Conversion of Acetylene to Benzene over Palladium Single-Crystal Surfaces. 1. The Low-Pressure Stoichiometric and the High-Pressure Catalytic Reactions

T. G. Rucker, M. A. Logan,[†] T. M. Gentle,[‡] E. L. Muetterties,[§] and G. A. Somorjai*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, Berkeley, California 94720 (Received: October 11, 1985)

Acetylene cyclotrimerizes to form benzene on palladium single crystals in ultrahigh vacuum (UHV) $(10^{-12}-10^{-8} \text{ atm})$ and at atmospheric pressures (10^{-1} -1 atm). The reaction is structure sensitive in both pressure regimes. In UHV the (111) face is the most active followed by the (110) and then the (100) surfaces. At high pressure the (111) and (100) surfaces have equal catalytic activity whereas the (110) face is one-fourth as active. In UHV the reaction products are benzene from cyclotrimerization, ethylene from hydrogenation, and hydrogen from decomposition. At high pressures only benzene was detected. The high-pressure catalytic reaction proceeds on the bare metal surface. The reaction also proceeds readily on Pd films and Pd supported on alumina.

1.0. Introduction

The rapid developments in ultrahigh vacuum (UHV) surface chemistry and high-pressure catalytic studies, both using singlecrystal surfaces, have led to a growing interest in comparing low-pressure and high-pressure reactions. Low-pressure reactions are mostly stoichiometric with one product molecule formed per metal atom. High-pressure reactions have many product molecules formed per metal atom and are thereby catalytic. Correlating the behavior of the same molecules in both stoichiometric and catalytic reaction conditions is important in predicting and modeling high-pressure reactions. Only a few reactions proceed readily in both of these conditions. An example of one reaction which occurs in both pressure regimes is the trimerization of acetylene on palladium.

The conversion of acetylene to benzene is a reaction which proceeds readily at pressures ranging from UHV $(10^{-12}-10^{-8} \text{ atm})$ to atmospheric pressures $(10^{-1}-1 \text{ atm})$ on palladium surfaces. This reaction provides a unique opportunity to investigate a synthetic reaction over 13 orders of magnitude of pressure. We found that the reaction also proceeds on a variety of palladium surfaces: single crystals, evaporated films, and small particles supported on alumina.

The cyclization of acetylene to benzene was first reported to occur in small yields by Berthelot¹ in 1866 at elevated temperatures (300-400 °C) in a glass vial. In the 1940's Reppe² discovered that certain homogeneous nickel complexes produced benzene from acetylene in good yield under mild experimental conditions. Since that discovery, other research groups have found numerous homogeneous transition-metal systems that catalyze unsubstituted and functionalized acetylenes to form benzene and benzene derivatives.^{3,4} For example, cobalt complexes such as $CpCo(CO)_2$ are used in cyclization steps in the synthesis of natural products such as steroids and vitamin B_6 .⁵ It has also been shown that palladium chloride will easily oligomerize acetylene.^{6,7}

It has been reported that, in solution, palladium on charcoal will trimerize acetylene in high yields.⁸ Also, it has been demonstrated that nickel supported on silica at 300 °C is a suitable Recently, cyclotrimerization of catalyst for this reaction.⁹ acetylene has been found on nickel⁹ and copper single crystals.¹⁰

Numerous research groups have extensively studied the reactivity and structure of acetylene on palladium and other tran-sition-metal surfaces.¹¹⁻²³ In the original UHV trimerization studies on Pd(111) by Tysoe et al.^{17,18} benzene formation was found by temperature-programmed desorption (TPD), angle-resolved photoemission spectroscopy (ARUPS), and molecular beam measurements. They concluded that the major surface species was a flat-lying acetylenic species at low temperature (<220 K),

while at higher temperatures an olefinic species predominated. They also proposed that the low-temperature acetylenic species is the precursor in the trimerization reaction, and that the two benzene desorption maxima in the TPD spectra are due to tilted and flat benzene molecules desorbing from the surface. Subsequent work by Sesselman et al.¹⁹ using UPS and metastable deexcitation spectroscopy (MDS) support the low-temperature formation of a π -di- σ -bonded species and the high-temperature formation of a different species (β -state). Here again, the lowtemperature species is the intermediate in the cyclotrimerization reaction. Electron energy loss spectroscopy (EELS) studies of C_2H_2 adsorption on Pd(111) by Kesmodel et al.²⁰⁻²² show formation of C-CH₃ species coadsorbed with CCH fragments. At higher temperatures (450 K) CCH becomes the dominant species. This group found no evidence for the trimerization reaction. This is in contrast to a recent EELS study by Marchon²³ where vibrational modes due to adsorbed benzene were observed at high C_2H_2 coverages.

