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# Temperature programmed desorption of co-adsorbed hydrogen and acetylene on Pd(111)

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## Abstract

Co-adsorbed acetylene and hydrogen react on Pd(111) to form ethylene and butene. Benzene is also formed and it is found that the low temperature ( $\sim 280$  K) desorption state observed on the clean surface is virtually unaffected by the presence of hydrogen whereas the higher temperature ( $\sim 520$  K) state is modified. However, adsorbing benzene onto a hydrogen pre-covered surface just affects the sticking coefficient but not its desorption properties. The effect of hydrogen on the high-temperature, acetylene-derived benzene desorption state is therefore ascribed to its influence on the chemistry of acetylene rather than being due to the effect of hydrogen on the benzene that has been formed. The reaction between hydrogen and acetylene to form ethylene is shown to be first order in hydrogen coverage and to proceed with an activation energy of  $\sim 23$  kJ/mol. The trailing edge of the ethylene desorption profile is proposed to be due to the loss of acetylene because of its conversion to a vinylidene species. A fit to the desorption profile using this model gives an activation energy for this reaction of  $\sim 16$  kJ/mol with a reaction pre-factor of  $\sim 600$  s<sup>-1</sup>.

**Keywords:** Alkynes; Hydrogen; Low-index single-crystal surfaces; Models of surface kinetics; Palladium; Surface chemical reaction; Thermal desorption spectroscopy

## 1. Introduction

The palladium-mediated conversion of acetylene to benzene is an attractive reaction since it occurs both in ultra-high vacuum (UHV), where approximately 30% of an acetylene overlayer reacts to form benzene during a thermal desorption sweep [1–3], and also catalytically at high pressure both on model single crystals [4] and supported catalysts [5]. The

general reaction pathway in ultra-high vacuum is now relatively well established. Adsorbed acetylene can initially dimerize forming a surface C<sub>4</sub> species which then reacts with acetylene synthesizing benzene [6–9]. In spite of the apparently relatively facile formation of benzene in TPD, the overall catalytic reaction rate is rather low [4] ( $\sim 10^{-2}$  reactions/site/s). However, experiments using high-surface-area, supported palladium display a high initial acetylene-to-benzene conversion rate which diminishes to a low, steady-state rate as the reaction proceeds suggesting that the reaction is being poisoned [5]. It has been shown that acetylene trans-

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forms into a vinylidene species following adsorption at room temperature [10] and the formation of this overlayer may be responsible for the decrease in the rate of benzene formation observed for the high-surface-area catalysts.

It is found that the addition of a small amount of hydrogen to the acetylene (a few percent) significantly enhances the rate of benzene formation [5]. In order to investigate the effect of hydrogen, we have studied co-adsorbed acetylene and hydrogen on a palladium single crystal surface using temperature-programmed desorption and, consonant with the existence of  $C_4$  species on the surface, we find  $C_4$  hydrocarbon formation as well as the desorption of ethylene due to the direct hydrogenation of acetylene.

In addition, palladium is an active and selective catalyst for the hydrogenation of acetylene to ethylene [11–13] so that an investigation of the kinetics of a mixed hydrogen + acetylene layer should also provide useful insights into this reaction.

## 2. Experimental methods

Experiments were carried out in an apparatus that has been described in detail elsewhere [14]. The stainless-steel, ultra-high vacuum chamber operated at a base pressure of  $2 \times 10^{-10}$  Torr following bake-out; it contained a four-grid, retarding-field analyzer (RFA) for LEED/Auger experiments and a quadrupole mass spectrometer for gas analysis and thermal desorption measurements. The computer-multiplexed mass spectrometer allowed up to sixteen different ion signals to be monitored sequentially. Thermal desorption spectra were collected using a heating rate of 8 K/s. Gases could be introduced either by means of a directional dosing source or by back-filling the chamber. The sample was exposed to acetylene using the directional doser in order to minimize background contamination of the chamber since it is pumped away relatively slowly. Since all experiments were carried out using an acetylene-saturated surface, the dosing time required to form a saturated overlayer using the source was measured using the method of King and Wells [15]. Comparison with previous measurements of acetylene adsorption kinetics [1,6] shows that an equivalent of a 3 L

exposure was used to attain acetylene saturation. The surface was exposed to hydrogen or deuterium by back filling the chamber and their exposures are uncorrected for ionization gauge sensitivity.

