH}_2$), and a part of the benzene formed by cyclotrimerization of acetylene desorbs. Because of these parallel processes, the different species involved, and the possible orientations the molecules may have, it is practically impossible to make a reliable assignment of the observed features in the STM pictures to chemical species. However, since the vinylidene fragment was detected spectroscopically,^{2,18} it can be expected that it constitutes the majority of the reaction product. Hence, the larger part of the bright protrusions within the disordered areas may be attributed to this species, but a clear distinction from the benzene molecules remaining on the surface to desorb around 500 K cannot be made. Finally, it cannot be excluded that a part of the new features is due to additional formation of benzene. An influence of the STM tip to the measured reactions is unlikely because STM scans taken at a different location were equivalent to those obtained at the end of each sequence.

4. Discussion

The STM data show that a visible reaction occurs in the acetylene/Pd(111) system under the following circumstances: (1) at 140 K, just before saturation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer, and (2) upon heating a saturated $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer to 230 K. From a comparison with literature data, the first reaction is assigned to the cyclotrimerization of acetylene to benzene and the second reaction to the isomerization and decomposition of acetylene and to the simultaneous low-temperature desorption of benzene. These results are summarized in the reaction scheme presented in Figure 8.

The STM pictures in Figure 3 show that the cyclotrimerization reaction at 140 K almost exclusively takes place in the disordered areas between the $(\sqrt{3} \times \sqrt{3})R30^\circ$ patches, *parallel to* the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase. The benzene formation stops as soon as the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase covers practically the whole surface. Exposing the surface to additional acetylene or heating to 200 K does not result in a further reaction. This clearly indicates that the acetylene molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains alone are not reactive, and consequently, the formation of benzene requires a different type of acetylene. In full agreement with the requirement of a critical acetylene coverage, the cyclotrimerization reaction starts when the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase is almost completed (Figure 3),⁸ suggesting that the adsorbed acetylene has to be compressed