This paper reports on the pressure dependence on the cyclotrimerization of acetylene to benzene on palladium surfaces in UHV conditions and at atmospheric pressures. In both pressure regions we assess the influence of surface topography and composition on the metal's catalytic activity.²⁴ The reaction is

- (2) Reppe, W.; Schlichting, O.; Klager, K.; Toepal, T. Justus Liebigs Ann. Chem. 1948, 560, 1.
 - (3) Parshall, G. W. Homogeneous Catalysis; Wiley: New York, 1980.
 - (4) Vollhardt, K. P. C. Angew. Chem., Int. Ed. Engl. 1984, 23, 539.
 (5) Vollhardt, K. P. C. Acc. Chem. Res. 1977, 10, 1.

 - (6) Maitlis, P. M. Acc. Chem. Res. 1976, 9, 93.
 - (7) Blomquist, A. T.; Maitlis, P. M. J. Am. Chem. Soc. 1962, 84, 2329.
 - (8) Bryce-Smith, D. Chem. Ind. (London) 1964, 239.
- (9) Bertolini, J. C.; Massardier, J.; Dalmai-Imelik, G. J. Chem. Soc., Faraday Trans. 1 1978, 74.
- (10) Avery, N. J. Am. Chem. Soc. 1985, 107, 6711.
- (11) (a) Gentle, T. M.; Muetterties, E. L. J. Phys. Chem. 1983, 87, 2469. (b) Gentle, T. M.; Muetterties, E. L. J. Am. Chem. Soc. 1983, 105, 304.
- (12) Somorjai, G. A. Chemistry in Two Dimensions: Surfaces; Cornell
- University Press: Ithaca, NY, 1981; and references therein. (13) Stroscio, J. A.; Bare, S. R.; Ho, W. Surf. Sci. 1984, 148, 499.
- (14) Muetterties, E. L.; Tsai, M.-C.; Keleman, S. R. Proc. Natl. Acad. Sci. U.S.A. 1981, 78, 6571.
 - (15) Gates, J. A.; Kesmodel, L. L. J. Chem. Phys. 1982, 76, 4281.
- (16) Bandy, B. J.; Chesters, M. A.; Pemble, M. E.; McDougall, G. S.;
 Sheppard, N. Surf. Sci. 1983, 139, 623.
 (17) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. J. Chem. Soc., Chem.
- Commun. 1983, 623.
- (18) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. Surf. Sci. 1983, 135, 128.
- (19) Sesselman, W.; Woratschek, B.; Ertl. G.; Kupers, J.; Haberland, H. Surf. Sci. 1983, 130, 245.
 (20) Kesmodel, L. L.; Waddill, G. D.; Gates, J. A. Surf. Sci. 1984, 138,
- 464.
- . (21) Gates, J. A.; Kesmodel, L. L. J. Chem. Phys. 1982, 76, 4281. (22) Gates, J. A.; Kesmodel, L. L. Surf. Sci. 1983, 124, 68.
- (23) Marchon, B. Surf. Sci. 1985, 162, 382.

[†]Present address: J. C. Schumacher Co., P.O. Box 1159, Oceanside, CA 92054.

¹Present address: Dow Corning Corp., Midland, MI 48640. [§]Deceased January 1984.

⁽¹⁾ Berthelot, M. Ann. Chem. 1867, 141, 173.

structure sensitive in both UHV and atmospheric pressure regimes. In UHV the (111) surface is the most active followed by the (110) and (100) surfaces, while at higher pressure the (111) and (100) are surfaces equal in activity followed by the (110). In both pressure regions the reaction most likely proceeds on the bare metal surface.

2.0. Experimental Section

The experiments with single crystals of palladium were performed in two separate UHV chambers described in detail elsewhere.^{25,26} One chamber was ion pumped and had a base pressure of 1×10^{-10} Torr. It was equipped with a four-grid retarding field electron energy analyzer (RFA) for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), and a quadrupole mass spectrometer and programmable peak selector for TPD. The crystal was spot-welded to a tantalum foil which masked the edges and was mounted on a high-precision manipulator. The crystal was heated by electron bombardment and cooled with a liquid nitrogen reservoir in direct contact with the crystal. In this configuration the crystal could be heated to 1000 K and then cooled to 130 K in 2.5 min. The crystal temperature was monitored by a chromel/alumel thermocouple spot-welded to the crystal. Two variable rate leak valves were employed for controlled dosing of the sample surface with the reactant gases.

TPD experiments comprised cleaning the surface with Ar^+ bombardment (5 × 10⁻⁵ Torr of Ar, 20 mA) and O₂ treatment at 850 K (5 × 10⁻⁷ Torr) followed by annealing at 950 K until the surface was free from contaminants such as carbon, sulfur, and silicon as monitored by AES. The crystal was then cooled, flashed to desorb any background gases, rapidly cooled, and dosed with the desired amount of reactant gases. While linearly heating at 25K/s the desorbing gases were monitored by the mass spectrometer.

