

# Preadsorbed Oxygen Atoms Affect the Product Distribution and Kinetics of Acetylene Cyclization to Benzene on Pd(111): A Laser-Induced Thermal Desorption/Fourier Transform Mass Spectrometry Study

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The study presented here focuses on determining the role of oxygen as a modifier on Pd(111) and its effects on the cyclization of acetylene to benzene. Laser-induced thermal desorption/Fourier transform mass spectrometry (LITD/FTMS) is used as a sensitive tool for measuring the in situ kinetics of benzene formation from acetylene on O/Pd(111). Low exposure of acetylene on O/Pd(111) leads to the anticipated formation of benzene and 1,3-butadiene. Though there is no evidence of furan formation on the surface, oxidation products, such as CO and H<sub>2</sub>O, are observed. An enhancement in the yield of benzene has been observed with increasing oxygen preexposure. Our evidence suggests that this enhancement is caused by oxygen-island compression of acetylene molecules into bare patches of Pd, which effectively increases the local coverage of acetylene in those regions. Isothermal kinetic studies of 1.1 langmuirs of acetylene on a 50% saturated layer of O on Pd(111) (from a 0.25 langmuir exposure of O<sub>2</sub> at 250 K) yield an  $E_a$  of  $37.8 \pm 3$  kJ/mol using initial rates (and  $36.2 \pm 3$  kJ/mol using a pseudo-first-order model). Both the activation energy and preexponential factor from a 50% saturation coverage of oxygen on Pd(111) correspond to the values expected for twice the acetylene exposure on a clean surface. The apparent contradiction between increased benzene yields and activation barrier for the O/Pd system can be rationalized by the compensation effect, where a more tightly bound reactant can lead to a greater entropy of activation.

## Introduction

The nature and reactivity of a metal surface can be greatly modified by the adsorption of a highly electronegative atom or molecule. Charge transfer from the metal to the electronegative adsorbate occurs readily and can significantly alter the electron density at an otherwise reactive metal surface site. Electronegative adatoms, such as oxygen, also tend to form 2-dimensional islands on fcc(111) metals,<sup>1</sup> the geometry of which can play a completely different role on the surface apart from any electronic perturbation generated by these species. As one might expect, the adsorption of oxygen on Pd(111) both raises the work function<sup>2</sup> and, at submonolayer coverages, also forms islands of p(2 × 2) structure.<sup>3</sup> The modifying nature of oxygen is even more revealing, though, with the coadsorption of hydrocarbons, where processes such as site blocking and oxidation can compete with reactions normally occurring on the “clean” surface.

Acetylene cyclization on Pd(111) has been well-characterized by several investigators using a number of different techniques.<sup>4–7</sup> A logical step in elucidating the mechanism of this reaction was to coadsorb electronegative atoms such as S, O, P, and Cl and monitor changes in surface electronic structure, reactivity, and kinetics.<sup>8</sup> Surprisingly, not much work has been done to thoroughly understand the reactivity of acetylene on O/Pd(111), and none before this study have even attempted to determine the kinetics of benzene formation. Temperature-programmed

reaction (TPR) spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used previously to investigate this system and the coverage dependence of acetylene and oxygen on benzene formation.<sup>2</sup> For a given exposure of acetylene, this study reported a slight increase in the yield of benzene at the lowest exposures of oxygen introduced, but overall the yield decreased with increasing exposure. Increasing acetylene exposure with a constant oxygen precoverage enhanced the yield significantly. A more recent theoretical study used Monte Carlo simulations to predict the benzene yields observed in the TPR study mentioned above, the results of which agreed with the experimental study.<sup>9</sup> Interestingly, in our laser-induced thermal desorption/Fourier transform mass spectrometry (LITD/FTMS) study, an enhancement in the benzene yield persisted through a wider range of oxygen exposures than was observed in the aforementioned study.<sup>2</sup> Earlier TPR studies also reported small amounts of furan (C<sub>4</sub>H<sub>4</sub>O) from low precoverages of oxygen, in addition to forming benzene and other oxidation products.<sup>10</sup> This furan formation is analogous to the heterocyclization of acetylene with coadsorbed S to yield thiophene<sup>11–13</sup> and, thus, might be expected on O/Pd(111), yet no furan signal was ever observed here using either LITD/FTMS or FT-TPR. Using saturation precoverages of oxygen, Nascente et al. previously studied acetylene adsorption on the O/Pd(111) surface with high-resolution electron energy loss spectroscopy (HREELS) and low-energy electron diffraction (LEED).<sup>14</sup> Focusing on the conversion of acetylene to ethylidyne (rather than benzene formation), their study concluded that the presence of preadsorbed oxygen induced ordering of this species, possibly by removing the near-surface hydrogen hindering periodic alignment.

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The LITD studies presented here focus on determining the role of oxygen as a modifier on Pd(111) and its effects on the cyclization of acetylene to benzene. LITD has the unique advantage of probing in situ reaction processes occurring on the surface which is most valuable for determining the mechanism and kinetics of benzene formation. We show that the yield of benzene *on the surface* generally increases with increasing preexposures to oxygen and that the difference in kinetics of benzene formation are quite notable on O/Pd(111) compared to that of a clean surface. The kinetics results contrast the effects of coadsorbed sulfur on Pd(111) which have no significant effect on benzene yield or rate of formation. The results suggest that the adsorbed oxygen forms islands on the surface and compresses the acetylene on clean Pd patches into regions of effectively high, local coverage.

