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Kinetics and Mechanism of Benzene Formation from Acetylene on Pd(111) Studied by Laser-Induced Thermal Desorption/ Fourier Transform Mass Spectrometry

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Abstract: The first *in situ* kinetics investigation of benzene formation from acetylene (2.5 L) on Pd(111) is reported. Laser-induced thermal desorption with Fourier transform mass spectrometry is used to monitor the surface molecular composition as a function of temperature and reaction time. The reaction occurs in a stepwise mechanism, the rate-determining step being the reaction of 1 equiv of acetylene with 1 equiv of C_4H_4 surface intermediate (formed at ~110 K) to form benzene. At low temperatures (≤210 K), the reaction is self-poisoning by site blocking, and the reaction ceases with excess acetylene remaining. Heating to 260 K, however, drives the reaction to completion. Below 210 K, the reaction is observed to be pseudo zeroth order in acetylene surface concentration, but follows pseudo-first-order kinetics overall. The activation barrier for benzene formation is 43.5 ± 4.5 kJ/mol with a preexponential of $10^{9.8\pm0.1}$ s^{-1}. Additionally, butadiene is observed, confirming the presence of C_4 species on the surface.

Investigations into the cyclization reactions of acetylene on Pd have been ongoing in various laboratories for the past decade.[1−27] An excellent review of this work recently appeared.[28] Previously, thermal desorption spectroscopy (TDS) studies showed low (210−250 K) and high (500 K) temperature desorption of benzene after adsorption of acetylene on Pd(111).[1−4] This represents an important class of reactions, since C−C bond formation and aromatization both occur under ultrahigh vacuum (UHV) conditions, seemingly similar to high pressure[9] and homogeneously catalyzed processes.[22,23]

Most studies of heterogeneous acetylene cyclization use the closet-packed (111) surface of Pd, since it is the most active for benzene formation.[9] Several important details regarding the mechanism of this reaction have been gleaned. Isotopic labeling experiments have conclusively shown that no C−C or C−H bond breaking takes place during benzene formation.[15] Molecular beam scattering studies conducted by Tysoe et al.[2] also showed desorption of benzene as well as possibly C_4H_X species when a Pd(111) surface was exposed to a beam of acetylene. The formation of furan[24] (C_4H_4O) and thiophene[11−14] (C_4H_4S) from O- and S-covered Pd surfaces, respectively, with coadsorbed acetylene has been interpreted as further evidence for a stepwise mechanism involving the formation of a C_4H_4 intermediate, although the possibility that these were products of side or competing reactions could not be ruled out. Additionally, *cis*-3,4-dichlorocyclobutene (DCB)[5,25] has been used as a precursor for benzene,[15,24] furan,[24] and thiophene[11] formation, further strengthening the hypothesis that C_4H_4 is an intermediate in all of these reactions. Near-edge X-ray absorption fine structure, high resolution electron energy loss, and angle resolved ultraviolet photoemission investigations[5,10,25] have suggested that the C_4H_4 surface intermediate produced after DCB adsorption is a tilted metallocycle. However, prior to this study, there has been little evidence regarding many details about the surface processes, such as the rate-determining step (if any)

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or the energetic barrier to reaction, since the evolution of gaseous benzene is desorption-rate limited.[1−4,9]

This investigation utilizes laser induced thermal desorption (LITD)[29,30] to desorb neutrals from the substrate into the gas phase where they are post-ionized with an electron beam and detected by Fourier transform mass spectrometry (FTMS).[31] This method has been shown to be useful for monitoring changes in surface molecular composition and can accomplish this feat at temperatures below those necessary for conventional thermal desorption.[30−34] Thus, one can probe reactions under conditions where all reactants and products remain on the surface. Recently, we utilized LITD/FTMS to observe the simultaneous formation of benzene and thiophene at 120 K from a 6 L (L = Langmuir = 10^{-6} Torr·s) acetylene precoverage on sulfided Pd(111).[17]