The high-pressure (HP) experiments on single crystals were performed in a combined high-pressure/UHV chamber which was pumped with a liquid-nitrogen-trapped oil diffusion pump and had a base pressure of 1×10^{-9} Torr. This chamber, in addition to the standard UHV surface science equipment such as a mass spectrometer, double-pass cylindrical mirror analyzer for AES, LEED optics, and Ar⁺ sputter gun, was equipped with a highpressure cell which, when raised, enclosed the crystal in a continuous flow batch reactor. The gas mixture in this loop was periodically sampled with a gas chromatograph (GC) with a 3-ft Poropak N column equipped with a flame ionization detector. The gases were circulated with a magnetically driven micropump. In this chamber, the single crystal was spot-welded to a rotatable manipulator by tantalum support rods. The crystal was resistively heated and the temperature monitored by a chromel/alumel thermocouple. The typical sequence for performing the highpressure reaction was as follows: after cleaning the surface as described above, the cell was raised. Acetylene was added to the loop until the desired pressure was reached and then N_2 (an inert carrier gas) was added to bring the total pressure to 20 psi. After the reaction, the loop was evacuated to a pressure of 1×10^{-3} Torr. After lowering the cell, UHV surface science techniques were used to analyze the surface. The initial rate of reaction was calculated from the slope of the product accumulation vs. time plot.

Blank experiments (without a Pd crystal) showed no activity, as did the experiments performed on Pd covered by graphitic carbon (obtained by heating the crystal in a hydrocarbon atmosphere at 800 K).

The supported catalyst studies were performed in a 2 cm diameter by 5 cm long stainless steel cylinder charged with 5 g of catalyst. This noncirculating batch reactor has a gas inlet, pressurizing hydraulic piston, and an evacuating mechanical pump at one end, and a two column gas chromatograph equipped with a flame ionization detector at the other. The temperature was

controlled by a ceramic block heater and monitored with a chromel/alumel thermocouple. The temperature was allowed to stabilize for 30 min prior to adding the acetylene. The Pd/Al_2O_3 was cleaned by flowing O₂ (420 K, 1 h), followed by hydrogen (450 K, 1 h) over the catalyst, and then heating in vacuo (480 K, 1 h). After adding the purified acetylene, the reaction mixture was periodically sampled and analyzed with the GC. The fourth system used in this series of experiments on the cyclotrimerization of acetylene was a film reactor. This system consisted of a glass bell jar with an area of 36 cm², and a volume of 1.2 L mounted on a liquid-nitrogen-trapped oil diffusion pump. The system also had an ionization gauge and a TC gauge to monitor the pressure in the operating regions. A visible layer of palladium was deposited onto the walls of the bell jar by resistively heating a piece of Pd foil (99.9% pure). After purified acetylene was added to bring the pressure to 250 mtorr, the reaction mixture was periodically sampled by a GC. All the reactions were performed at room temperature. After each reaction the bell jar was again coated with twice the original amount of Pd (as measured by time) to cover the carbonaceous deposit from the previous reaction. After two reactions, the bell jar was cleaned in aqua regia, followed by an ethanol rinse and drying. Blank experiments showed no activity of the uncoated surface.

Acetylene(Matheson) was passed through a 195 K acetone/dry ice bath prior to use in order to remove the acetone stabilizer and then vacuum distilled into a glass bulb. Benzene was dried over calcium hydride. Spectroscopic grade ethylene was used without further purification. The palladium single crystals were spark erosion cut from single-crystal rods (Metals Research Ltd.) to within $\pm 1^{\circ}$ of the desired orientation and prepared by standard metallographic techniques, which produced optically flat and ordered surfaces. Palladium supported on alumina (5%) was obtained from Aldrich (lot no. CK0220 KE).

3.0. Results

We have investigated the conversion of acetylene to benzene over a 13 orders of magnitude pressure range $(1 \times 10^{-12}-1 \text{ atm})$ using palladium catalysts (single crystals, films, and alumina supported). The experiments are divided into two classes:

(1) At low pressures $(1 \times 10^{-12} - 1 \times 10^{-8} \text{ atm})$ the reaction is stoichiometric and the formation of benzene is monitored by temperature-programmed desorption of molecular benzene after dosing with acetylene at 130 K.

(2) At high pressures $(1 \times 10^{-1}-1 \text{ atm})$ the reaction is catalytic and benzene formation is monitored by gas chromatography.

3.1. Low-Pressure, Stoichiometric Reaction Studies over Palladium Single-Crystal Surfaces. Following the adsorption of acetylene on the Pd single-crystals acetylene, ethylene, benzene, and hydrogen were detected as desorption products. For a better understanding of the reaction ethylene, benzene, and hydrogen were adsorbed separately on the clean Pd crystals. Table I lists the adsorbate molecules, the desorption products and temperatures, relative amounts, and the activation energies of desorption for the (111), (100), and (110) palladium single-crystal surfaces.

