Adsorbate Ordering Effects in the Trimerization Reaction of Acetylene on Cu(100)

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The trimerization of acetylene to benzene on a Cu(100) surface is reported. The reaction occurs at both room temperature and at or below 200 K depending on the coverage. The reaction yield exhibits a strong coverage dependence, with the yield increasing as the initial acetylene coverage increases. The maximum yield for the room temperature reaction is 30%. The structural properties of the acetylene overlayer have been investigated by LEED, and the results correlated with the reaction yield observations. The results are discussed in light of the coverage dependence of the benzene yield for the same reaction on Cu(110) and Pd(111). It is found that the structural arrangement of the acetylene overlayer on the three different surfaces explains the different coverage dependences of the reaction yield. A unique feature is observed in the thermal desorption data for this system; the mass 26 signal mimics the trimerization reaction rate at high coverages. This is most likely due to the exothermicity of the benzene reaction, leading to the desorption of vibrationally hot benzene molecules, or the transfer of energy to nearby acetylene molecules, resulting in simultaneous desorption.

1. Introduction

A general strategy for surface science is to study simplified model systems that can be characterized in great detail by the wide array of available experimental probes. Presumably the detailed characterization of well-defined systems and the determination of the underlying physics will lead to the development of general principles that will aid in the understanding of more complex, "real world" systems. The goal of understanding heterogeneously catalyzed reactions is perhaps the most mentioned example. In this regard, the choice of model system is then crucial to developing interesting insights into more complex phenomena.

One such model reaction that has received a great deal of attention is the trimerization reaction of acetylene to form benzene on metal substrates (for a recent review, see ref 1). This system is interesting for several reasons. The study of the series of ethane, ethylene, and acetylene on metal single-crystal surfaces provides insight into the chemistry of single, double, and triple C−C bonds on surfaces. In addition, this reaction is exciting in that rather than decomposition to simpler fragments, the carbon backbone is increased in length by a factor of 3. It is very rare to see the formation of more complex molecules on metal surfaces under UHV conditions. Furthermore, on surfaces where this reaction occurs, the intermediate to benzene formation has been identified as a C_4 species.[1,2] Because it is stable, it has been possible to study the intermediate in great detail by conventional UHV techniques. Also, recent STM investigations are currently yielding atomic-level detail of the motions of individual acetylene molecules on metal surfaces.[3–5] Thus, this reaction embodies the characteristics of

being simple enough to study in detail and yet complex enough to demonstrate interesting chemistry.

The behavior of acetylene under UHV conditions on single-crystal substrates is, in general, complex. Acetylene adsorption has been studied on over 14 low-index faces of transition and noble metals. The potential for carbon−carbon and carbon−hydrogen bond cleavage leads to a wide range of possible products, several of which are typically observed at varying temperatures/coverages on any given metal (for a review, see ref 6). The trimerization reaction, however, has proven to be a highly surface-sensitive reaction. It has been shown conclusively to occur on only two well-defined elemental single-crystal metal surfaces to date, namely Pd(111) and Cu(110). Recently, several bimetallic model catalysts have been shown to catalyze the reaction. Under UHV conditions, the Au/Pd(111) system[7] and the Pd/Au(111) system[8] under appropriate preparation conditions can show enhanced benzene yield relative to the Pd(111) surface. Sn/Pd-supported bimetallic catalysts can also catalyze the reaction under high-pressure conditions.[9] In addition, the Sn/Pt(111) system has shown activity toward benzene formation both under UHV[10] and high-pressure conditions,[11] an interesting result as the Pt(111) surface is highly selective against benzene formation. The trimerization of acetylene and related alkynes has also been observed on TiO_2 under UHV conditions.[12,13]

The results of over 10 years of investigation of this reaction on Pd(111) by several research groups has been recently reviewed by Lambert et. al.[1] On Pd, the reaction is specific to the (111) surface; it does not occur on the (110) or (100) surfaces. Under UHV conditions, the reaction proceeds by the association of two acetylene molecules to form a C_4 intermediate, which then reacts with a third acetylene molecule to form benzene. The reaction shows a pronounced coverage depen-

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dence, with a threshold coverage necessary for the onset of benzene formation. Thermal desorption experiments have shown that benzene is formed only for initial acetylene coverages above 0.3 ML (monolayer) and reaches a maximum yield of 25% for a saturated acetylene layer (0.46 ML). It was also observed that for low-temperature adsorption (175 K), acetylene forms an ordered overlayer at 0.3 ML, as evidenced by the observation of a $(\sqrt{3} \times \sqrt{3})R45°$ LEED pattern.[14] Thus, the onset of the trimerization reaction and the formation of long-range order in the acetylene overlayer coincide. Another interesting observation was made. It was possible to force the trimerization reaction to proceed at lower acetylene coverages by the adsorption of a spectator molecule, NO. The NO formed segregated islands, which then forced the acetylene into a higher local coverage, allowing the trimerization reaction to proceed.