Reported here is the first *in situ* UHV kinetics study of benzene formation from acetylene on clean Pd(111) by LITD/FTMS. Our results favor a stepwise mechanism which is ultimately desorption limited, as well as providing accurate values for the kinetic parameters for benzene formation on the surface. The acetylene initial exposure is 2.5 L with the Pd sample held at 80 K. Using the initial rates of reaction at various temperatures from 165 to 200 K, an activation barrier of 43.5 ± 4.5 kJ/mol (95% confidence limits) is obtained. Under these conditions, no desorption of reactants or products takes place and the reaction eventually ceases while the acetylene concentration is still at 65−85% of its initial value, presumably due to depletion of reactive sites. The stoichiometry of the slow step, however, is shown to involve the conversion of 1 equiv of acetylene (plus some unobserved surface intermediate, presumably C_4H_4) for each equivalent of benzene formed. Thus, the reaction shows pseudo-zeroth-order dependence on acetylene surface concentration (present in excess), but psuedo-first-order behavior overall for the increase in benzene product. Fitting the data to a pseudo-first-order model yields a preexponential factor of $10^{9.8\pm0.1}$ s^{-1} (also 95% confidence limits). Butadiene was also detected on the surface by LITD, confirming the presence of C_4 species, but no C_8 species were observed. These results correlate well with conclusions drawn from high pressure heterogeneous catalysis studies[9] as well as homogeneously catalyzed, solution-phase chemistry.[22,23]

Experimental Section

The Pd(111) surface is supported at the end of a long motion bellows in a UHV chamber (base pressure = 2×10^{-10} Torr). The surface is cleaned by Ar^+ (500 eV) bombardment to remove tightly bound species, such as sulfur, and heating in oxygen (sample temperatures elevated to 600 °C) to remove residual carbon. The elemental composition of the surface is monitored by Auger electron spectroscopy.

The acetylene is spectral grade (99.96% pure) with an acetone stabilizer impurity. Acetone (and benzene, if present) is removed by passing the acetylene through a CO_2-ice/acetone-cooled trap. (Purity is checked with FTMS prior to and during use.) Acetylene is admitted to the chamber with a sapphire sealed variable leak valve. All adsorption takes place with the sample held at 80 K.

A detailed explanation of the apparatus will be published later. Briefly, a Nd:YAG laser (1064 nm, 5 ns, ca. 10^7 W/cm^2 power density, and 1 mm spot diameter) is focused onto a Pd single crystal with a polished (111) plane exposed. Adsorbed molecules are vaporized from the surface as neutrals without substrate (Pd) ablation. The neutrals are post-ionized by an electron beam (70 eV) and detected by FTMS with a 0.5 T magnetic field. FTMS yields complete mass spectra of the post-ionized species, ranging from *m/z* 10 to 800. The desorbed species have been shown to be representative of the surface composition in the majority of cases.[31−34]

Careful calibration of the relative sensitivities of LITD/FTMS to adsorbed acetylene and benzene has been achieved by monitoring the uptake of each species, individually and together, on the Pd surface at 80 K. A constant pressure of one species is maintained while monitoring the LITD/FTMS signal as a function of time for exposures up to about 2 L. (Exposure values are corrected for ion gauge sensitivities−1.66 for acetylene and 5.18 for benzene.[35a]) These curves are linear with $R^2 \geq 0.9$. Uptake curves of benzene onto Pd at 80 K predosed with 0.1 and 3 L of acetylene were also linear. Also, the benzene signal was monitored for a constant coverage of benzene while increasing the coadsorbed acetylene. Addition of 3 L of acetylene increased the benzene signal only slightly relative to the same amount of benzene on a clean Pd surface. This demonstrates that the change in the benzene signals during the kinetics studies described here (where the acetylene coverage changes very little) should remain linearly dependent on the surface benzene concentration. The isothermal kinetics studies are conducted by ramping quickly (10 K/s) to the desired temperature and holding as the laser is rastered across the surface, striking a different spot and acquiring a complete mass spectrum for each laser shot.