3.1.1. Pd(111). On the Pd(111) face, dosing 6 langmuirs of acetylene produced benzene with two distinct desorption peaks at 250 and 490 K. The low-temperature peak was 2.5 times larger than the high-temperature peak (Figure 1). Acetylene, ethylene, and hydrogen were also detected as desorption products. Acetylene and ethylene desorbed at 190 and 310 K, respectively. Hydrogen, the only other product detected, had a broad desorption peak from 430 to 830 K, with a maximum at 450 K (Table I). At low acetylene coverages (0.5 langmuir) the temperatures of the benzene desorption maxima remained unchanged. The amount of benzene formed decreased, with the area under the high-temperature peak decreasing more rapidly than the area under the low-temperature peak. No C₄ products were detected.

To determine whether the products formed before or during desorption we allowed C_6H_6 , C_2H_4 , and H_2 to adsorbed separately on clean Pd(111) at 130 K, and TPD spectra of each were taken as a function of coverage. Benzene undergoes reversible and irreverible chemisorption, with the fraction of reversibly bound

⁽²⁴⁾ Logan, M. A.; Rucker, T. G.; Gentle, T. M.; Muetterties, E. L.; Somorjai, G. A., J. Phys. Chem., following article in this issue.

⁽²⁵⁾ Friend, C. M.; Muetterties, E. L. J. Am. Chem. Soc. 1981, 103, 773.
(26) Cabrera, A. L.; Spencer, N. D.; Kozak, E.; Davies, P. W.; Somorjai, G. A. Rev. Sci. Instrum. 1982, 53, 1893.

TABLE I: Desorption Products from Acetylene, Ethylene, and Benzene over Pd(111), Pd(100), and Pd(110) Single Crystals in UHV

crystal face	dose molecule	desorption product	desorption temp, K	E_{α} , kcal/mol	rel areas ^b	
(111)	C ₂ H ₂	H ₂	450 (430-830)	26.3	2.0	
· · ·		$\overline{C_2H_2}$	190	10.8	1.0	
		C_2H_4	350	20.3	0.4	
		C ₆ H ₆	250, 490	14.3, 28.7	1.7	
	C_2H_4	C_2H_4	300	17.3		
	C ₆ H ₆	H ₂	545 (520-720)	32.0		
		C ₆ H ₆	260, 520	14.9, 30.5		
(100)	C_2H_2	H ₂	420 (495-625 sh)	24.5	1.3	
		C_2H_2	180 (250 sh)	10.2	1.0	
		C_2H_4	305	17.6	.2	
		C_6H_6	260, 380, 470	14.9, 22.1, 27.5	.1	
	C_2H_4	C_2H_4	260, 310	14.9, 17.9		
	C ₆ H ₆	H ₂	575 (655 sh)	33.8 (39.3)		
		C ₆ H ₆	220, 375, 525	12.5, 21.8, 30.8		
(110)	C_2H_2	H ₂	490	28.7	0.7	
		C_2H_2	180 (to 500 sh)	10.2 (29.3 sh)	1.0	
		C_2H_4	260	14.9	0.2	
		C_6H_6	250, 420	14.3, 24.5	0.1	
	C_2H_4	C_2H_4	260	14.9		
	C ₆ H ₆	H_2	475, 535	27.8, 31.4		
		C ₆ H ₆	250 (to 425 sh)	14.3 (to 24.8)		

^aRelative areas are determined by integrating peak are and normalizing to acetylene. Corrected for mass spectrometer sensitivity. ^b For C_2H_2 adsorption.



Temperature (K)

Figure 1. Presented in this figure are the thermal desorption spectra for 6 langmuirs of acetylene dosed at 130 K on Pd(111). The heating rate was 25 K/s. Benzene from cyclotrimerization, ethylene from hydrogenation, and hydrogen from decomposition were detected.

benzene increasing with exposure. At low coverages (1.0 langmuir) there was primarily decomposition as characterized by a broad hydrogen trace extending from 520 to 720 K with a maximum at 545 K. Benzene had two weak desorption peaks at 260 and 520 K. With exposures greater than 2 langmuirs the hydrogen spectrum remained unchanged and the benzene maxima occurred at 235 and 510 K with a 1:10 intensity ratio. Acetylene and ethylene were not observed as desorption products. Dosing hydrogen on the clean surface yielded a single desorption peak of H₂ at 310 K. The peak does not shift with increasing hydrogen exposure. With ethylene (1.0 langmuir), reversible desorption occurred at 300 K with hydrogen desorbing at 370 and 430 K in a 1:1 ratio. Higher coverages of ethylene (>2 langmuirs) increased molecular desorption of ethylene exposure.