### Experimental Section

The experiments are performed in an ultrahigh-vacuum chamber ( $3 \times 10^{-10}$  Torr) equipped with LEED, Auger electron spectroscopy (AES), ion sputtering, and adsorption/desorption measurements utilizing both conventional and laser-induced heating methods coupled with Fourier transform mass spectrometry. Details of the apparatus are published elsewhere.<sup>15</sup> The Pd(111) crystal is cleaned by repeated cycles of Ar<sup>+</sup> bombardment to remove any tightly bound species, such as sulfur, until no impurities are detectable by analysis with AES. Residual carbon is then removed from the surface by repeated cycles of O<sub>2</sub> treatments, whereby the surface is heated to 900 K in the presence of oxygen ( $5 \times 10^{-8}$  Torr with dosing tube) for 2 min, followed by a 1 min anneal at 1200 K. Sample cleanliness is monitored by dosing O<sub>2</sub> between 250 and 300 K followed by TDS and monitoring the desorption of O<sub>2</sub> and CO.

The oxygenated surface was prepared by backfilling the chamber with O<sub>2</sub> while holding the sample temperature constant at 250 K. It has been established that, at 300 K, O<sub>2</sub> on Pd(111) forms a well-ordered  $p(2 \times 2)$  LEED pattern.<sup>3</sup> Dissociation of molecular oxygen on Pd(111) begins at 180 K and is completed by  $\sim 200$  K,<sup>16,17</sup> though, the maximum coverage of atomic oxygen occurs on this surface when dosing O<sub>2</sub> at 300 K (rather than dosing at low temperatures and annealing to dissociate).<sup>18</sup> The sticking probability of O atoms is high at 300 K until 4 langmuirs, where the surface saturates and the sticking probability drops to zero ( $\theta_s = 0.25$  ML). Our own temperature-programmed desorption (TPD) studies monitoring O<sub>2</sub> desorption from O<sub>(a)</sub> show that an exposure of 0.25 langmuir corresponds to roughly 50% saturation (0.12 ML). Following exposure to oxygen, the surface was then immediately cooled to 100 K. LEED was used to confirm the existence of a  $p(2 \times 2)$  lattice in the overlayer following this procedure.

The acetylene is spectral grade (99.96%) with an acetone stabilizer impurity. Acetone (and benzene, if present) is removed by passing the acetylene through a CO<sub>2</sub>-ice/acetone-cooled trap and determined free of impurities by gas-phase, FT mass spectral analysis. Following oxygen preadsorption, the surface is exposed to acetylene by backfilling the chamber. The sample temperature is held constant at 100 K during the exposure. At this temperature and low coverage, acetylene sticks to the Pd(111) surface with near unit probability.<sup>19</sup> Exposures (langmuir =  $10^{-6}$  Torr·s) have been corrected for ion gauge sensitivities. The values used for acetylene (1.66), benzene (5.18), 1,3-butadiene (2.9), and CO (1.0) were obtained directly from the literature.<sup>20–22</sup>

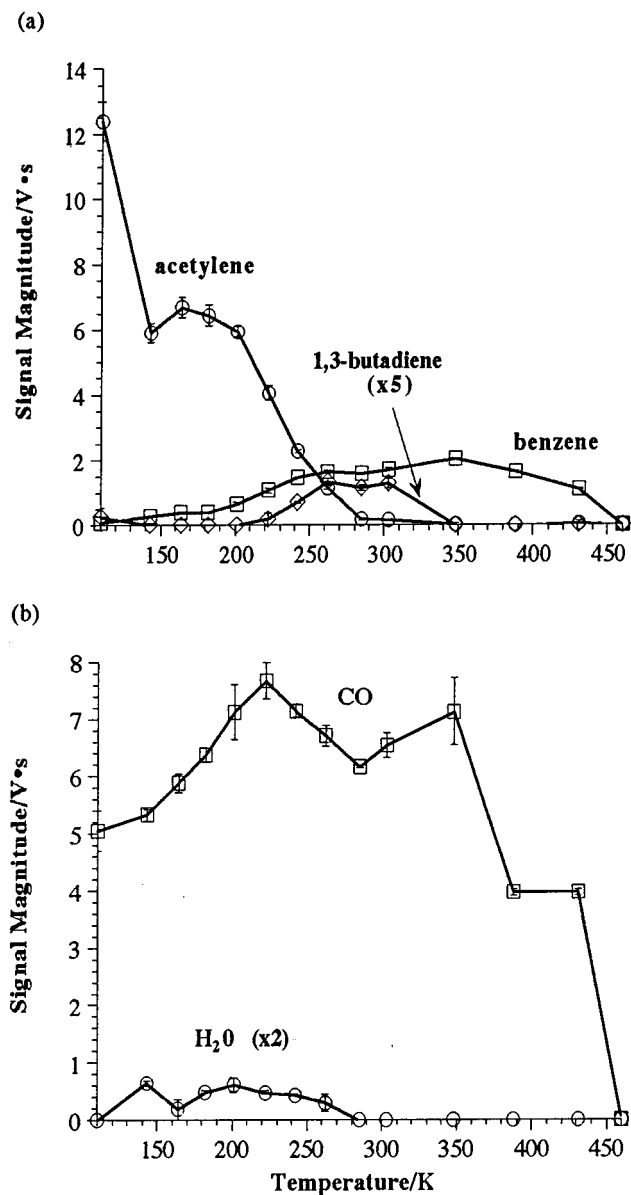
One of our most useful experiments is the *LITD T-jump survey* monitoring all masses. During these experiments, the