The trimerization of acetylene is also known to occur on the Cu(110) surface. The reaction was first reported by Avery in 1985,[15] and has recently been studied in detail by Lomas et al.[2] Lomas et al. have shown that the reaction proceeds via an associative mechanism to form a C_4 intermediate, as on the Pd-(111) surface. However, there is little coverage dependence of the benzene yield, with nearly complete conversion of 85% of the adsorbed acetylene to benzene in a single thermal desorption cycle for initial coverages below 0.4 ML, with the yield falling slightly at the saturation coverage of 0.5 ML. On Cu(110), a $c(2 \times 2)$ pattern is observed for acetylene adsorption at 120 K at coverages above 0.15 ML, which increases with quality until saturation of the monolayer at 0.5 ML. The formation of a LEED pattern corresponding to the maximum coverage but observable at low coverage is indicative of attractive interactions leading to islanding of the adsorbed acetylene molecules.[16]

It appears that the ordering of the acetylene overlayer plays a key role in determining the trimerization yield. The necessity of bringing two acetylene molecules close enough to form the intermediate is a key feature of the reaction. The probability to form benzene increases the closer the acetylene molecules are packed together on the surface. For the Pd(111) surface, the LEED results indicate overall repulsive interactions, which lead to no benzene formation at low coverages. For Cu(110), the observed islanding of the acetylene at low coverages explains both the high yield and the minor coverage dependence of the yield on this surface.

These interesting results have prompted our investigation of this reaction on the Cu(100) surface. We report the observation of the trimerization reaction on the Cu(100) surface for the first time. The structure of the acetylene overlayer is investigated via LEED crystallography, and the coverage dependence of the reaction is studied via thermal desorption spectroscopy. A clear picture emerges where the coverage dependence of the acetylene overlayer structure explains the probability of trimerization to benzene.

2. Experimental Section

The experiments were performed in a stainless steel UHV chamber equipped with a four-grid LEED apparatus, a quadrupole mass spectrometer, and an Auger spectrometer. The sample, a commercially prepared Cu(100) single crystal, was attached to a cryostat that allowed cooling to 90 K via liquid nitrogen and resistive heating. The sample temperature was measured by a type C thermocouple. Following initial crystal cleaning, the sample was routinely cleaned by 10 min of Ar^+ sputtering followed by annealing to 800 K for 5 min. The experimental apparatus allowed for high-quality thermal desorption spectra (TDS) to be obtained. The mass spectrometer

was differentially pumped and equipped with a nose cone with an aperture of 1 mm. During a TDS experiment, the sample was positioned within 2 mm of the nose cone. Furthermore, to eliminate any possible electron-induced reaction, the nose cone was biased at −45 V to block any electrons from the mass spectrometer ionizer from reaching the sample. The coverage was measured by a differential reflectivity technique. A visible light source ($\lambda = 632.8$ nm) was reflected off of the crystal surface, and the reflectivity change for p-polarized light was monitored as a function of acetylene exposure. For adsorption of acetylene into the chemisorbed state, the reflectivity change was found to correlate linearly with the coverage.[17] This allowed for an accurate correlation of the exposure to the coverage (within 0.0l ML). For details of this aspect of the experiment, see refs. 17 and 18. Absolute coverages are reported relative to the surface Cu atom density.

The trimerization reaction channel on the Cu(100) surface was identified by thermal desorption spectroscopy. Benzene is identified via its parent ion at m/e 78. The acetylene is identified by its parent ion at m/e 26. These studies were performed by exposing the clean crystal to acetylene at 120 K and subsequently performing a TDS run to 420 K. The benzene and acetylene mass fragments were detected simultaneously. At the completion of a single run, the crystal was cleaned by ion bombardment. This procedure was repeated for several different initial acetylene exposures.

The benzene yield was measured by the following procedure. The m/e 26 signal was integrated to give the total desorbed acetylene. Benzene does have a mass fragment at m/e 26, but based on the measured cracking pattern of benzene and the amount of benzene detected, this leads in the worst case to an error of only 2% in the acetylene desorption yield and we, therefore, ignore it. The m/e 78 signal is integrated to give the proportional amount of benzene desorbed. This number is then corrected for the mass spectrometer sensitivity to benzene relative to acetylene. The relative sensitivity of the mass spectrometer to the two molecules is estimated from the ionization cross sections of the molecules,[19,20] the measured cracking pattern, and the transmission and gain factors of the spectrometer as a function of fragment mass. Using this procedure, the percent yield of the reaction, defined as the percentage of initially adsorbed acetylene that reacts to form benzene, can be calculated. The major source of error in this procedure is the estimate of the relative sensitivity of the mass spectrometer to the two different species. Any error introduced by the estimation of the relative sensitivities will be the same for all runs, so that any observed trends will be real.

3. Results

Molecular Acetylene: Thermal Desorption Results. The adsorption and thermal evolution of acetylene on the Cu(100) surface has been investigated by HREELS by Marinova et al.[21] In this study it was observed that acetylene adsorbs molecularly at low temperatures (140 K) but is strongly distorted with a C−H stretch frequency indicating rehybridization to close to sp^3 and a C−C stretch frequency indicative of a bond order of 1.5. The acetylene was stable on the surface to about 300 K, at which temperature a new hydrocarbon species was detected. This species was thought to be CCH, but CCH_2 could not be ruled out on the basis of the observed frequencies. Further heating to 375 K resulted in simultaneous desorption of molecular acetylene and decomposition to the new hydrocarbon species.