3.1.2. Pd(100). On the Pd(100) surface, following an exposure of 6 langmuirs of acetylene a broad, continuous benzene desorption peak was observed from 250 to 490 K with three maxima at 260, 380, and 470 K (Figure 2). At exposures below 3 langmuirs no benzene was detected. This surface formed one-twentieth as much benzene as the (111) crystal face. With a 6-langmuir dose of acetylene, in addition to cyclotrimerization, reversible desorption, hydrogenation, and decomposition were also observed. Acetylene desorbed at 180 K with a shoulder at 250 K, and ethylene desorbed



Temperature (K)

Figure 2. The desorption products for 6 langmuirs of acetylene dosed on the Pd(100) surface are presented. The heating rate was 25 K/s. Benzene, ethylene, hydrogen, and acetylene were the only molecules desorbing from the surface.

in a single peak at 305 K. The hydrogen desorption from the decomposition reached a maximum at 420 K, followed by a broad plateau from 495 to 625 K. At low coverages of acetylene (1.0 langmuir) there was primarily decomposition. No C₄ fragments were detected. Benzene dosed on the crystal at low coverages (1.0 langmuir) yielded a weak maximum at 310 K, with a tail extending to 535 K. At an exposure of 6.0 langmuirs, three poorly resolved benzene maxima at 220, 375, and 525 K were observed, along with a hydrogen peak at 575 K which had a high-temperature shoulder at 665 K. When hydrogen alone was dosed on the surface, at all coverages it desorbed at 310 K in one peak. Ethylene (0.5 langmuir) gave molecular desorption at 260 and 310 K in a 1:5 ratio with hydogen desorbing at 365 K. Larger ethylene doses increased the low-temperature reversible desorption peak without affecting the hydrogen desorption. No benzene was detected from ethylene.

3.1.3. Pd(110). The Pd(110) surface produced one-sixth the amount of benzene as the (111) face and three times more benzene than the (100) face. On the (110) face, benzene desorbed at 250 and 420 K in a 1:3 ratio after a 6-langmuir dose of acetylene (Figure 3). With acetylene coverages below 3 langmuirs, no benzene was detected. Molecular desorption of acetylene occurred at 180 K with a broad shoulder plateau extending to 500 K. Ethylene desorbed at 260 K, and hydrogen in a broad peak centered at 490 K. When the surface was dosed with 6 langmuirs of benzene, molecular desorption occurred at 250 K, with a shoulder extending to 425 K. At low coverages (1.0 langmuir)





Temperature (K)

Figure 3. This figure presents the products and desorption temperatures from the stoichiometric reaction of 6 langmuirs of acetylene dosed on the Pd(110) surface at 130 K. The heating rate was 25 K/s. Benzene has two desorption maxima at 265 and at 425 K. Ethylene desorbs at 265 K and reversible molecular desorption of acetylene occurs at 175 K. Hydrogen has a single maxima at 495 K. No other products were detected.



Figure 4. The relative amount of benzene formed on single crystals in UHV and at atmospheric pressures is shown here. In UHV the (111) face is the most active followed by the (110) and then the (100). At higher pressures (1 atm,) the (111) and the (100) faces show equal activity and the (100) is one-fourth as active.

a single peak at 260 K was observed. The hydrogen from decomposed benzene had maxima at 475 and 535 K which increased in area with increasing amounts of benzene up to 3 langmuirs, after which they remained constant. Hydrogen desorbed at 310 K at low coverages when adsorbed on the clean surface, and the desorption temperature decreased with increasing coverage.

3.1.4. Summary of Low-Pressure Cyclotrimerization Studies. Benzene forms from adsorbed acetylene on all three low Miller index planes of palladium. The cyclotrimerization of acetylene was most facile on clean Pd(111) followed by the (110) face which was 18% that of the (111) surface and then the (100) surface, which formed 5% as much as the (111) face (Figure 4). On the (111) surface, benzene formed at exposures above 0.5 langmuir. On the other surfaces, only after exposures greater than 3 langmuirs of acetylene did benzene become observable. Ethylene and hydrogen desorption were detected on all surfaces at all coverages and no C₄ products were seen.

3.2. High-Pressure Catalytic Reaction Studies on Palladium Single-Crystal-Crystal Surfaces. We have extensively studied the cyclotrimerization of acetylene on three low Miller index planes of palladium ((111), (110), and (100)) at high pressures (200 to 1200 Torr) in the temperature range of 273-573 K. For all the temperature and pressure conditions used in this study, benzene was the only product detected. Due to the large acetylene peak in the GC trace, ethylene could not be detected below 5 mol % relative to acetylene. As observed in UHV conditions, the reaction



Figure 5. The activation energy for the catalytic reaction of 2 kcal mol⁻¹ is determined by calculating the slope of the log turnover frequency plotted vs. 1/T. This value is obtained on all three low Miller index planes of palladium.