The palladium single crystal was attached to 2 mm Mo rods by means of 0.25 mm Mo wires and mounted on an XYZ-rotary motion feedthrough. It could be resistively heated and also be cooled by being brought into thermal contact with a liquid-nitrogen-filled reservoir. Specimen cleaning was achieved by heating the sample to  $\sim 700$  K in a pressure of  $\sim 1 \times 10^{-6}$  Torr of oxygen introduced via the dosing source. Sub-surface carbon contamination was particularly troublesome, and it was found that a sensitive index of cleanliness was to saturate the surface with oxygen and monitor the resulting desorption spectrum. Initially only CO desorbed; subsequently some  $O_2$  desorption was observed along with some CO and finally only  $O_2$  was detected with no trace of CO indicating a completely carbon-free surface. Isotopically labelled acetylene ( $^{13}C_2H_2$ , Aldrich, 99.999%) was used directly from the glass bottle and hydrogen and deuterium (Aldrich, CP grade) were used without any further purification. The purity of all gases was checked periodically using mass spectroscopy and, in all cases, gas exposures have not been corrected to take account of ionization gauge sensitivities.

## 3. Results

Multimass thermal desorption spectra were collected for co-adsorbed acetylene (using isotopically labelled acetylene ( $^{13}C_2H_2$ )) and hydrogen. Surfaces were prepared by first exposing the Pd(111) sample to hydrogen at 180 K by back filling the chamber and subsequently saturating the surface with acetylene via the dosing source using the equivalent of a 3 L exposure ( $1 L = 1 \times 10^{-6}$  Torr  $\cdot$  s). It was shown, by measuring acetylene adsorption kinetics using the capillary array dosing source by the method of King and Wells [15], that acetylene adsorption was not effected by the presence of pre-adsorbed hydrogen even with a saturated hydrogen overlayer. This procedure therefore leads to a saturation coverage of acetylene identical to that for a clean Pd(111) surface ( $\theta = 0.46$  [1] where coverages are referenced to the

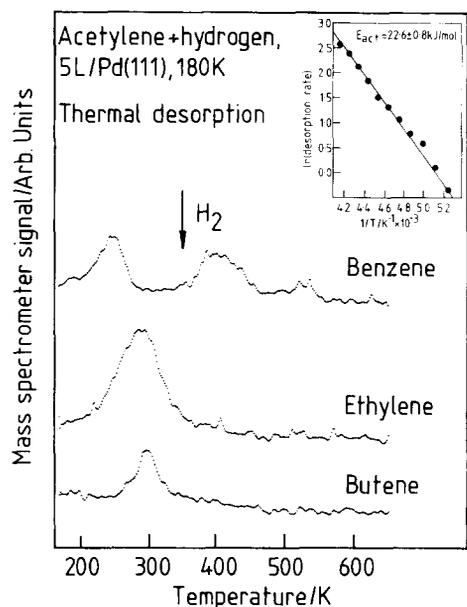


Fig. 1. Benzene, ethylene and butene thermal desorption spectra obtained after pre-exposing the surface to 5 L of hydrogen and then 3 L of acetylene. A leading-edge plot for the desorption of ethylene is shown as an inset.

palladium site density on the (111) face) for the various hydrogen coverages. In addition, it was shown by comparing the hydrogen or deuterium thermal desorption traces both with and without acetylene post-dosing, that no hydrogen was displaced from the surface by dosing with acetylene. Typical desorption product distributions are displayed in Fig. 1 for a surface pre-saturated with hydrogen (5 L  $H_2$ ) where exposures are uncorrected for ionization gauge sensitivity. Benzene formation is still detected although the shape of the desorption curve is significantly modified compared to that for clean Pd(111). In particular, the intensity of the 520 K peak which, for clean Pd(111), is approximately equal in intensity to the 280 K feature is significantly attenuated and is replaced by a feature at  $\sim 410$  K. Note that the position of the 280 K state is identical to that seen for clean Pd(111).

A peak is also found with its major intensity at 30 amu corresponding to ethylene desorption ( $^{13}C_2H_4$ ) and the nature of this species is confirmed by comparing the relative desorption yield at the various fragment masses of ethylene with the fragmentation pattern of ethylene itself. This result agrees with that

found previously [6]. This feature is sufficiently intense to allow the activation energy for ethylene formation to be measured from the leading-edge region of the desorption spectrum. The resulting “leading-edge” plot is shown as an inset in Fig. 1 and the measurement of the slope of this curve yields an activation energy of  $22.6 \pm 0.8$  kJ/mol for acetylene hydrogenation to ethylene on Pd(111). The maximum coverage decrease over the temperature range used for this plot was less than 10%.