Results and Discussion

The experiments discussed here utilize a 2.5-L exposure of acetylene (corresponding to ~0.33 monolayer, i.e. saturation of the first layer[2]) on clean Pd(111) held at 80 K. Figure 1 shows three spectra, each obtained using a single laser shot at a fresh spot. Note that the spectra are obtained at different sample temperatures. Since the efficiency of laser desorption is dependent on the initial substrate temperature, one must correct for this dependence in order to compare the absolute signal intensities between spectra obtained at different temperatures. We find that the LITD signal as a function of initial temperature is fairly constant for acetylene and benzene at temperatures between 80 and 150 K. However, as one approaches temperatures near the onset of conventional thermal desorption, the LITD signals increase sharply. Once conventional thermal desorption begins, the LITD/FTMS signals decrease due to depletion of the surface concentration.

The peak observed in Figure 1a at *m/z* 26 is representative of acetylene, while the small peak appearing at *m/z* 28 is due to CO, having a measured exact mass of 27.993 ± 0.005 (CO 27.994, N_2 28.011, and C_2H_4 28.034) as determined by internal calibrants ($C_2H_2^+$, $C_4H_2^+$, $C_4H_3^+$, $C_4H_4^+$, $C_6H_5^+$, and $C_6H_6^+$) in subsequent spectra. This small amount of CO adsorbs onto the cooled sample from the chamber background. Unlike NO, CO should not appreciably affect the acetylene chemistry, especially at these levels.[36−38] Figure 1b is a spectrum obtained after warming to 200 K for about 1 min. The peak observed at *m/z* 78 and its molecular fragmentation pattern, appearing at

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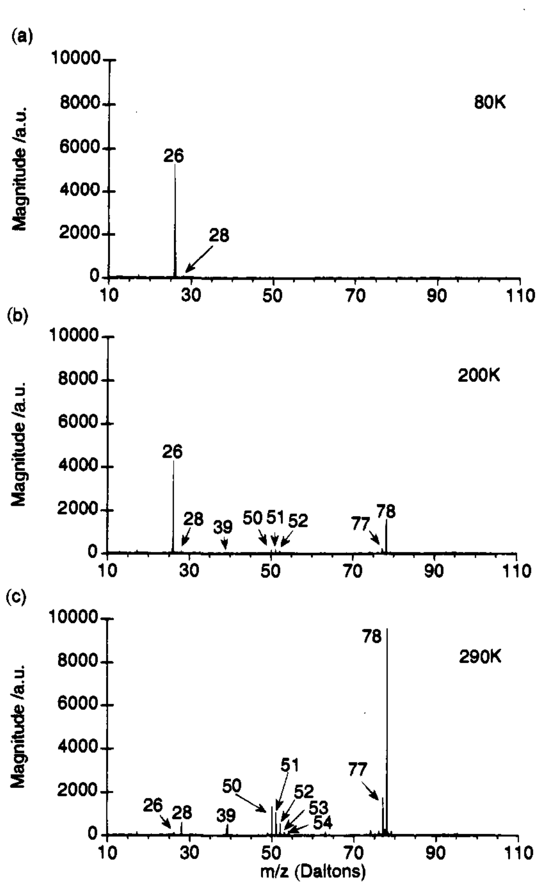

Figure 1. A clean Pd(111) crystal is dosed with acetylene (2.5 L) at 80 K and examined by laser-induced thermal desorption/Fourier transform mass spectrometry (LITD/FTMS). Spectra a−c are obtained with the sample held at 80, 200, and 290 K, respectively. (a) At 80 K, the peaks indicate that only acetylene (*m/z* 26) and CO (*m/z* 28) are present on the surface. (b) After warming to 200 K, the peak appearing at *m/z* 78 is indicative of benzene, and *m/z* 39, 50, 51, 52, and 77 are the electron ionization fragments of benzene. (c) As the temperature is increased to 290 K, peaks appearing at *m/z* 53 and 54 are representative of 1,3-butadiene. The loss of acetylene (*m/z* 26) and gain in CO (*m/z* 28) and benzene are also observed.