Figure 6. Plotting the turnover frequency as a function of acetylene pressure shows that the cyclotrimerization reaction is first order in acetylene on all three surfaces. The (111) face is more active than the (110) face.

showed structure sensitivity for the formation of benzene (Figure 4). It was found that the (111) and the (100) surfaces were approximately equal in catalytic activity and the (110) surface was one-fourth as active. The (111) and (100) surfaces had a turnover frequency (TF.) of 0.048 molecule site⁻¹ s⁻¹ and the (110) face had a TF of 0.014 molecule site⁻¹ s⁻¹ (200 Torr of acetylene, 850 Torr of N₂ or Ar at 575 K). The turnover frequency is defined as the number of molecules formed per metal atom per second assuming 1.5×10^{15} metal atoms cm⁻² on the single-crystal surface. Turnover frequency was constant for over 10 h of reaction time, and the rates shown in Figures 4-6 were obtained within the first 3 h. No correction was made for the different number of surface atoms on the various faces. On the more active surfaces the reaction had up to 50% conversion of acetylene to benzene or roughly a 20 mol % yield of benzene. At these conversion percentages, the reaction was limited by either surface poisoning or by product concentration. The slope of the turnover frequency plotted vs. 1/T, assuming Arrhenius kinetics, yields the apparent activation energy of the reaction, calculated as 2 kcal mol⁻¹ on all three surfaces (Figure 5). Plotting the reaction rate as a function of acetylene pressure showed that the reaction was first order in acetylene with the rate law (Figure 6)

rate = $kP_{C_2H_2}$

Analysis by AES and CO titration after the reaction found a partially carbon-covered surface. After the crystal was heated to 650 K and exposed to 1×10^{-6} Torr of hydrogen, the surface remained carbon covered, implying a stable graphitic overlayer.



Time (minutes)

Figure 7. On palladium films coated on glass, benzene forms from acetylene at room temperature with 250 mTorr of acetylene ($\sim 10-20$ monolayers). Other products detected were ethylene and ethane which are formed with hydrogen from decomposed acetylene. Relative product distribution is measured by GC counts and corrected for GC sensitivity.

CO titration determines the percentage of bare metal sites since CO does not adsorb on carbon overlayers at low pressure. After the trimerization reaction (200 Torr of acetylene, 850 Torr of N_2 , 300 K 3-h reaction time), it was estimated that only 5–7% of the Pd(111) surface was composed of bare metal sites, while the same conditions yielded 12–15% bare sites on Pd(100) and less than 2% on the (110) face, the least active surface.

From TPD studies it was determined that CO binds more strongly to the partially carbon-covered metal than C_2H_2 does. In order to determine if the reaction proceeded on the bare metal or a carbonaceous overlayer, we added 0.2 Torr of CO into the circulating gases of a reaction at room temperature 3 h after the start of the reaction. The reaction was immediately quenched and the rate of benzene formation was zero. Subsequent heating of the crystal to 485 K, which is above the desorption temperature of CO, restored the reaction rate to within 15% of its original value. At lower reaction temperatures the poisoning rate of the reaction decreased as determined by higher reaction rates and less carbon buildup.

At the beginning of the cyclotrimerization reaction a small amount (10^{-4} times the amount of benzene) of C₄ products was detected. This peak disappeared 1 h into the reaction. Using ethylene as the reactant gas, instead of acetylene, produced only very small quantitites of benzene (2% of the amount as from C₂H₂) and ethane showed no activity for the formation of benzene. A mixture of methylacetylene and acetylene produced only benzene.

3.3. High-Pressure Reaction Studies on Palladium Films and Alumina-Supported Palladium Particles. We have also extended this study to palladium surfaces other than single crystals. The other two surfaces investigated in this study are palladium films coated on glass and palladium supported on alumina. Both of these surfaces catalyze benzene formation.

In the Pd film reactor, the chamber was filled to 0.25 Torr of acetylene and the reaction mixture periodically sampled. Benzene, ethylene, and ethane were the only observed products, and all formed within 15 min. The reaction continued until all of the acetylene was consumed (approximately 100 min). Roughly equal mole percentages benzene and ethylene formed with less ethane being produced (Figure 7). Under these isothermal conditions the turnover frequency was about 0.01 molecule site⁻¹ s⁻¹ assuming a Pd film area of 36 cm² and a Pd atom concentration of 1×10^{15} atom cm⁻² (actual number of active metal sites not determined due to unknown surface morphology).

Analysis of surface carbon coverage after the reaction was not possible.



Figure 8. This figure shows the relative product distribution of acetylene over palladium supported on alumina at 2 atm. At temperatures below 470 K there is limited conversion of acetylene to benzene and ethylene. At temperatures above 470 K the relative amount of benzene increases.

amounts of benzene formed (Figure 8). As in the film reactor, significant amounts of ethylene formed, with a higher percentage of benzene forming at elevated temperatures. At 430 K acetylene was found to completely react to form C_6H_6 , C_2H_4 , and C_2H_6 .