In addition, a relatively small peak is detected corresponding to the formation of a  $C_4$  hydrocarbon in accord with the presence of stable  $C_4$  species on the surface [16]. The mass distribution for this molecule for a mixed acetylene ( $^{13}C_2H_2$ ) + deuterium surface is shown in Table 1. In this case, the maximum detectable mass is at 64 amu corresponding to the formation of  $C_4H_4D_4$ , that is,  $d_4$ -butene. The relatively large intensities at lower masses suggests that there may be some hydrogen deuterium exchange for this molecule. Note that mass spectrometer ionizer fragmentation of  $C_4$  species may contribute to the ethylene signal. However, the integrated intensity of the  $C_4$  trace is significantly smaller than that for ethylene and does not effect the assignment of the 30 amu trace to ethylene. Only desorbing  $C_2$ ,  $C_4$  and  $C_6$  hydrocarbons were found.

The peak temperature of the ethylene state is at 295 K and that due to the  $C_4$  hydrocarbon is cen-

Table 1

Table showing the integrated intensity distribution in temperature programmed desorption for the reaction of  $^{13}C$ -acetylene with deuterium on Pd(111)

| Mass (amu) | Relative intensity (%) |
|------------|------------------------|
| 68         | 0                      |
| 67         | 0                      |
| 66         | 0                      |
| 65         | 0                      |
| 64         | 88                     |
| 63         | 73                     |
| 62         | 100                    |
| 61         | 72                     |
| 60         | 26                     |
| 59         | 0                      |
| 58         | 0                      |
| 57         | 0                      |
| 56         | 0                      |
| 55         | 0                      |

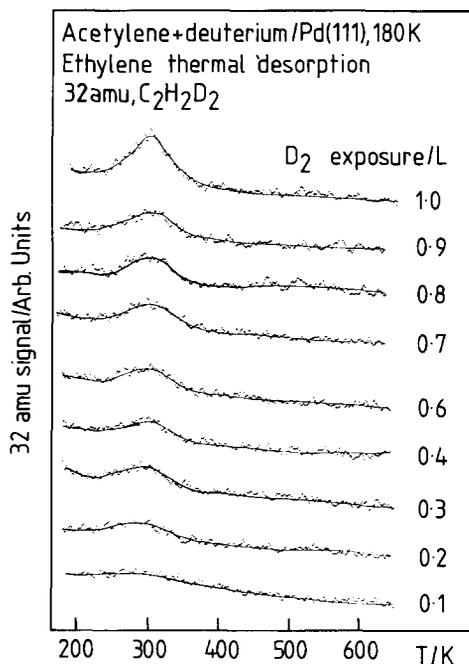


Fig. 2. 32 amu ( $d_2$ -ethylene) thermal desorption spectrum obtained by pre-dosing a Pd(111) surface with deuterium followed by exposure to  $^{13}\text{C}$ -acetylene (3 L) displayed as a function of deuterium exposure. The deuterium coverages corresponding to the various exposures in order of increasing exposure are 0.18, 0.31, 0.42, 0.50, 0.64, 0.70, 0.74, 0.78 and 0.8.

tered at 300 K. The peak position for hydrogen desorption is also marked on the spectra at  $\sim 350$  K and this serves to illustrate that a significant amount of hydrogen remains on the surface even though the rate of formation of hydrogenation products decreases. These results suggest that the precursors to ethylene and  $\text{C}_4$  hydrocarbon formation (adsorbed acetylene and a surface cyclobutadienyl species respectively) are being removed causing the product desorption rate to decrease. It has previously been shown that adsorbed acetylene converts to vinylidene on heating an acetylene-covered surface to somewhat above room temperature [10] and these effects will be discussed in greater detail below.