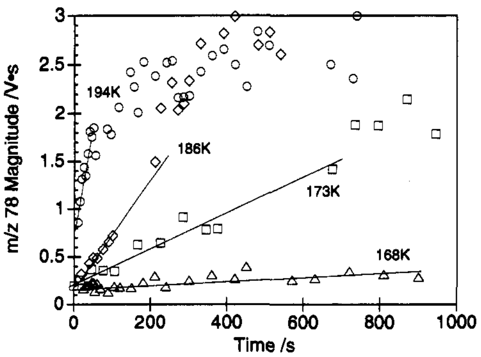

Figure 2. The *m/z* 78 signal as a function of time at temperature, indicating the isothermal formation of benzene from acetylene (2.5 L) on Pd(111), is plotted at several temperatures. The solid line indicates the initial rate at which benzene formation occurs. Only data from the first 50% of the reaction at each temperature are used to estimate the initial rates.

m/z 39, 50, 51, 52, and 77, are indicative of benzene formation. Loss of acetylene is also observed. In fact, the actual decrease in acetylene surface concentration is larger than indicated by comparing the peak heights between Figure 1a and 1b, since the higher initial temperature in Figure 1b leads to slightly more efficient removal of adsorbed acetylene during LITD. The efficiency of benzene removal does not change appreciably between 80 and 200 K.

Figure 1c was obtained after heating the sample to 290 K. The peaks appearing at *m/z* 53 and 54 are indicative of butadiene. No such peaks are observed when benzene alone is heated on Pd(111). The butadiene may be due to hydrogenation of a C_4H_4 surface intermediate. Also, additional loss of acetylene and gain in benzene (and CO from adsorption of background) are observed. However, the removal of benzene is significantly more efficient at 290 K than at 200 K, so the magnitude in Figure 1c must be reduced by approximately 40% for direct comparison with Figure 1a or 1b. After this correction, one can compare the initial signal for acetylene to the final signal for benzene. We find that, after correcting for our relative sensitivities, the ratio of acetylene in Figure 1a to benzene in Figure 1c is approximately 2.8. If one assumes that no other species are present on the surface after dosing at 80 K, then the conversion efficiency of the acetylene to benzene is slightly greater than 100%! However, we have previously shown that heating to 120 K already results in small signals for benzene and thiophene on sulfided Pd(111).[17] We note here that, on clean Pd(111) with a 2.5-L exposure of acetylene, one sees a very small signal for benzene and a significant decrease in the signal for acetylene after brief heating to 110 K. The signal for benzene, however, does not increase appreciably with time until temperatures in excess of 150 K (as demonstrated by the kinetic data discussed later). This LITD/FTMS signal for benzene obtained on clean and sulfided Pd(111) below 150 K is likely due to a laser-driven surface reaction of C_4H_4 with acetylene. Laser-driven reactions during LITD have been observed previously.[39] It is unlikely that such associative reactions would have high yields, since time scales are short and decomposition and desorption, which are both single step, first-order processes, are in direct competition for reactants. If C_4H_4 does form in substantial amounts after short time at 110 K, it is likely that some forms already at 80 K during acetylene adsorption and positioning of the sample. Thus, our initial LITD experiment (Figure 1a) may probe a surface where some acetylene has already reacted to C_4H_4. Unfortunately, except for the very inefficient benzene desorption, we currently cannot monitor the surface C_4H_4 concentration. (Previous studies have shown these types of reactions to be very sensitive to the details of laser heating, so relative yields and signal intensities vary widely from shot to shot, making quantitative measurements difficult.[39]) This makes it difficult to assess the efficiency of benzene formation other than to say that it is nearly quantitative. We see no evidence for significant desorption of benzene at temperatures below 380 K using the very slow, stepwise heating conditions described above. TDS, however, shows significant benzene desorption between 210 and 280 K. Since the amount of benzene remaining on the surface at 290 K in our experiments represents nearly quantitative conversion of the initial acetylene, we must conclude that the low-temperature (210−280 K) desorption of benzene (attributed to tilted benzene) is sensitive to reaction conditions such as heating rate.