4.0. Discussion

The most interesting feature of the acetylene-palladium chemistry is the low-pressure stoichiometric, and high-pressure catalytic, formation of benzene on a variety of surfaces (single crystals, films, and supported on alumina). The trimerization under UHV conditions has been studied by our group and other.^{11,24,17-20} These studies have detected benzene formation with ultraviolet photoelectron spectroscopy, TPD, metastable deexcitation spectroscopy, EELS, and other techniques.^{11,17,19,23} One exception is the EELS study by Kesmodel et al.²⁰ They only observed the formation of surface CH, CCH, and =C-CH₃ fragments and no benzene. Subsequent EELS work by Marchon,23 found evidence for benzene at higher acetylene coverages. Ours is the first systematic study of this unique reaction at both high pressures and in UHV. In UHV there is structure sensitivity for the reaction, with the (111) face the most active followed by the (110) with one-sixth the activity and the (100) with one-twentieth the activity of the (111) surface (Figure 4). At low pressures, the activity was determined by comparing the area under the thermal desorption traces, and at high pressures, the activity was determined by comparing the turnover frequency.

In UHV, benzene desorbs with two maxima at 250 and 450 K, on the (111) face when formed from acetylene. When the surface was dosed with benzene there were desorption maxima at the same temperatures, suggesting that benzene formation is desorption rate limited rather than reaction rate limited. Thus, acetylene forms benzene upon adsorption and it exists in that form on the metal surface. Similar thermal desorption traces of H_2 from the C_2H_2 and C_6H_6 doses further substantiate this proposition. In both cases hydrogen desorbs in a broad high-temperature peak centered around 450-540 K. These similarities between benzene desorption traces exist on the other surfaces (Table I). The low and high-temperature maxima in the benzene desorption show that benzene forms readily and also that some benzene formed decomposes on the metal surface. The TPD spectra obtained for hydrogen, ethylene, and benzene correlate well with previous studies.²⁷⁻³⁰

Using Redhead's³¹ method of calculating activation energies of desorption for the UHV reactions from desorption maximum

- (30) Wadill, G. D.; Kesmodel, L. L. Phys. Rev. B 1985, 31, 4940.
- (31) Rehead, P. Vacuum 1962, 12, 203.

Palladium supported on alumina also formed benzene. In contrast to the Pd film, this reactor had to be heated to 430 K to see appreciable amounts of benzene. At room temperature small

⁽²⁷⁾ Cattania, M. G.; Penka, V.; Behm, R. J.; Christmann, K.; Ertl, G. Surf. Sci. 1983, 126, 382.

 ⁽²⁸⁾ Behm, R. J.; Christmann, K.; Ertl. G. Surf. Sci. 1980, 99, 320.
 (29) Stuve, E. M.; Madix, R. J. J. Phys. Chem. 1985, 89, 105.

TABLE II: Relative Catalytic Rates, according to Open Active Sites

crystal face	turnover frequency ^a	percentage of open sites	catalytic rates ^b
(111)	0.048	7	0.96-0.68
(100)	0.048	12-15	0.40-0.32
(110)	0.014	2	0.7

^a Percentage of open sites determined by CO titrations after 3 h of reaction time. ^b Units of molecules/(site-s). ^c Units of molecules/(open site-s).

vielded activation energies for benzene formation of 15 and 30 kcal mol⁻¹ for the low- (260 K) and high- (520 K) temperature peaks on the (111) surface (preexponential is 1×10^{13}). Contrasting these values with those from the high-pressure data shows large differences in activation energy. At high pressure, the cyclotrimerization reaction has an activation energy of 2 kcal mol⁻¹ (Figure 5). For a high-pressure reaction this is an extremely low value. For comparison, the formation of methane from CO and H₂, a facile reaction on iron, has an E_a of 24 kcal mol⁻¹ and H₂/D₂ exchange on Pt has a 4 kcal mol⁻¹ activation energy.^{32,33} This low activation energy could suggest formation of benzene on an overlayer of ethylidyne or other carbonaceous fragments onto which it would be loosely bound. From CO titrations it can be seen that the reaction rate is dependent on the number of metal sites available. As mentioned previously, on the (111) and the (100) surfaces approximately 5-7% and 12-15% of the surface was bare after 3 h of reaction time and on the less active (110) surface only 1-4% of the surface was bare. The differences in bare metal sites on the (111) and (100) surfaces which have similar turnover frequencies are most likely due to different poisoning rates. Also, when CO was added to the room temperature reaction 1 h after the start, the rate decreased to almost zero. Subsequent heating to 485 K, which is above the desorption temperature of CO, restored the rate to within 15% of its original value. CO binds only to the metal surface and since it binds more strongly than acetylene, it would displace acetylene. The CO titrations, CO poisoning experiments, and the structure sensitivity show that the bare metal atom is the active site for the high-pressure reaction.