We have studied this system utilizing thermal desorption spectroscopy. Selected TDS spectra for increasing coverages
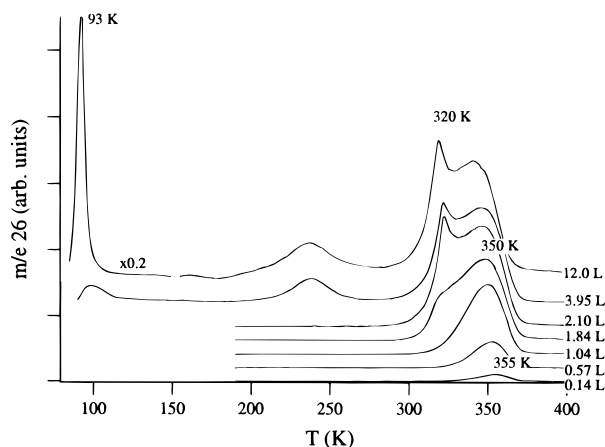
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Figure 1. Acetylene thermal desorption spectra for increasing exposure. Heating rate is 1.1 K/s. Acetylene is monitored via *m/e* 26. Successive traces are offset vertically for clarity.

are shown in Figure 1. The spectra indicate that acetylene adsorbs into three main energetically different states as a function of coverage. At low exposure, the acetylene desorbs from a chemisorbed state at 355 K. At low exposure, this peak is well-described by first-order kinetics. The desorption energy is found to be 109.0(4) kJ/mol, and the desorption prefactor is estimated to be $10^{15.7(1.4)}$. Increasing the exposure leads to growth of this feature, but the peak desorption temperature decreases, consistent with short-range repulsive interactions among nearby molecules. Near saturation of the chemisorbed feature there is an interesting development: a sharp spike grows in at about 320 K, which is partially resolvable from the main chemisorbed peak and correlates with the benzene desorption. There are several possible explanations for this feature that will be discussed later. At higher exposures, the chemisorbed state saturates and a new state is occupied, the "weakly chemisorbed" state, which desorbs at 240 K. The third major feature, consisting of acetylene bound in multilayers, is found at 90 K.

It is known that one reaction channel available to acetylene on the Cu(100) surface is a decomposition/isomerization leading to a strongly bound surface species. We have measured the amount of acetylene that decomposes on the surface rather than desorbing. For repeated saturation exposures of acetylene and subsequent thermal desorption without cleaning the crystal, the amount of desorbed acetylene decreases for each subsequent run. We estimate that about 5% of the acetylene overlayer undergoes decomposition from these results.

Ordering of the Acetylene Overlayer: LEED Results. The development of the LEED pattern is shown in Figure 2. The acetylene coverages quoted are based on a calibration of the relative coverage versus exposure using an optical reflection technique and Auger spectroscopy and taking the saturation coverage to be 0.25 ML on the basis of our LEED results. No pattern is observed for adsorption at 90 K, in accordance with previously reported results for adsorption at 60 K.[22] However, dosing at 275 K resulted in the LEED patterns shown. Adsorption at this temperature restricts acetylene to occupying the chemisorbed state. This temperature was chosen specifically to prevent adsorption into the weakly chemisorbed state and yet to remain below the temperature where the decomposition/isomerization channel opens. Thus, all ordered overlayers observed here relate to acetylene situated in the chemisorption sites. At coverages near 0.12 ML, an intensity pattern begins to emerge with nearly radial symmetry that approximates a doughnut with a discernible inner radius corresponding to one-half the reciprocal lattice vector of the clean substrate (Figure

2a). Increasing the coverage to near 0.18 ML resulted in increased intensity of the $(^1/_2,^1/_2)$ and $(0,^1/_2)$ spots but still a generally diffuse pattern (Figure 2b). Cooling the sample down to 90 K at 0.18 ML coverage resulted in a somewhat sharper LEED pattern with spots in the $(^1/_4,^1/_2)$ positions becoming discernible. Subsequent exposure increased the sharpness of the observed pattern, and the pattern developed continuously to that displayed in Figure 2c. The LEED pattern shown was obtained at the saturation coverage of 0.25 ML and was the sharpest one observed. This LEED pattern could also be observed by dosing at 90 K and annealing the crystal to 275 K. Heating the crystal to 400 K resulted in the return of a sharp p(1 × 1) pattern, indicative of desorption of the majority of the acetylene.

Trimerization Reaction: Thermal Desorption Results. The previously cited HREELS study[21] did consider the possibility of acetylene trimerization, however, the authors were unable to positively identify this reaction channel for two reasons. First, for preadsorbed benzene, the observed vibrational modes coincided with some of the modes of the acetylene decomposition product, and second, preadsorbed benzene was found to desorb below room temperature.

We have identified the presence of this reaction channel and characterized it via TDS measurements. Figure 3a shows the TDS spectra for simultaneously acquired *m/e* 26 (acetylene) and *m/e* 78 (benzene) for varying initial acetylene exposures. An interesting feature present in Figure 3a is the simultaneous desorption of benzene and a correlated peak in the *m/e* 26 spectra. This correlation is quite clearly demonstrated for the higher exposure runs. It cannot be accounted for by the ground-state cracking pattern of benzene. The 26/78 cracking ratio for gas-phase benzene is 0.05; this can only explain less than 5% of the "extra" *m/e* 26 signal. There are two possible reasons for this correlated feature in the *m/e* 26 signal. First, there could be some factor that leads to both an increased probability of benzene formation and simultaneous acetylene desorption. The second possibility is that the reactively formed benzene desorbs with a large amount of internal energy, which alters the cracking pattern significantly. We can estimate from the TDS data that the 26/78 cracking ratio must change by a factor of about 20 to account for the observed *m/e* 26 signal.