entire Pd sample is resistively heated to a selected temperature and allowed to equilibrate for 1 min before firing the laser (Nd:YAG, 20 mJ/pulse, 5 ns pulse width). Each spectrum is obtained from a single laser shot, aimed at a different position on the surface (laser spot size  $\approx 1$  mm<sup>2</sup>), and each spectrum produced is a complete mass spectrum of all the ions trapped in the mass spectrometer analyzer cell. Several spectra are taken at each temperature and the signal magnitudes averaged. The LITD/FTMS signals are typically proportional to the surface concentrations for each species;<sup>15</sup> therefore, relative yield information can be obtained from a single spectrum. The kinetic experiments are run in a fashion similar to the LITD survey. The Pd sample temperature is rapidly increased and held constant at some temperature where the kinetics of the reaction can be easily monitored. The surface is not allowed to equilibrate at the designated temperature, and laser shots are taken immediately after temperature has been reached. Depending on how fast the reaction proceeds at a particular temperature, the laser is fired at a repetition rate consistent with the rapid initial change in surface composition. Over time, the reaction rate decreases and shots are taken less frequently.

### Results and Discussion

**A. LITD Surveys.** *The Cyclization of Acetylene Leads to the Formation of Benzene and Other Oxidation Products.* The LITD/FTMS survey in Figure 1 looks very similar to that of a low exposure of acetylene on clean Pd(111). In this case, however, the Pd surface has been predosed with a 0.25 langmuir exposure of O<sub>2</sub> yielding an approximate oxygen atom coverage of 0.12 ML. On this modified Pd surface, significant yields of oxidation products (CO and H<sub>2</sub>O) are observed at low temperature, in addition to the predictable addition products (benzene and 1,3-butadiene) also observed. The oxidation products are formed at low temperatures and remain on the surface until they are thermally desorbed. The low-temperature signals for these masses are most likely due to reaction at defect sites, since acetylene does not begin decomposing until  $> 200$  K. Surprisingly, no signal for furan (C<sub>4</sub>H<sub>4</sub>O) was ever observed using LITD/FTMS or FT-TPR, though there have been reports of furan forming from acetylene on O/Pd(111) using TPD.<sup>2</sup> On this point, a slight contrast exists between acetylene cyclization on O/Pd(111) vs S/Pd(111).<sup>13</sup> Cyclization on S/Pd leads to the formation of thiophene (C<sub>4</sub>H<sub>4</sub>S), as well as benzene. Not only was thiophene observed in LITD, but the yield and rate of formation were comparable to those of the efficient benzene formation. On the other hand, even with the high sensitivity of LITD, we were unable to detect even a femtomole of furan from acetylene on O/Pd(111). With TPD, Omerod and Lambert report to have observed a very small amount of furan using the same oxygen precoverages and acetylene exposures as in this LITD study. These LITD studies were repeated several times using various exposures of both acetylene and preadsorbed oxygen, and we feel confident that if any furan formation occurred, LITD would have provided sufficient evidence to agree with conclusions drawn by these investigators.

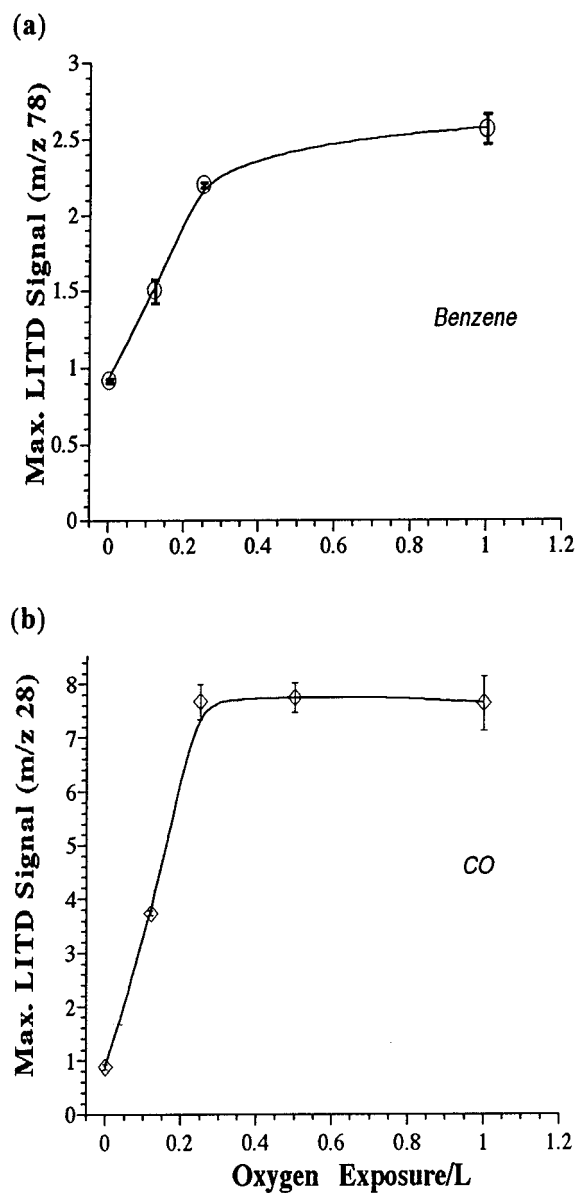
*The Yield of Benzene Changes with O Exposure.* It was of interest to determine the extent to which preadsorbed O atoms affected the yield of benzene. A series of LITD/FTMS *T-jump* surveys, like that shown in Figure 1, were taken using the same acetylene exposure with varying amounts of preadsorbed oxygen. Figure 2 summarizes those results. Each data point in the plot represents the maximum (corrected) LITD signal for (a) *m/z* 78 and (b) *m/z* 28 for each exposure of oxygen used. (This maximum was typically taken from data near 350 K.)