The low activation energy for this reaction can also be explained by incorporating an adsorption equilibrium constant into the rate law.³⁴ The apparent activation energy, which is determined from the slope of the ln k vs. 1/T plot, equals the combination of the surface process activation energy and the heat of chemisorption. We were unable to extend the experimental parameters to regions of high acetylene surface coverage to test this hypothesis.

The (110) surface, the least active face, is the most open surface and leads to the highest decomposition rate of both acetylene and benzene as seen by the low percentage of bare Pd atoms. Therefore, the amount of irreversibly bound carbon in the catalytic steady-state reaction limits the rate by blocking sites.

If the percentage of open or active sites is taken into account, the reaction still exhibits structure sensitivity (Table II). The (111) surface is still the most active, followed by the (110) and then the (100) face. This is the same order of activity as seen in UHV. The relative values of the activity differ; however, this may be due to the innaccuracy in determining the percentage of open sites with CO titrations.

Product distributions at low and high pressures differ. In UHV, in addition to benzene formation, approximately 20% as much ethylene forms. At high pressure on single crystals less than 5% ethylene forms. Hydrogen could not be detected at high pressure. The presence of hydrogen would lead to rapid hydrogenation to ethylene and ethane. Also a rougher surface which has more Rucker et al.

decomposition would allow self hydrogenation. In UHV no C_4 fragments were detected whereas at atmospheric pressures small amounts (<0.1% of the benzene formed) of C_4 fragments were observed during the first hour of the reaction, but they were subsequently reduced in concentration during the reaction.

Benzene formation was detected on Al_2O_3 -supported palladium and on palladium films on glass. Quantitative data was difficult to obtain. Nevertheless, these experiments show that the cyclotrimerization proceeds readily on a variety of palladium surfaces.

The most difficult question to address is that of possible mechanisms for the reaction. It is likely that several mechanisms exist and there may be a gradual transition from one to another as a function of pressure. One possible reaction path involves a metallacyclopentadiene as an intermediate. In organometallic chemistry numerous studies have investigated possible routes for [2+2+2] cycloadditions.⁵ Spectroscopic evidence (NMR, IR) suggests that two acetylenes sequentially displace two ligands to form a metallacyclopentadiene intermediate. This is followed by the insertion of another acetylene to form either a metallacycloheptatriene and then benzene, or to form benzene through a Diels-Alder-type addition.³⁵ The first portion of this mechanism is well understood, but the addition of the final acetylene is very rapid and the pathway has not been determined. Another reaction scheme involves the concerted trimerization of three acetylene molecules.³⁶ One could also suggest the formation of a cyclobutadiene intermediate on the surface.^{37,38} Since no C_4 products were detected at low pressure and only small amounts at high pressure this mechanism seems improbable and has been ruled out in the homogeneously catalyzed reaction.³⁷ Analysis of product distribution and yields does not provide enough information to propose a mechanism but allows us only to rule out various possibilities.

5.0. Conclusions

From this surface science study of acetylene chemistry on palladium surfaces numerous important results were obtained which are outlined below.

The cyclotrimerization of acetylene proceeds readily in ultrahigh vacuum and at atmospheric pressures.

The reaction is structure sensitive in both pressure regions. (a) In UHV the activity ratio of the (111):(110):(100) faces is 100:18:5. (b) At atmospheric pressures the (111) and the (100) surfaces have equal activity followed by the (110) surface which is one-fourth as active. If the percentage of open or active sites is taken into account the reaction exhibits the same structure sensitivity ordering as in UHV [(111) > (110) > (100)].

At atmospheric pressures the reaction proceeds on the bare metal surface, with an activation energy of 2 kcal/mol and with a first-order pressure dependence in acetylene.

On single crystals in UHV acetylene produced benzene, ethylene by hydrogenation, and hydrogen from decomposition. At high pressures on single crystals only benzene was detected.

Acetylene also cyclotimerizes on Pd film and on small Pd particles supported on alumina.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. T.M.G. thanks Dow Corning Corp. for a graduate fellowship. We also thank Richard Wilmer for his assistance on the film reactor.

Registry No. HC=CH, 74-86-2; H_2C =CH₂, 74-85-1; C_6H_6 , 71-43-2; Pd(111), 7440-05-3.

⁽³²⁾ Garfunkel, E. L. Ph.D. Thesis, University of California, Berkeley, 1983.

 ⁽³³⁾ Zaera, F. Ph.D. Thesis, University of California, Berkeley, 1984.
 (34) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980.

⁽³⁵⁾ See ref 5 and 6 and references therein.

⁽³⁶⁾ Schrauzer, G. N.; Glockner, P.; Eichler, S. Angew. Chem., Int. Ed. Engl. 1964, 3, 185.

⁽³⁷⁾ Pollock, D.; Maitlis, P. M. Can. J. Chem. 1966, 44, 2673.

⁽³⁸⁾ Whitesides, G. M.; Ehmann, W. J. J. Am. Chem. Soc. 1969, 91, 3800.