To determine whether the desorption of reactively formed benzene was desorption limited or reaction rate limited, TDS experiments were carried out for benzene adsorbed directly onto the clean Cu surface. It is found that pure benzene desorbs at or below 246 K, depending on the coverage. Therefore, the benzene evolution observed under reactive conditions is reaction rate limited, and the *m/e* 78 curve directly reflects the kinetics of the trimerization reaction.

The reaction yield as a function of initial coverage is shown in Figure 3b. The reaction yield was calculated as described in the Experimental Section. From the figure it is clear that there is a strong coverage dependence of the reaction yield on the initial coverage, with the yield reaching a maximum value of approximately 30% for the saturated acetylene overlayer. At saturation coverage, we estimate that about 5% acetylene undergoes decomposition to an irreversibly bound hydrocarbon species. Thus, the benzene channel is the major reaction on this surface.

Low-Temperature Acetylene Trimerization. When the crystal is held at temperatures below about 240 K, it becomes possible to adsorb additional acetylene on the surface, as evidenced by the "weakly chemisorbed" feature in the TDS spectrum at 240 K. It is found that the total amount of additional
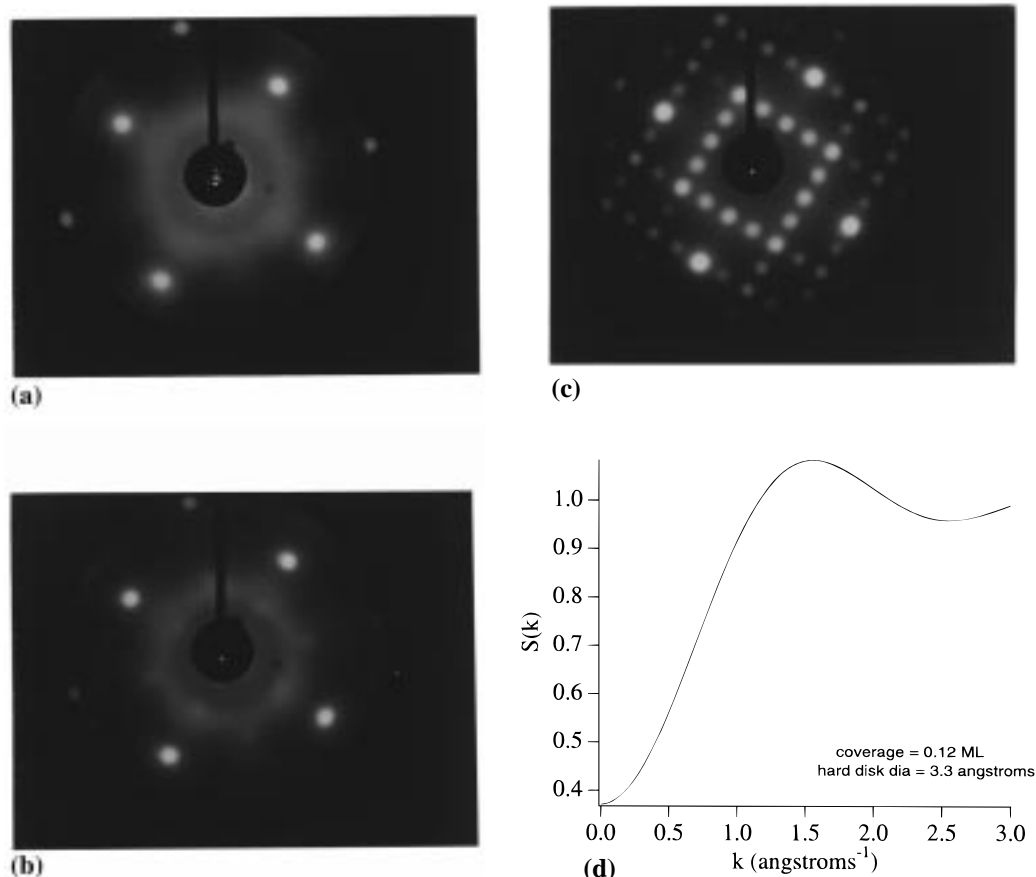
Figure 2. Coverage development of ordering of acetylene on Cu(100) (a) 0.12 ML, (b) 0.18 ML, (c) 0.25 ML (saturated chemisorbed overlayer). (d) Simulated radial dependence of $S(k)$ for the hard-disk model. Incident beam energy = 52.0 eV, T_{ads} = 275 K.
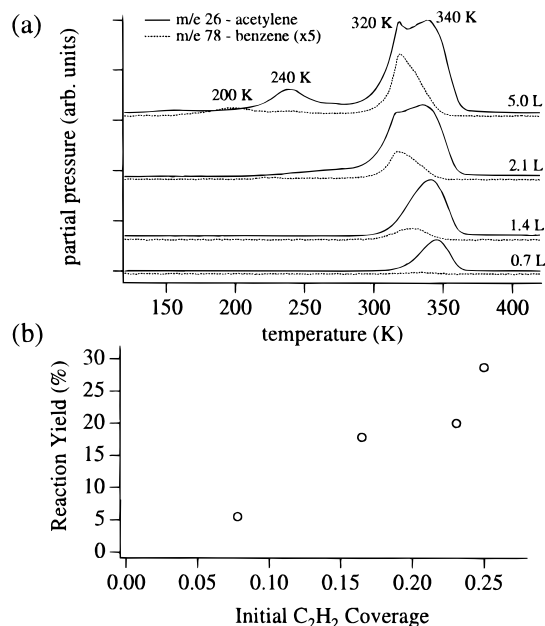