**Figure 1.** LITD/FTMS survey of acetylene on O/Pd(111). This survey was selected to show the loss of acetylene with the formation and growth of (a) cyclization and (b) oxidation products. The data were obtained using a 1.2 langmuir exposure of acetylene on a Pd(111) surface precovered with a 0.25 langmuir exposure of oxygen atoms (corresponding to 50% saturation coverage, roughly 12% of a monolayer). The values shown here have been corrected for both ion gauge sensitivity and percent total fragmentation.

The curve is not representative of any fit to the rise in either yield; it has been added merely to guide the eye. It is clear from the plot that, for the same exposure of acetylene, the yields of both benzene and CO increase with oxygen exposure, saturating above 0.25 langmuir. (Note the 1.5-fold increase in the benzene signal from clean to 0.12 langmuir O exposure.) Though not shown, it is interesting to point out that the onset temperature for benzene formation shifts to lower temperature as the exposure of oxygen increases. From the survey data then, it appears that the presence of preadsorbed oxygen enhances and facilitates the formation of benzene.

Electronegative atoms, such as oxygen, tend to form islands on unreconstructed fcc(111) surfaces.<sup>1</sup> At low exposures, oxygen chemisorbs onto Pd(111) in a  $p(2 \times 2)$  overlayer occupying 3-fold coordination sites; the formation of large



**Figure 2.** Yield of benzene and CO vs oxygen exposure. The plots show the maximum yield of (a) benzene and (b) CO as a function of oxygen exposure from a 1.2 langmuir exposure of acetylene. In both (a) and (b), the yield of product increases steeply with exposure to oxygen, saturating above 0.25 langmuir. Values have been corrected for ion gauge sensitivity and percent total fragmentation.

ordered islands by the oxygen atoms was indicated by LEED patterns exhibiting a fairly well-defined  $(2 \times 2)$  structure well before reaching the saturation coverage of  $\theta = 0.25$  ML.<sup>3</sup> The current and past results seem to indicate that when acetylene is coadsorbed, the molecules adsorb initially to either the oxygen islands or the clean Pd patches but then migrate to clean patches and cyclize to benzene. Ormerod et al. have compared changes in work function as a function of acetylene exposure for both a clean and O-saturated Pd(111) surface and find that the initial rate of work function decrease in both cases is the same.<sup>2</sup>

This suggests that the initial sticking probability for acetylene on O/Pd(111) is unaltered from that on the clean surface, which helps to support the scenario described above. As the oxygen exposure increases, below saturation, these islands either grow in size laterally or simply multiply, and this effectively compresses acetylene into regions of high, local coverage. This compression effect has been observed for NO/Pd(111)<sup>23</sup> and

also O/Pd(111),<sup>2</sup> though, as will be discussed in the following section, this LITD study presents the first quantitative measurement of this effect. Because benzene formation is very sensitive to the concentration of acetylene molecules,<sup>6</sup> this compression facilitates benzene formation over that of a clean surface with the same nominal acetylene exposure.

The LITD results seem to contrast the TPR studies by Ormerod et al. mentioned earlier.<sup>2</sup> In those studies, the yield of benzene increased slightly only at very low acetylene and oxygen exposures but then decreased with increasing oxygen exposure for a given exposure of acetylene. With LITD, the yield of benzene was shown to increase over a wider range of oxygen exposures, saturating above 0.25 langmuir of oxygen. Keeping in mind that LITD probes species on the surface (whereas TPD monitors what is desorbing), it is quite possible that the amount of benzene *desorbing* in TPR decreases but that the *formation on the surface* (and probed by LITD) is truly enhanced by the presence of coadsorbed oxygen.

As stated previously, no signal for furan was ever observed in LITD or TPD. This, again, is in contrast to the Ormerod study where small amounts of furan were detected. Their desorption trace had a peak centered about the thermal desorption temperature of furan, indicating that the presence of such is limited by desorption and that reaction to form furan occurs at some temperature below 300 K. With the exposures of oxygen and acetylene used in our study, however, evidence suggests there is virtually no reactive acetylene near the oxygen islands to cyclize and form furan at the appropriate temperature. At low temperatures, acetylene will initially adsorb onto either the oxygen islands or the bare Pd. Ultimately, though, it appears that most of the acetylene will migrate to clean patches on the surface and form benzene, and some of that which has settled at defect sites or edges of oxygen islands will react at low temperatures to yield CO and H<sub>2</sub>O. (Recall from the LITD survey in Figure 1b that combustion products were observed in substantial amounts as low as 110 K, indicating that reaction of acetylene and oxygen occurs almost immediately upon adsorption.) Our results indicate that, as the temperature is increased, there is no acetylene available to cyclize with oxygen near these reactive island sites and, as a result, no furan is formed.