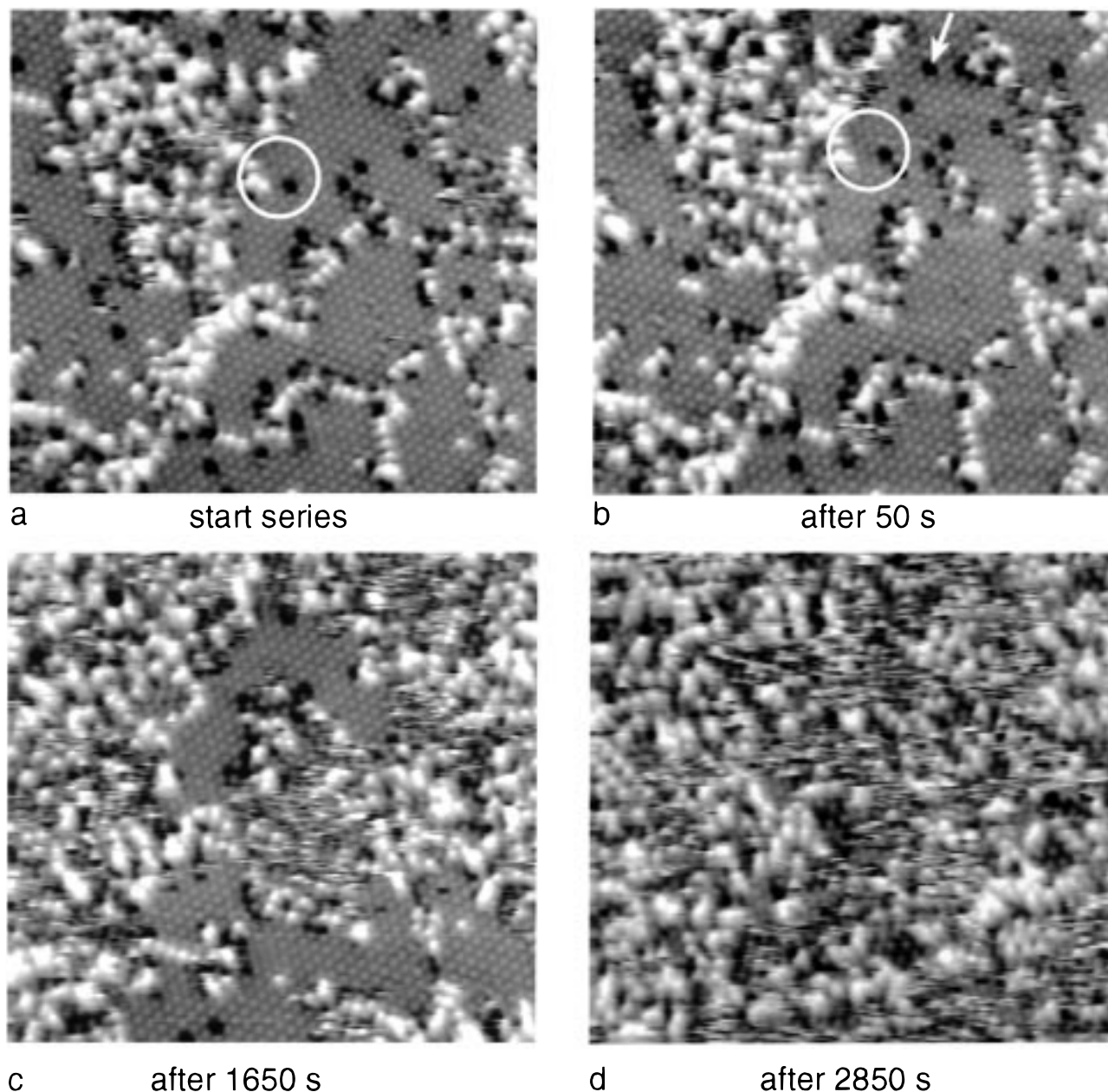


Figure 7. Selected STM images of a saturated layer of acetylene on Pd(111) at 230 K, showing the thermal decay of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains (210×210 Å, 8 nA, 440 mV). Scanning rate: 50 s/frame. Changes within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands can be recognized in frames a and b: the circle marks a moving hole, and the arrow indicates a newly created hole.

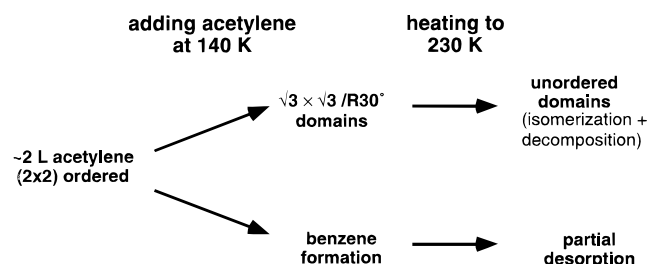


Figure 8. Proposed reaction scheme for acetylene on Pd(111) on the basis of the structures observed in the STM experiments.

first. The STM data, however, do not allow for a further identification of the reactive species, nor has a different acetylene species been identified spectroscopically. This leads to a scenario that a transient adsorption state, formed during the compression of the (2×2) to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration, is essential for the cyclotrimerization reaction to

occur. This could, for instance, be a π -bonded species, in contrast to the di- σ -bonded type in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains.^{6,21,29} A reaction of such a transient species with molecules at the edges of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains cannot be excluded, but at least one of the three molecules finally reacting to benzene has to be different from those in the ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains.

In contrast to our interpretation, it was concluded earlier that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase is reactive, based on an experiment in which a $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer of C_2H_2 was exposed to an equal amount of C_2D_2 .⁷ The idea behind that experiment is that the C_2D_2 adsorbed afterward cannot be in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration any more and must assume a more weakly bound configuration. Because the benzene formed in this experiment contains significantly more hydrogen than deuterium atoms, it was concluded that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase is reactive, and a more weakly bound acetylene phase is not required. Our STM data show, however, that the benzene

formation takes place while the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase is developing, implying that *not all* acetylene molecules have to be part of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase when the corresponding LEED pattern is observed. It is proposed here that those acetylene molecules that are not part of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains are responsible for the cyclotrimerization reaction.

The nonreactivity of the acetylene molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration provides also a natural explanation for the limited conversion of acetylene to benzene.^{6,7,9} This was previously explained by a random orientation of acetylene molecules along the three main axes of the surface, resulting in a limited number of configurations favorable for the cyclotrimerization reaction.³¹ In this case benzene would form also in the interior of ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands, which is not the case. Moreover, because of the above-mentioned rotation of the acetylene molecules, which starts already at $T > 44$ K,²² their relative rotational orientation cannot be limiting for the reaction. The requirement of a transient species for the cyclotrimerization, in a reaction accompanying the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains, accounts for both the stability of ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands of acetylene up to 230 K and the formation of only a small amount of benzene at 140 K.