Figure 2 shows a plot of the benzene signal as a function of time at several temperatures from 168 to 188 K utilized for isothermal kinetics studies. (Additional temperatures were investigated but are not shown for clarity.) The activation barrier for benzene formation can be determined from a plot of the natural logarithm of the initial rate of benzene formation vs the inverse temperature, without any need for assumptions about the order or mechanism of the reaction, as follows.

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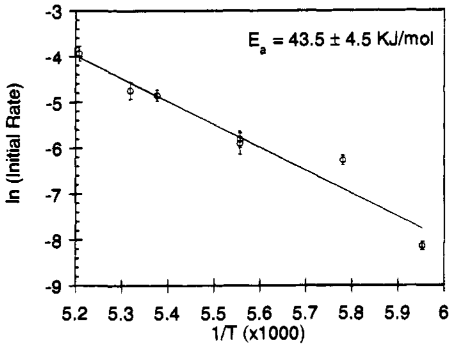

Figure 3. The Arrhenius plot of benzene formation from acetylene (2.5 L) using initial rates (shown in Figure 2).

Assuming an irreversible reaction,

$$xX + yY \rightarrow Z \qquad (I)$$

the initial rate of reaction (κ_i) 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:

$$\kappa_i = k[X]_0^n \cdot [Y]_0^m \qquad (II)$$

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. Substituting for

$$k = \nu e^{-E/RT} \qquad (III)$$

where ν is the Arrhenius preexponential factor, E is the activation barrier for the process, R is the gas constant, and T is the absolute temperature, and taking the natural logarithm of both sides gives:

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

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 $\ln(\kappa_i)$ 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 utilized.

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 data from the first half of the reaction (benzene signals less than 50% of the final benzene signal) by fitting to a straight line. This is indicated on Figure 2. Figure 3 shows a plot of the natural log of the initial rates vs inverse temperature and a weighted linear least-squares fit to these data gives an activation energy of 43.5 ± 4.5 kJ/mol (95% confidence) for benzene formation. The activation energy is the only parameter calculated from the initial rates.

The activation energy reported by Rucker et al. for formation of benzene at high acetylene pressures (250 Torr) and in the presence of nitrogen at 1040 Torr is 8.4 kJ/mol,[9] which is considerably lower than that observed here. However, the activation energies measured under high pressure conditions are a combination of the surface activation energy with the reactant adsorption/desorption equilibria occurring.[40] Specifically, for a first-order reaction (the case here, as reported by Rucker et al.[9]), Satterfield has shown that the energy of activation observed at high pressure is the difference between the activation energy for the surface process and the reactant heat of adsorption.[40] Employing the laser desorption technique, we measure the activation energy for the surface process directly. One can then use the surface-only value from our results with the combined value from the high pressure studies to obtain an estimate of the binding energy for acetylene: ~35 kJ/mol. This is, however, an unreasonably low value (by a factor of 2–5) for the heat of adsorption for acetylene on Pd(111).[21] Rucker et al. speculated that the reaction they observed at high pressure might be occurring on an overlayer of ethylidyne or other carbonaceous species.[9] An acetylene adsorption/desorption equilibrium occurring on this carbonaceous overlayer would explain the low acetylene adsorption energy, even if the surface reaction were occurring on small bare Pd patches.[40] This assumes that surface diffusion is not rate limiting—a reasonable assumption at the temperatures employed in those studies.

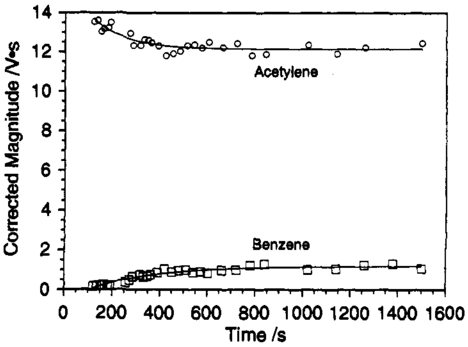

Figure 4. Plot of the acetylene and benzene signals as a function of time after heating acetylene on Pd(111) to 186 K. The data are indicated by squares for benzene (mass 78) and circles for acetylene (mass 26), while the solid curves are exponentials characteristic of first-order kinetics, but with a non-zero end point added in the acetylene fit. The signal magnitudes have been corrected for relative sensitivities and plotted to scale.