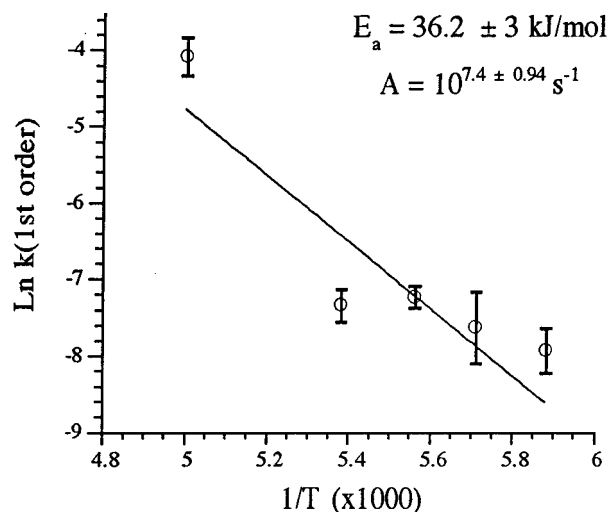
**B. LITD Kinetics.** *The Kinetics of Benzene Formation Are Altered by the Presence of Preadsorbed Oxygen.* To determine the kinetics of this reaction, the LITD/FTMS signals for benzene were measured as a function of time under isothermal conditions for several different temperatures. Using LITD/FTMS, Abdelrehim et al. previously determined that the formation of benzene from acetylene on clean Pd(111) followed pseudo-first-order kinetics.<sup>5</sup> The reaction appears to be zeroth-order in acetylene, present in excess, and pseudo-first-order with respect to the C<sub>4</sub>H<sub>4</sub> intermediate. It was then natural to assume pseudo-first-order kinetics when plotting the data for benzene formation on an oxygenated surface. For a reaction converting species X into the species Z,



product formation, assuming a pseudo-first-order process, follows

$$[Z]_t = [Z]_{\infty}(1 - e^{-kt}) \quad (\text{II})$$

where  $[Z]_t$  is the concentration of product at any time,  $t$ ,  $[Z]_{\infty}$  is the concentration of product after the reaction has gone to completion, and  $k$  is the pseudo-first-order rate constant. The



**Figure 3.** Arrhenius plot of benzene formation from acetylene on O/Pd(111) using first-order kinetics. The plot of above gives the activation energy and preexponential factor for benzene formation from a 1.1 langmuir exposure of acetylene on a Pd(111) surface precovered with a 0.25 langmuir exposure of oxygen atoms (corresponding to 50% saturation coverage) assuming first-order kinetics.

experimental data for the time evolution of the benzene signal is fit to eq II using both  $[Z]_{\infty}$  and  $k$  as adjustable parameters.

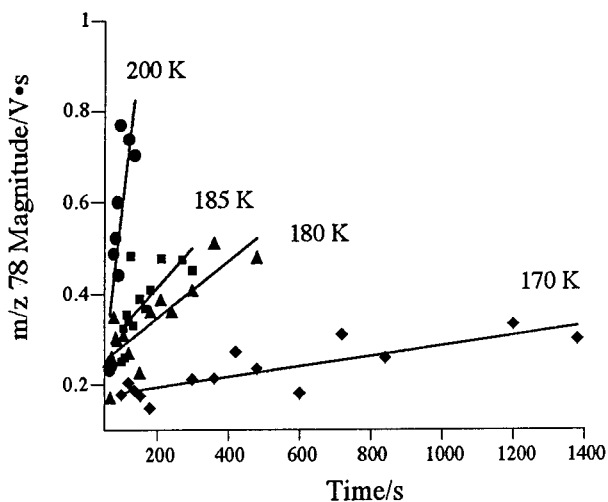
The first-order rate constants obtained with this method were used to construct an Arrhenius plot (shown in Figure 3) to determine the kinetic parameters for benzene formation. It is often not the case, however, that the mechanistic details surrounding a reaction are known, and to use a straightforward Arrhenius treatment (as above) requires that assumptions be made about the order of the reaction. However, by simply using the *initial rates* of the reaction, the activation barrier for benzene formation can still be determined without knowing the details of the mechanism. Assuming an irreversible reaction,



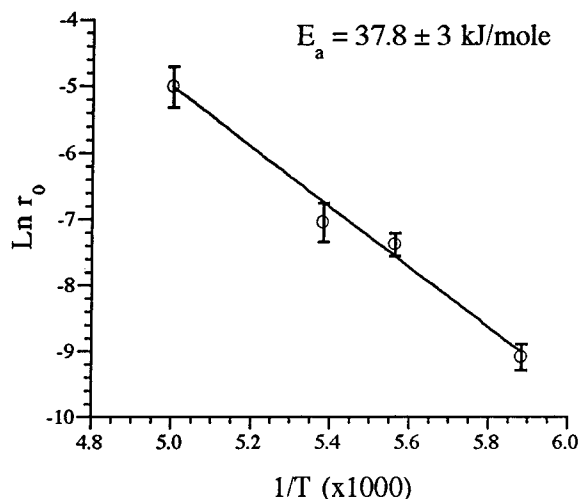
the initial rate of reaction ( $r_0$ ) equals the initial rate of formation of Z and is simply the reaction rate constant ( $k$ ) multiplied by the initial concentrations of reactants, each raised to a power appropriate for the reaction mechanism and kinetic dependence. Substituting for  $k$  and taking the logarithm gives