Figure 3. (a) Simultaneously acquired acetylene and benzene thermal desorption spectra. Solid line: acetylene (m/e 26). Dotted line: benzene (m/e 78). T_{ads} = 120 K. Heating rate is 1.1 K/s. (b) Percent reaction yield of benzene as a function of initial acetylene coverage for benzene originating from the chemisorbed acetylene overlayer.

acetylene adsorbed is nearly one-fifth of the acetylene in the 0.25 ML structure. Some of the acetylene adsorbed in this coverage regime is also capable of trimerizing to benzene. Since benzene desorbs from the clean surface at or below 250 K, the benzene evolution in this coverage regime does not necessarily

reflect the reaction kinetics. The benzene yield in the low-temperature/high-coverage regime is also substantial. We find that 36% of the acetylene adsorbed above 0.25 ML is converted to benzene. The fact that the reactively formed benzene desorbs at lower temperatures than from a clean surface is attributable to steric effects which lower the effective desorption barrier. One possible explanation is that with large amounts of acetylene also present on the surface, the benzene is unable to lie completely flat and maximize its adsorption energy. This effect is seen also for benzene on Pd(111).[1]

4. Discussion

4.1. Acetylene Overlayer Structure: Coverage Dependence. Interpretation of Intermediate Coverage Diffuse LEED Results. The diffuse LEED pattern observed at intermediate coverages (Figure 2a) can be understood in a semi-quantitative way by a simple hard-disk model. Consider an isolated acetylene molecule on the surface with its ability to scatter electrons contained in the form factor $F(\mathbf{k})$, where ideally this is calculated in a rigorous, multiple scattering formalism. If the lateral potential of the surface is turned off, then $F(\mathbf{k})$ averaged over all orientations becomes a radially symmetric function. In addition, the probability of finding a nearby acetylene molecule is given by the pair correlation function $g(r)$, which in the absence of a lateral potential becomes a radially symmetric function as well. In a simple model, the interactions of acetylene with its neighbors is approximated as a hard disk of diameter a. Under these approximations, the scattered intensity can be written as[23]

$$I(k) = N|F(k)|^2 S(k)$$

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where

$$S(k) = 1 + 2\pi\rho \int_0^\infty r(g(r) - 1)J_0(kr)\mathrm{d}r$$

In eq 1 N is the total number of scatterers, $S(k)$ is the structure factor, ρ is the number of scatterers per unit area, and J_0 is the zero-order Bessel function. It is then necessary to deduce the functional form of the pair correlation function. In the limit of low density, $g(r)$ becomes simply $e^{-V(r)/kT}$, where $V(r)$ is the intermolecular pair potential.[24] For a hard disk, $V(r)$ is ∞ for $r \le a$ and 0 for $r > a$. This leads to $g(r)$ being 0 for $r \le a$ and 1 for all other r. The physical interpretation of this is that the acetylene molecules are situated randomly on the surface except that they can never approach each other closer than a. This leads to the structure factor being given by

$$S(k) = 1 + 2\pi\rho \int_0^a (-1)rJ_0(kr)\mathrm{d}r$$

The intensity pattern calculated from eq 2 is then shown in Figure 2d for a 0.12 ML coverage and a hard-disk diameter of 3.3 Å. It is interesting to note that in the above formula all the structural information is contained in the integral. In the low-coverage limit, a change in the coverage simply scales the diffraction features while their positions in reciprocal space are unaltered. A change in the hard-sphere diameter does lead to a shifting of the diffraction features in reciprocal space, however. We have numerically integrated eq 2 for various values of a from 1 to 4 times the Cu(100) nn distance of 2.55 Å. We then calculate the position of the first diffraction maximum as a function of a. We find that to negligible error over the stated range, the position of the first-order maximum k_0 as a function of the hard disk diameter is

$$k_0 = 0.817\frac{2\pi}{a}$$

Thus, the position of the first-order maximum is located at a distance slightly less than the reciprocal lattice vector associated with the distance a. The position of the first-order maximum from Figure 2b is measured to be 1.55(16) Å^{-1}, which according to eq 3 yields a hard-disk diameter of 3.31(35) Å. Our interpretation of the diffuse LEED pattern at low to intermediate coverage is that the dominant forces ordering the structure of acetylene are short-range repulsive interactions that restrict the approach of the acetylene molecules to no closer than the hard-disk diameter. For farther distances, the site occupation is approximately random, leading to the radially symmetric pattern. It will be seen later that the saturation structure leads to acetylene molecules at 5.10 Å apart. Thus, while this simple hard-sphere model can qualitatively account for the observed diffraction pattern, the model underestimates the hard-disk diameter by 35%.