A feature characteristic for C_4 dimers is not identified in the STM pictures but has not been spectroscopically identified in the acetylene/Pd(111) system either. The main arguments for a C_4 intermediate are based on the formation of butadiene in the presence of excess hydrogen³² and of furan,³³ thiophene,^{34,35} and pyridine³⁶ in the presence of oxygen, sulfur, and HCN, respectively. That coupling of acetylene to C_4 dimers can occur at 140 K on a Pd(111) surface, a requirement for the cyclotrimerization reaction, is indicated by the low temperature (120 K) for thiophene formation.³⁵ An assignment of the bright protrusions in Figure 6, after completion of the reaction, to the C_4 intermediate is rejected because (1) it is inconsistent with the UPS and HREELS data, which indicate that benzene is formed,^{3,8,19} and (2) no visible reaction occurs in the STM experiments until a temperature of 230 K is reached, and according to the available TPD data, benzene formation must have taken place at that temperature. It is concluded that the amount of C_4 dimer remains small, probably because the insertion of the third acetylene is fast.

The amount of acetylene that converts to benzene in the STM experiments remains well below 10%, as estimated from the amount of acetylene and benzene molecules observed in the STM pictures, while conversions of 20–35% were estimated with XPS.^{6,8,9} Although these numbers probably represent an upper limit,³⁷ a second reason for the difference may be the different pressures and surface temperatures at which the acetylene was dosed. According to the mechanism presented above, the selectivity toward benzene is determined by the rate of formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains with respect to that of coupling of acetylene molecules in the disordered phase of acetylene. The probability for the former process is independent of the amount of the transient, reactive species, while the latter process becomes more probable when more reactive molecules are present. (This is also reflected in the critical coverage for benzene formation.) Therefore, the formation of $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains is favored when less reactive molecules are available, which is the case at lower dosing pressures. Some support for this viewpoint comes from STM experiments in which the acetylene was dosed at higher pressure which also showed a larger amount of benzene, but more data are needed to confirm this. Furthermore, as mentioned earlier, it cannot be excluded that a part of the benzene molecules

observed in TPD is formed during the desorption. The STM pictures taken at 230 K show that at that temperature the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase becomes reactive and that both an unordered phase and mobile acetylene molecules are present, which is quite similar to the circumstances that led to the formation of benzene at 140 K.

5. Conclusions

The acetylene/Pd(111) system has been investigated with scanning tunneling microscopy (STM), both as a function of acetylene coverage at 140 K and as a function of temperature for a saturated surface. Adsorption of acetylene on Pd(111) at 140 K initially results in the formation of an ordered (2×2) layer, which is compressed into a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure upon further exposure of acetylene. The cyclotrimerization of acetylene to benzene takes place in a parallel process in the disordered areas between the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains, just before completion of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains, and stops when saturation is reached. The acetylene within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains is stable up to 230 K, even with background pressures of 5×10^{-7} Torr of acetylene. This provides strong evidence that the cyclotrimerization of acetylene to benzene at 140 K requires a transient state of acetylene, in contrast to the present viewpoint that acetylene in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration is reactive. Since the reactive type of acetylene is only a minority species on the surface, it is expected that it is hard to characterize spectroscopically. The fact that the formation of benzene and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ domains are directly competing reactions also explains the limited conversion of acetylene to benzene.

The majority of the acetylene molecules are adsorbed in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ configuration and become reactive at 230 K, when isomerization, decomposition, and possible formation of additional benzene take place. This reaction occurs patchwise, by a gradual shrinking of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ ordered domains, while a new disordered phase is formed. A further identification of the STM features in the disordered areas is not possible, due to the many different processes occurring under those circumstances. The conditions under which the cyclotrimerization and isomerization reactions of acetylene on Pd(111) are observed by STM agree well with those found in previous spectroscopic studies.

Acknowledgment. T.V.W. Janssens thanks the Alexander-von-Humboldt Stiftung for a Research Fellowship.

References and Notes

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- (37) In refs 6 and 8, the amount of benzene formed from acetylene was estimated from the decrease of the C XPS signal upon annealing to 600 K. At these temperatures the decreasing C XPS signal may be caused by additional factors, such as desorption of acetylene or other reaction products such as ethylene, and by bulk dissolution of carbon. That not only benzene desorption is taking place upon annealing to 600 K is supported by the gradual decrease of the C XPS signal, whereas a stepwise behavior is expected from the two distinct benzene desorption peaks in TPD. We assume therefore that the conversion factor of 20–35% represents an upper limit.