A value of 43.5 kJ/mol for the activation energy of the surface process is not unreasonably low, since energy is not expended in breaking C–C or C–H bonds,[15] and the carbon atoms in acetylene adsorbed on Pd(111) are already substantially rehybridized to sp^2.[21] The barrier may be due to one or a combination of diffusion, rehybridization, and C–Pd bond breaking or weakening. Adsorbed C_4H_4 from the decomposition of dichlorocyclobutene has been shown to be a metallocycle with multiple bonds to the surface and is tilted, rather than parallel to the surface.[5,25] This is not consistent with any C_4H_4 portion of benzene in its preferred binding site on Pd(111).[21] The same study showed acetylene is bonded with the molecular plane 15–30° from the surface normal. (Adsorbed acetylene is not linear.) Thus, benzene formation must be preceded by a change in orientation of both the acetylene and the C_4H_4.

One can also infer mechanistic details of the reaction by studying the rate curves. Figure 4 shows the benzene and acetylene signals as a function of time after warming to 186 K. The signal magnitudes are corrected for our relative sensitivities toward each species. The actual data are indicated by squares

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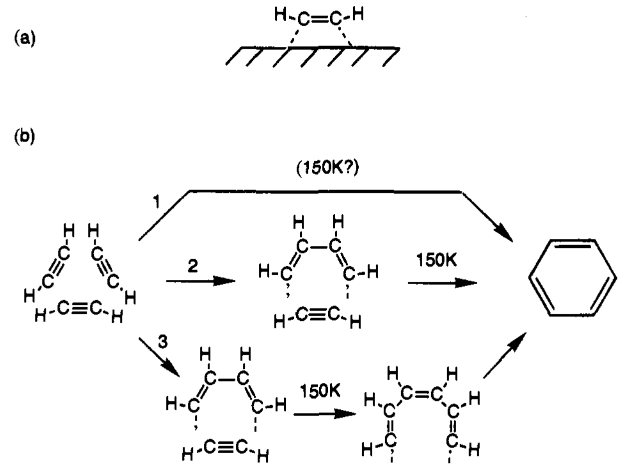

Figure 5. (a) A cartoon showing the approximate adsorption geometry for acetylene on a Pd surface (adapted from ref 21). (b) Three possible pathways for benzene formation from acetylene. Path 1 represents a concerted mechanism for benzene formation. Path 2 shows an intermediate step resulting in the formation of a C_4H_4 surface intermediate, and the final step is a Diels−Alder addition of acetylene to C_4H_4. Path 3 is similar to Path 2 but the reaction of acetylene with C_4H_4 results in insertion into the C−Pd bond forming an expanded metallocycle. Our data support a rate-determining step (becoming appreciable above 150 K) involving 1 equiv of acetylene for each equivalent of benzene formed. Only Paths 2 and 3 are consistent with such a mechanism, and only if the steps marked with 150 K are rate-determining.

for benzene (mass 78) and circles for acetylene (mass 26), while the solid curves are exponentials characteristic of pseudo-first-order kinetics, but with an arbitrary non-zero final concentration included as an additional fitting parameter for the acetylene signal. At this temperature, no thermal desorption occurs (except where LITD is performed). The rate constants for benzene formation and acetylene loss are the same, within experimental error, indicating that both are resulting from the same process. Interestingly, the total benzene formed at any time is approximately equal to the total amount of acetylene consumed at each point in the reaction (acetylene change/benzene change = 1.4 ± 0.3). Stoichiometrically, this is not feasible unless the reaction proceeding is the addition of acetylene to a preexisting C_4H_4 surface intermediate to form benzene, hence the ~1:1 relationship of the benzene-formed to acetylene-lost observed in Figure 4. Additional evidence for such a mechanism is provided by the fact that the acetylene signal loss observed as the temperature is ramped from 80 to 150 K is approximately twice that of the signal loss observed in Figure 4.