The underestimation of the hard-disk diameter is due to the simplifications made to develop the model, and it is instructive to consider these in more detail. One might anticipate that the assumption of low coverage would lead to large inaccuracies in the calculation of k_0, but this is not the case. It has been shown, e.g., in extensive calculations on liquids, that the position of the first order maximum is dependent essentially upon the repulsive part of the intermolecular potential and is very weakly dependent upon the density,[25] varying only 7% up to a density of one-half of the close-packed density. We note that the coverage in Figure 2b is about one-half of the saturated coverage. In developing the model, it was assumed that the form factor $F(k)$ was radially symmetric and the acetylene could
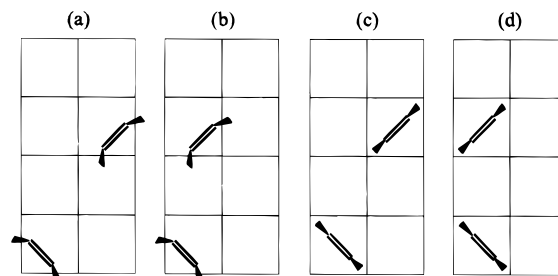

Figure 4. Four possible saturated chemisorbed acetylene overlayer structures. Structures a and b correspond to acetylene in the local C_s binding site, and structures c and d correspond to acetylene in the local C_{2v} binding site as described in the text.

occupy any randomly chosen position on the surface. However, it is clear that for an isolated acetylene molecule, $F(k)$ will not be radially symmetric and each molecule will be strongly localized to a specific bonding site. Considering this, it seems surprising that a diffraction pattern with approximate radial symmetry is observed at these intermediate coverages.

As will be discussed in the next section, there is evidence that the local binding site of an acetylene molecule is either the low-symmetry site shown in Figure 4a,b or the higher symmetry site shown in Figure 4c,d. At low coverages, an acetylene molecule can orient itself in more than one way in any given substrate primitive cell. This leads to some averaging of the structure factor so that it can approach radial symmetry. Also, as long as a second acetylene molecule is further apart than the hard-disk diameter, there are more possible relative orientations than the square lattice presented by the substrate would suggest. These considerations clarify how such a simple model is able to capture the qualitative aspects of the diffraction pattern at relatively high densities and also points out the inadequacies. The lack of considering any polar angle dependence of the form factor $F(k)$ is another simplification which limits the accuracy of the calculated intensity.

Long-Range Order Near Saturation Coverage. The saturation pattern shown in Figure 2c leads to a simple and unambiguous interpretation. The diffraction positions observed in a LEED pattern can be simply interpreted to yield the symmetry and dimensions of the overlayer unit cell. Note that while the relative intensities of the observed spots vary as a function of the incident electron energy, no additional spots are observed over the energy range of 40−180 eV. The Cu(100) substrate provides a square lattice. All the observed spots can be accounted for by a p(2 × 4) overlayer lattice, allowing for the presence of two domains oriented at right angles to each other. Then it is necessary to account for the missing spots that are predicted by such an overlayer but are not observed. The answer lies in the presence of a glide plane lying along the long real space axis. If the real space p(2 × 4) unit cell is oriented with the long axis lying along the [01] direction, such a glide plane results in every spot with indices (0,k), with k odd to be missing,[26] with the indices referring to the overlayer reciprocal lattice points. Then the sum of such a pattern with an equivalent domain at right angles accounts simply for the observed pattern. The appearance of a glide plane in the space symmetry is fortunate in that it allows the absolute coverage to be determined with little doubt. The glide plane necessarily restricts the number of acetylene molecules in the overlayer unit cell to be an even number. This restriction requires that there are at least two acetylene molecules in the unit cell.

To further narrow down the possible surface structure, we consider two possibilities for the local binding site geometry

for the acetylene molecule. Utilizing SEXAFS and NEXAFS, Arvanitis et al.[22,27,28] have found the acetylene to be coordinated to three Cu surface atoms in a di-σ + π bonding arrangement (nomenclature from ref 6). The point group of acetylene in this binding site is C_s. The C—C bond lies parallel to the surface at 1.30 Å above the surface Cu plane. The bond length is 1.42 Å, indicating significant stretching of the gas-phase C—C bond length of 1.21 Å.[29] The positions of the hydrogen atoms cannot be determined by the above experimental techniques, however, they can be estimated. The observed hydrogen stretch indicates a high degree of rehybridization, close to sp^3,[21] which implies significant bending of the hydrogen away from the surface. A recent theoretical study optimizing the hydrogen position for the experimentally determined binding site places the molecular plane of acetylene at 60° to the surface with a C—C—H bond angle of 120°, where a C—H bond length of 1.09 Å was assumed.[30] We then use these dimensions to fix the hydrogen positions.

A recent STM study has found a different local binding site for acetylene. Stipe et al.[4,5] observed the acetylene to be centered above the 4-fold hollow site with the molecular plane aligned across the diagonal of the square formed by four Cu atoms. In this configuration, the acetylene is expected to be coordinated to four Cu atoms. The point group symmetry of acetylene in this site is C_{2v}.