$$\ln(r_0) = \{\ln(\nu) + \ln([X]_0^n) + \ln([Y]_0^m)\} - E/RT \quad (\text{IV})$$

where  $[X]_0$  is the initial concentration of X, etc., and the exponents  $n$  and  $m$  may or may not be equal to the stoichiometric coefficients  $x$  and  $y$  depending on the details of the reaction mechanism,  $\nu$  is the Arrhenius preexponential factor,  $E$  is the activation barrier for the process,  $R$  is the gas constant, and  $T$  is the absolute temperature. The three terms in brackets on the right in eq IV should be essentially independent of temperature for a small temperature range. Thus, a plot of  $\ln(r_0)$  vs  $1/T$  should yield a straight line with a slope of  $-E/R$ . One can then calculate the activation energy without having to make any assumptions about the mechanism. However, the intercept can no longer be used to obtain the preexponential factor unless the details of the kinetic dependence and initial concentrations are known. One must also assume that the reaction follows van't Hoff-Arrhenius behavior and that the exponents in the rate law do not change significantly over the temperature range used.



**Figure 4.** Initial rates of benzene formation at several temperatures. The figure above plots the  $m/z$  78 signal as a function of time under isothermal conditions for different temperatures. The data were obtained using a 1.1 langmuir exposure of acetylene on a Pd(111) surface precovered with a 0.25 langmuir exposure of oxygen atoms (corresponding to 50% saturation coverage). The solid lines indicate the initial rate at which benzene formation occurs, which clearly show a temperature dependence on the rate of formation. Only data from the first 50% of the reaction at each temperature are used to estimate the initial rates.



**Figure 5.** Arrhenius plot of benzene formation from acetylene on O/Pd(111) using method of initial rates. Above is a plot of the natural log of initial rates,  $r_0$ , vs inverse temperature and gives the activation energy for benzene formation from a 1.1 langmuir exposure of acetylene on a Pd(111) surface precovered with a 0.25 langmuir exposure of oxygen atoms (corresponding to 50% saturation coverage). The data shown here were obtained using initial rates; however, the same activation energy was calculated assuming first-order kinetics (see Figure 3).

The initial rate of benzene formation at each temperature is measured by observing the benzene signal (as a function of time after heating to the reaction temperature) until the reaction ceases. The initial rate of formation is then estimated using the data from the first half of the reaction (benzene signals less than 50% of the final benzene signal) and applying a straight-line fit, as shown in Figure 4. Figure 5 shows a plot of the natural log of the initial rates vs inverse temperature and a weighted linear least-squares fit to these data. From a 1.1 langmuir exposure of acetylene after 0.25 langmuir exposure of  $O_2$  (yielding 0.12 ML of O atoms, i.e., 50% of saturation) on Pd(111), this treatment yields an  $E_a$  of  $37.8 \pm 3$  kJ/mol (95%

confidence) for benzene formation. This value is in excellent agreement with the  $E_a$  of  $36.2 \pm 3$  kJ/mol determined using the first-order treatment described above. Also from the first-order plot, a value of  $10^{7.4 \pm 0.94} \text{ s}^{-1}$  for the preexponential factor,  $\nu$ , was obtained and will be used in comparison in the next section with  $\nu$  obtained from benzene formation on clean Pd(111).

*A Comparison between Kinetics on Clean and Oxygenated Pd(111).* It was shown previously that the preadsorption of oxygen enhances the formation of benzene from acetylene on Pd(111). Recall that, in Figure 2, the yield of benzene increased with increasing oxygen exposure for the same exposure of acetylene (1.2 langmuirs), reaching a saturation point beyond 0.25 langmuir of oxygen. In fact, relative to the clean surface, the maximum benzene signal increased by a factor slightly greater than 2 with an oxygen preexposure of 0.25 langmuir (the same exposure conditions used in these kinetic experiments). It was also noted that the onset of benzene formation shifted to lower temperatures with increasing oxygen exposure. On the basis of these results, one might first assume that the presence of oxygen lowers the activation barrier leading to benzene formation, thus facilitating the reaction and enhancing the yield. Compared to the same acetylene exposure on a clean surface, however, the activation energy for benzene formation is actually greater on O/Pd(111) by a factor of 1.5 (for the clean surface,  $E_a = 24.4 \pm 3.9$  kJ/mol and  $\nu = 10^{3.1 \pm 0.1} \text{ s}^{-1}$ ).<sup>6</sup> By considering  $E_a$  only, the increase in barrier height seemingly contradicts the notion that benzene formation is promoted by the presence of oxygen. However, the increase in  $E_a$  is compensated by concomitant and substantial increase (4 orders of magnitude) in the preexponential factor, corresponding to a gain in entropy for the transition state; thus, transmission to products becomes more favorable.