These observations support a stepwise process with C_4H_4 forming at low temperature (~100 K) and no further reaction until the temperature exceeds 150 K when a single equivalent of acetylene reacts with the preexisting C_4H_4 surface intermediate to form C_6H_6. This precludes a concerted mechanism (refer to Figure 5) as well as a mechanism where the formation of C_4H_4 is the slow step. Note that, due to the true multiplex nature of FTMS, the benzene and acetylene data were obtained simultaneously (see Figure 1) facilitating this direct comparison, since there can be no doubt that the mass spectrometer and laser parameters are identical for the two species. The major source of uncertainty in these values comes from the uncertainties in the ion gauge relative sensitivities for acetylene (1.7−1.9) and benzene (4.3−5.2).[35] Taking the "worst-case" values, one can only reach a 1.9:1 stoichiometry, still not sufficient to accommodate any mechanism where the slow step for benzene formation is the first acetylene coupling to form C_4H_4, all of which would require a minimum of 3:1 stoichiometry in our observations. One other possible mechanism not yet discussed is that of three acetylenes linking to form a C_6 metallocycloheptatriene or metallocyclooctatriene at low temperature followed by ring contraction to eliminate the metal atoms and form benzene at 150 K. The simultaneous loss of acetylene observed at 150 K would then have to be attributed to coincidental desorption, or perhaps to further reaction due to increased availability of reactive ensembles as the benzene might take up less surface area than the expanded metallocycle ring. If significant amounts of this C_6H_6 intermediate were present on the surface, however, we might expect to see some signal for the dihydrogenated form, 1,3,5-hexatriene, m/z 80, during LITD, just as we see some dihydrogenated C_4H_4 desorb as 1,3-butadiene at m/z 54. However, no peaks above mass 78 are observed, so it appears that this mechanism does not significantly contribute to benzene formation.

Under the conditions of our experiments, it appears that acetylene is present in large excess compared to the C_4H_4 intermediate. Hence, the reaction appears pseudo zeroth order with respect to acetylene and should be first order with respect to C_4H_4. Rucker et al. observed first-order dependence on acetylene pressure for benzene formation in elevated pressure studies, consistent with the hypothesis that addition of a single acetylene to an existing C_4H_4 is the rate-determining step at high pressures, as well.[9] The large excess of acetylene remaining after the reaction has ceased must be attributed to a process which is limited by the number of active sites present on the surface, since more C_4H_4 would otherwise form at low temperature and be subsequently converted to benzene. We observe an overall decrease of ~1/3 of the original acetylene concentration. At this exposure, Tysoe et al. have concluded, based on a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern, that the acetylene coverage is one acetylene molecule per three Pd surface atoms.[2] Since three acetylenes are required for each benzene, the active site concentration under these conditions would be $1/(3 \times 3 \times 3) = 0.037$ monolayer, assuming very little of the acetylene had converted to C_4H_4 prior to our spectrum obtained at 80 K. Rucker et al. report that the reaction is limited by surface poisoning or by product accumulation in high pressure studies of acetylene on Pd(111), as well.[9,15]

The spectra in Figure 1 were obtained by heating 2.5 L of acetylene dosed at 80 K in steps of 20 K with several LITD spectra obtained at each temperature. The previous time-dependent studies showed that the benzene formation reaction reached a plateau within 20 s at 200 K. The spectrum in Figure 1b was obtained after >1 min at this temperature and subsequent spectra at 200 K showed no change, indicating that the reaction had indeed ceased before this spectrum (Figure 1b) was obtained. Note that the spectrum obtained at 200 K shows significantly less benzene than that obtained after warming to 290 K, shown in Figure 1c. (The signal in Figure 1c must be reduced by about 40% due to the higher initial temperature for LITD). When the temperature is >210 K, some mechanism (perhaps benzene diffusion away from the specific active sites or rearrangement to expose more bare Pd ensemble sites) exposes more active sites for further benzene formation. This continues until the acetylene LITD signal drops to zero, indicating no more surface acetylene present. Thus, as the temperature is raised, the benzene surface concentration continues to increase (see Figure 1c), reaching a maximum by 260 K and then falling after heating above 380 K (where desorption of flat-lying benzene becomes appreciable[15]). (It should perhaps be mentioned that dosing a clean Pd(111) surface with benzene at 80 K followed by warming produced no detectable acetylene, so that, as expected from the thermodynamics, no contribution from the backwards reaction is evident.)