Given the two proposed local binding sites of acetylene in its chemisorbed state, it is highly unlikely that there are four acetylene molecules per p(2 × 4) unit cell. Any such configuration would require some or all of the Cu atoms in the unit cell to be coordinated to more that one acetylene molecule at saturation coverage, which implies a significant change in the bonding as a function of coverage. Our LEED results argue strongly against such a possibility. There is no evidence in the LEED pattern for a change in periodicity of the acetylene unit cell or a change in symmetry of the p(2 × 4) unit cell for coverages between 0.18 and 0.25 ML, corresponding to a 40% increase of the coverage. It seems highly unlikely that a shift from two to four molecules per unit cell is occurring and that we have misassigned the absolute coverage. We, therefore, set the number of acetylene molecules in the unit cell at 2, yielding a saturation coverage of 0.25 ML. This result compares well with the results of Marinova et al.[31] Measuring the Auger intensity for a saturated acetylene monolayer and comparing to the Auger intensity for a saturated monolayer of oxygen for which the coverage is known, they estimate the acetylene saturation coverage at 0.24 ML.

The two proposed binding sites lead to four possible structures for the saturated acetylene overlayer based on the symmetry requirements imposed by the LEED data. These are shown in Figure 4. Structures a and b belong to the space group *pg*, structure c belongs to space group *p2gg*, and structure d belongs to space group *p2mg*.

To further distinguish between these four structures, we have calculated several intermolecular distances. These distances are displayed in Table 1. If the local binding site is the site with C_s symmetry, then structures a and b are possible. Both structures are very similar in terms of intermolecular distances. Both structures have identical nn C distances and nn "center of molecule" distances. The hydrogens at closest approach are 8% farther apart for structure b. For higher order distances measured from the center of the C—C bond, it can be seen from Table 1 that there is a compensation in the bond distances. That is, the nnn distance is closer for structure b but the 3nn distance is closer for structure a, etc. There is evidence in the coverage

TABLE 1: Intermolecular Distances[a]

		structure a	structure b	structure c	structure d
carbon	nn	4.22	4.22	4.22	4.10
hydrogen	nn	3.44	3.72	3.94	3.00
acetylene	nn	5.10(2)	5.10(2)	5.10(2)	5.10(4)
	nnn	5.33(2)	5.20(2)	5.70(4)	7.20(4)
	3nn	6.22(2)	6.54(2)	9.20(4)	10.20(4)
	4nn	8.37(2)	7.96(2)	10.20(4)	11.40(8)

[a] Inter-acetylene distances refer to the distance between molecules measured from the center of the C—C Bond. Distances reported in Å.

dependence of the LEED pattern and the TDS data for repulsive interactions at close distances for acetylene molecules. However, taking the van der Waals radius of a hydrogen atom at 1.0 Å[32] and noting that the closest approach of H atoms in both structures is significantly greater than 2.0 Å, it is not possible to distinguish between the two structures based on steric arguments.

If the local binding site is the site with C_{2v} symmetry, then structures c and d are possible. Of these two sites, structure c appears to be the most probable. This structure has farther nn distances between both carbon and hydrogen than structure d. It also has fewer nn molecules. Therefore, it is more consistent with the observation of repulsive intermolecular interactions. Also, the STM data[4,5] provides convincing evidence of a C_{2v} site symmetry. However, none of the structures can be rigorously excluded on the basis of the LEED data.

4.2. The Trimerization Reaction and Its Coverage Dependence. In this section we will concentrate on the acetylene trimerization in the chemisorbed layer. The correlation of the LEED results with the reaction yield results provide a satisfying picture that compares well with the yield vs coverage results on Pd(111) and Cu(110). For the Cu(100) system, there is no threshold for reaction. Short-range repulsive interactions lead to a low probability of reaction at low coverages. The probability is not zero, however, because the repulsion is only short range. The partial ordering observed at lower coverage in LEED indicates that it is possible (on average) for some acetylene molecules to approach sites as close as about two lattice units. Heating the surface gives some of these pairs enough thermal energy to then approach nn sites and react. Increasing the surface coverage increases these nearby "pairs", which can then go on to react.

The LEED results also shed light on the interesting correlation between the benzene reaction and the simultaneous peak observed in the *m/e* 26 TDS data. To discuss this, first we will assume that the signal is due to simultaneously desorbing acetylene. Under this assumption, we will consider two possible scenarios. One possible explanation is that at the higher coverages a new overlayer structure, which we will term a "compression structure", is formed, forcing the closer approach of adsorbate molecules. It is well-known that nn repulsive interaction can lead to two peaks in a TDS spectrum for coverages above 0.5 ML on a square lattice, even though the molecules remain bound in the same local site over the entire coverage range.[33] In our case, with a saturation coverage of 0.25 ML, addition of more molecules would force occupation of nn or nnn lattice cells. At high coverages, the formation of a "compression structure" would lead to a lower activation barrier to desorption due to short-range repulsions and to a high benzene reaction rate due to the closer approach of acetylene pairs. However, our LEED results indicate that this is not the case. The LEED results show that nn and nnn lattice cells are

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not occupied to any significant extent in the overlayer and the saturation coverage is insufficient to force occupation of these sites.