Oxygen is a highly electronegative adatom and is expected to induce changes in the electronic structure of Pd upon adsorption. It is unlikely, though, that these changes are responsible for the increase in activation energy observed for benzene formation on O/Pd(111). First, consider the interaction of acetylene with Pd in the absence of preadsorbed oxygen atoms. It has been shown that exposure to acetylene decreases the Pd(111) work function.<sup>2</sup> This decrease is the consequence of a net electron transfer from acetylene to Pd and is consistent with an increase in Fermi energy. The  $E_a$  for benzene formation increases with increasing acetylene coverage, and it has been argued that this is likely due to an increased degree of back-bonding and a stronger C–Pd interaction with increasing Fermi energy.<sup>6</sup> Preadsorption of oxygen, however, results in net electron transfer from the metal to the oxygen atoms and consequently decreases the surface Fermi energy (for any given acetylene exposure, the work function for O/Pd(111) lies higher in energy relative to the same coverage of acetylene on a clean surface).<sup>2</sup> A decrease in Fermi energy effectively reduces the back-bonding interaction between Pd and acetylene, and thus, the  $E_a$  would be expected to decrease on a surface precovered with oxygen. This is contrary to our observations.

As mentioned earlier, oxygen atoms tend to form islands on Pd(111) at coverages below saturation. Our results suggest that these oxygen islands effectively compress the acetylene molecules into regions of high, local coverage and that this compression facilitates benzene formation over that of a clean surface. Acetylene coverage dependence on benzene formation kinetics has been studied extensively using LITD/FTMS, the findings from which have made a significant impact on our understanding of acetylene cyclization on Pd(111).<sup>5,6</sup> The

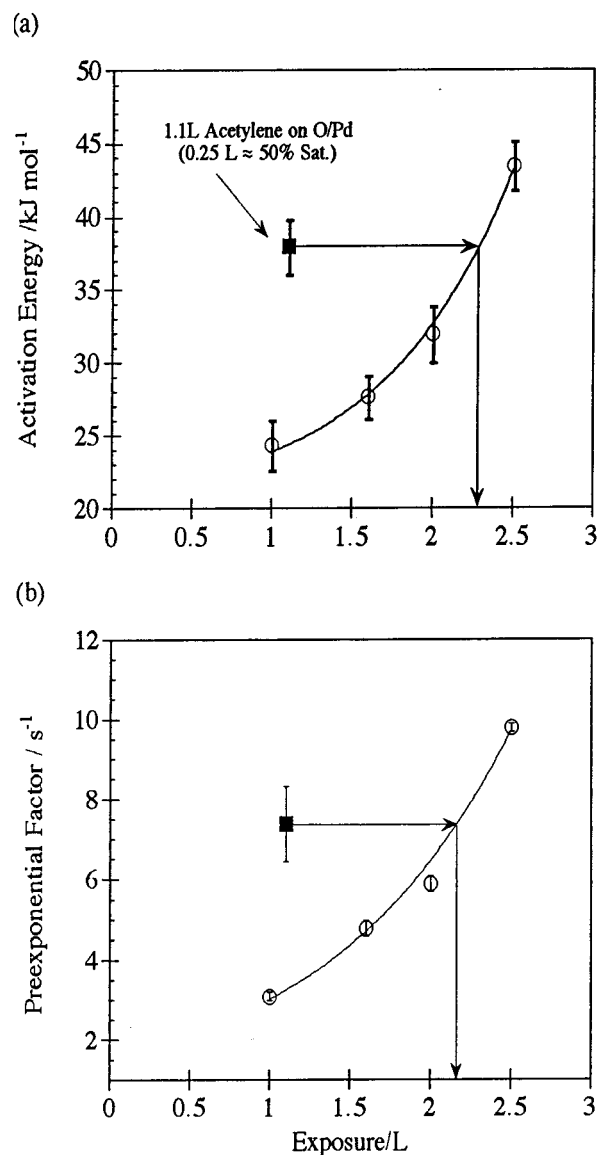
results from these studies provide a basis for comparison with results from the kinetics on O/Pd(111) and offer, as well, an explanation for the observed increase in kinetic parameters. A summary of the relevant conclusions (as they pertain to the results of this study), drawn from refs 5 and 6, will be provided in the next paragraph.

The coverage dependence of the activation energy and preexponential factor for acetylene cyclotrimerization on clean Pd(111) was obtained from isothermal rate studies using LITD/FTMS. Increasing the initial acetylene exposure from 1.0 to 2.5 langmuirs caused an increase in the rate of benzene formation by a factor of 10–50 and an increase in the relative yield of benzene by a factor of 4. The activation barriers for benzene formation increase from  $24.4 \pm 3.9$  kJ/mol (95% confidence) for 1.0 langmuir exposure of acetylene to  $43.5 \pm 3.9$  kJ/mol for the 2.5 langmuir exposure. The preexponential factors, assuming pseudo-first-order kinetics, increase from  $10^{3.1 \pm 0.1} \text{ s}^{-1}$  for the 1.0 langmuir exposure to  $10^{9.8 \pm 0.1} \text{ s}^{-1}$  for the 2.5 langmuir exposure. Since the activation barrier and preexponential factors both increase substantially with increasing acetylene exposure, effects due to crowding or changes in diffusion kinetics cannot account for the change in reaction kinetics observed. The increase in activation energy is most likely due to an increased barrier to C–Pd bond stretching or breaking to form a transition complex with the correct geometry for benzene formation. The corresponding change in preexponential factor with respect to the activation energy has previously been described in terms of the *compensation effect*,<sup>24,25</sup> where a more tightly bound reactant can lead to a greater entropy of activation. An increased barrier to C–Pd bond breaking, due to stronger bonding at higher coverages, is also consistent with the calculated electronic structure of acetylene adsorbed on Pt(111).<sup>26,27</sup>