Since the mechanism above implies that the reaction observed during the isothermal kinetics experiments (at 165–200 K) is the addition of one acetylene to one C_4H_4 intermediate, the data obtained were fit assuming pseudo-first-order and second-order kinetics for a statistical comparison. With LITD, one can readily observe the surface acetylene and benzene, but the C_4H_4 appears to be too tightly bound to undergo efficient intact desorption, even under the conditions of laser heating. Small amounts of C_4H_4 might be evolved, but would be difficult to detect, since the electron beam fragmentation of benzene also leads to a small amount of $C_4H_4^+$. Since the acetylene evolution is somewhat complex, we choose to use kinetic models that only incorporate the concentration of product, benzene. The evolution of products assuming a pseudo-first-order process goes as follows. For a reaction converting species X into the species Z,

$$X \rightarrow Z \qquad \text{(V)}$$

the evolution of product formation follows

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

since the product concentration, assuming no competing reactions, can be related to the initial reactant concentration by

$$[X]_t = [X]_0 - [Z]_t \qquad \text{(VII)}$$

and

$$[X]_0 = [Z]_\infty \qquad \text{(VIII)}$$

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, k is the pseudo-first-order rate constant, $[X]_0$ is the initial reactant concentration, and $[X]_t$ is the reactant concentration at time t.

Assuming second-order behavior,

$$X + Y \rightarrow Z \qquad \text{(IX)}$$

if the initial concentrations of X and Y are not nearly equal, then pseudo-first-order kinetics are obtained. If the initial concentrations of X and Y are assumed to be equal, one finds

$$[Y]_t = [X]_t = [X]_0 - [Z]_t \qquad \text{(X)}$$

and, again assuming no competing reactions,

$$[X]_0 = [Z]_\infty \qquad \text{(XI)}$$

yielding

$$[Z]_t/\{[Z]_\infty([Z]_\infty - [Z]_t)\} = kt \qquad \text{(XII)}$$

The experimental data for the time evolution of the benzene signal is fit to eq VI and eq XII using both $[Z]_\infty$ and k as adjustable parameters. A comparison of the χ^2 values using the F distribution favors the pseudo-first-order model over the second-order treatment (at the ~65% confidence level), as expected from the acetylene time-dependence. One can then fit the isothermal data sets using a pseudo-first-order model incorporating the activation barrier determined using initial rates and solve for the preexponential factor for each set. The weighted average of these preexponential factors is $10^{9.8\pm0.1}$ s^{-1} (95% confidence level).

Conclusions

These investigations have further increased our understanding of the acetylene/Pd(111) system's kinetic and mechanistic pathways for benzene formation. The activation energy (43.5 ± 4.5 kJ/mol) and preexponential factor ($10^{9.8\pm.1}$ s^{-1}) were extracted from isothermal kinetics studies. In addition, the rate-determining step was observed to be the addition of a single acetylene molecule to a C_4H_4 surface intermediate to form benzene. These results are in general agreement with previous studies and consistent with homogeneously catalyzed cyclization of alkynes by transition metal complexes[22] where, for Pd(II) complexes, the final step has been shown to be addition of a C_2 alkyne to a C_4 metallocyclopentadiene moiety.[23] Pseudo-first-order kinetics are favored for the formation of product, which is likely the result of a limited number of C_4H_4 intermediates formed at ~110 K at reaction sites suitable for benzene formation. The reaction ceases with a large excess of acetylene present at temperatures <210 K due to active-site blocking. This is consistent with results from high pressure studies at elevated temperatures showing the reaction was desorption-rate limited. The observation of butadiene confirms the presence of C_4 species on the surface.

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