The second possibility is as follows. It is conceivable that once the well-ordered chemisorbed acetylene layer is formed, some acetylene adsorbs randomly into some weakly bound state but does not alter the structure of the chemisorbed monolayer and is not directly evidenced in the LEED data. Upon heating this, acetylene could react with acetylene in the chemisorbed layer to form benzene or desorb. Then, presumably the 320 K peak could be due to this "weaker" bound state. From the TDS measurements, the amount of acetylene that must exist in such a state can be measured. It turns out that at saturation of the chemisorbed layer, one-fifth of the total desorbed acetylene comes at 320 K. If we attribute adsorption of acetylene into this hypothetical state as being responsible for the increased benzene yield as well, then at least one acetylene molecule for each desorbed benzene must come from this state. This leads to about 30% of the total adsorbed acetylene being in this state prior to the TDS cycle. The bonding energy of acetylene in this state can then be estimated at 85 kJ/mol by the common Redhead analysis[34](prefactor $= 10^{13}$ assumed). This bonding strength is significant, being 70% of the bonding energy of the acetylene desorbing at 350 K, and if this state indeed exists, it indicates significant interaction with the substrate. Thus, given the amount of acetylene that must be present in this hypothetical state to explain the observations, one would expect to see an altering of the overlayer structure at high coverages. Again, the LEED data shows no evidence for this.

The lack of evidence for a structural explanation leads us to consider an alternative mechanism. As already mentioned, the correlation between the two features cannot be explained by the cracking ratio of ground-state benzene. The correlation is most likely due to the exothermicity of the trimerization reaction. The energetics involved in the reaction can be estimated. The ΔH of reaction from acetylene to benzene in the gas phase is -602 kJ/mol.[35] The ΔH of acetylene adsorption is -109 kJ/mol from our TDS results, and the ΔH of benzene adsorption can be estimated to be approximately -65 kJ/mol using the standard Redhead analysis of our TDS data. This means that the formation of an adsorbed benzene molecule from adsorbed acetylene releases 340 kJ/mol of energy. Desorption of the benzene molecule requires 65 kJ/mol, leaving 275 kJ/mol of energy to be dissipated. Therefore, it is reasonable that some of this energy ends up as internal energy within the benzene molecule. The correlation could then be due to vibrationally hot benzene desorbing before it can equilibrate with the surface. If the benzene desorbs with a large amount of internal energy, this will alter the cracking ratio. It is known that reactively formed surface species can desorb without equilibrating with the surface; such an effect is seen in the angular dependence of reactively formed N_2 desorbing from the NO/Pd(110) system.[36]

However, if hot benzene were the only mechanism responsible for the "extra" m/e 26 signal, then then the "extra" signal should be proportional to the m/e 78 signal. Then it should be possible to subtract out the correlated peak in the m/e 26 spectrum and get a smooth curve indicative of pure acetylene desorption. However, we find that it is not possible to remove the 320 K feature completely from the m/e 26 spectrum by subtraction for any proportionality constant. We, therefore, cannot rule out the possibility that some of the energy from the reaction is transferred to nearby acetylene molecules, causing them to desorb simultaneously. A reaction-assisted desorption mechanism has recently been suggested for the desorption of

N_2O from Si as well.[37] Either one of these two possibilities would explain the correlation between the m/e 78 and 26 signals without the need to invoke an additional binding site. It should be possible to gain further insight into these possibilities via angle-resolved TDS measurements.

5. Conclusion

We conclude this discussion by summarizing the principle findings of these experiments and the insight gained into this reaction. The trimerization reaction of acetylene to benzene has been observed on the Cu(100) surface, this being the third elemental metal single-crystal face and the first (100) face known to catalyze this reaction under UHV conditions.

Molecularly adsorbed acetylene can adsorb in three energetically different states, the chemisorbed state (340 K), the weakly chemisorbed state (240 K), and the multilayer state (90 K). For adsorption into the chemisorbed state, the acetylene forms a well-ordered overlayer at coverages approaching 0.25 ML. The structure of this overlayer has been determined by LEED. At lower acetylene coverages, we have proposed a structural model for the overlayer that is consistent with the diffuse LEED patterns observed. At lower coverages, the overlayer shows short-range order that is dominated by short-range repulsive forces. The analysis of the diffuse LEED pattern suggests that this distance is 3.3 Å, however, it may be closer to 5.1 Å as the well-ordered overlayer results indicate. Beyond this distance the distribution is at least approximately random. At coverages approaching 0.25 ML, these repulsive interactions cause the overlayer to adopt a well-ordered arrangement on the surface. At saturation coverage, the repulsive interactions force the overlayer to adopt a structure with long-range order; the LEED data allows this structure to be identified.

The trimerization reaction yield shows a strong coverage dependence but does not show a threshold as in the case of Pd(111). We find that the coverage dependence of the reaction yield can be correlated well with the LEED observations; the repulsive interactions among neighboring acetylene molecules leads to little probability of trimerization at low coverage, while at higher coverages, the acetylene molecules are forced together in a closer arrangement and the reaction yield increases. The LEED observations also shed light on an interesting feature observed in the TDS data for this system. At higher coverages where the benzene yield is high, a feature is observed in the m/e 26 signal with kinetics that mimic the trimerization reaction rate. The most likely explanation for this phenomenon is that the exothermicity of the trimerization reaction leads to direct desorption of vibrationally excited benzene, with the possibility that some of the energy is transferred from the benzene to nearby acetylene monomers, resulting in their desorption.

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