It appears that the effect of preadsorbing oxygen, below saturation coverage, mimics the behavior observed in the acetylene coverage-dependent study. Figure 6 is a comparison of kinetic parameters for acetylene on clean vs oxygen-covered Pd(111). The data points (hollow circles) within the curved line represent the (a)  $E_a$  and (b)  $\nu$  obtained for different exposures of acetylene on clean Pd(111) (the curves are exponentials with an arbitrary offset at zero coverage used to guide the eye and not intended to imply the true functional dependence).<sup>6</sup> In both (a) and (b), solid squares represent the values obtained on the oxygenated surface. The oxygen values are clearly higher than those for the same exposure of acetylene on a clean surface. More importantly, both  $E_a$  and  $\nu$  from a 50% saturation coverage of oxygen on Pd (from 0.25 langmuir exposure of  $\text{O}_2$ ) correspond to the values expected for twice the acetylene exposure on a clean surface (indicated by arrows). This strongly suggests that oxygen is indeed behaving in such a way to force acetylene into regions of local, high coverage. The fact that both parameters, activation energy and preexponential factor, agree with the same higher exposure data provides further evidence of the compensation effect. The principles governing the compensation effect are directly responsible for the increased yields of benzene despite the rise in activation energy. Although the barrier to benzene formation increases on O/Pd(111), transmission to products is still favored by the resulting gain in preexponential factor.

## Conclusions

Low exposure of acetylene on O/Pd(111) leads to the anticipated formation of benzene and 1,3-butadiene. Oxidation products, such as CO and  $\text{H}_2\text{O}$ , were also observed. Even with



**Figure 6.** Comparison of clean vs oxygen-covered Pd(111) for the formation of benzene from acetylene. The plots above compare the (a) activation energy and (b) preexponential factor for benzene formation from acetylene on an oxygenated Pd(111) surface to that on a clean surface. The data points within the curve (hollow circles) represent the values obtained for the corresponding exposures of acetylene on clean Pd(111). In both (a) and (b), the values obtained on the oxygenated surface are higher than for the same exposure of acetylene on a clean surface. The data suggest that the oxygen compresses acetylene into areas of effectively higher, local concentrations.

the high sensitivity of LITD/FTMS we were unable to detect any signal for furan. This is in contrast to what was observed in the case of acetylene on S/Pd(111) where, in addition to benzene, acetylene also cyclizes with surface-bound sulfur atoms to form thiophene. For the same exposure of acetylene, the yields of both benzene and CO increase with increasing preexposure to oxygen, saturating above 0.25 langmuir. Our experimental evidence suggests that the yield enhancement is due to compression of acetylene by preadsorbed oxygen. Saturation of CO at such low oxygen exposures indicates that the formation of CO is limited by the amount of carbon on the surface. The kinetics of benzene formation on O/Pd(111) provide yet another striking contrast to the chemistry observed on S/Pd(111).<sup>13</sup> The presence of S does not significantly alter the kinetics of benzene formation. On O/Pd(111), however,

the effect of this coadsorbate is quite profound. Isothermal kinetic studies of 1.1 langmuirs of acetylene on a 50% saturated layer of O on Pd(111) (from a 0.25 langmuir exposure of O<sub>2</sub> at 250 K) yield an  $E_a$  of  $37.8 \pm 3$  kJ/mol using initial rates. This  $E_a$  value is almost a factor of 2 higher than the  $E_a$  for the same acetylene exposure on clean Pd(111). Assuming first-order kinetics yields essentially the same activation energy as the initial rate treatment, in addition to providing a preexponential factor for comparison with that from the clean Pd kinetics. Both  $E_a$  and  $\nu$  from a 50% saturation coverage of oxygen on Pd correspond to the values expected for twice the acetylene exposure on a clean surface. The kinetics of the O/Pd system mimic the trend observed in the acetylene coverage-dependent study by Abdelrehim et al., which further supports the argument of acetylene compression by oxygen. The apparent contradiction between increased benzene yields and activation barrier for the O/Pd system can be rationalized by the compensation effect, where a more tightly bound reactant can lead to a greater entropy of activation.

LITD/FTMS studies of this system are ongoing. We anticipate learning more about the effects of acetylene and preadsorbed oxygen from similar coverage-dependent investigations as were carried out on the clean Pd(111) surface. Preliminary survey results of benzene formation from increasing acetylene exposures on O/Pd(111) indicated that the yield actually decreased for exposures of 1–3 langmuirs with 50% saturation coverage of oxygen. If accurate, these results suggest that the reaction is self-poisoned by the effectively high, local concentrations of acetylene induced by the preadsorption of oxygen. Needless to say, a more thorough investigation is currently underway. In the interest of possibly probing reaction intermediates, future studies will also incorporate both Fourier transform reflection/absorption infrared spectroscopy (FT-RAIRS) and scanning tunneling microscopy (STM) to isolate intermediate species too tightly bound to be removed from the surface intact.

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## References and Notes

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