In order to establish whether vinylidene itself can react with chemisorbed atomic hydrogen during the thermal desorption sweep, the Pd(111) surface was saturated with acetylene at 180 K ( $\theta = 0.46$ ) and then annealed to 300 K (adsorbed acetylene converts to vinylidene under these conditions). The sample is then cooled to 180 K and exposed to 2 L of  $\text{D}_2$  and a

thermal desorption experiment is carried out. A large 4 amu signal is detected with a peak temperature at  $\sim 350$  K confirming that a substantial amount of hydrogen has adsorbed onto the vinylidene-covered surface. However, no hydrogenation products and, in particular, ethylene are detected indicating that the rate of vinylidene hydrogenation is substantially lower than that of hydrogen desorption. These results confirm that the conversion of acetylene to vinylidene would indeed result in a decrease in the rate of ethylene formation.

A series of ethylene thermal desorption spectra are shown in Fig. 2 (32 amu;  $^{13}\text{C}_2\text{H}_2\text{D}_2$ ) collected as a function of deuterium exposure and after then saturating the surface with acetylene ( $\theta = 0.46$ ). The deuterium exposures are marked adjacent to each spectrum and the corresponding deuterium coverages are indicated in the figure caption [23–25]. No significant signal is detected at 33 amu indicating that there is no substantial exchange between the acetylenic hydrogens and adsorbed deuterium. The low-coverage spectra exhibit a peak centered at  $\sim 290$  K which increases slightly in intensity and posi-

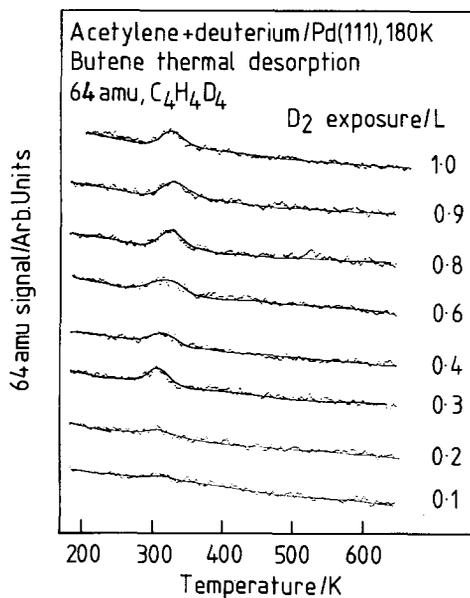


Fig. 3. 64 amu ( $d_4$ -butene) thermal desorption spectrum obtained by pre-dosing a Pd(111) surface with deuterium followed by exposure to  $^{13}\text{C}$ -acetylene (3 L) displayed as a function of deuterium exposure. The deuterium coverages corresponding to the various exposures in order of increasing exposure are 0.18, 0.31, 0.42, 0.50, 0.64, 0.70, 0.74, 0.78 and 0.8.

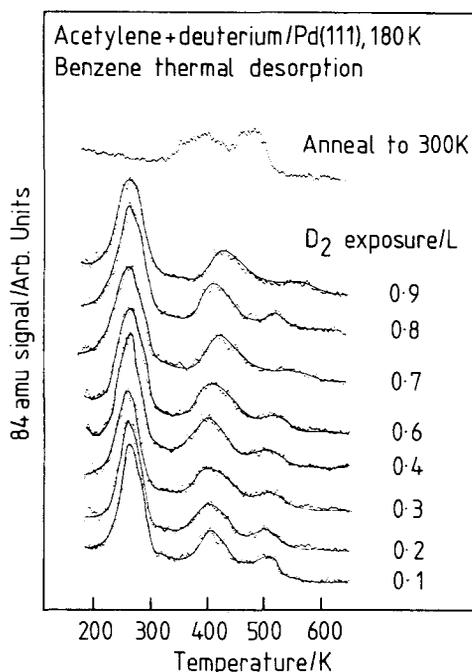


Fig. 4. 84 amu ( $^{13}\text{C}_6\text{H}_6$ ) thermal desorption spectrum obtained by pre-dosing a Pd(111) surface with deuterium followed by exposure to  $^{13}\text{C}$ -acetylene (3 L) displayed as a function of deuterium exposure. Shown also is a spectrum obtained by dosing with acetylene alone and by heating slowly to 300 K prior to collecting the spectrum. The deuterium coverages corresponding to the various exposures in order of increasing exposure are 0.18, 0.31, 0.42, 0.50, 0.64, 0.70, 0.74, 0.78 and 0.8.

tion with increasing deuterium coverage so that following a 1 L deuterium exposure ( $\theta(\text{D}) = 0.8$  [23–25]) the peak temperature has shifted to 320 K. These spectra are in agreement with previous results [6].

Fig. 3 displays the corresponding butene (64 amu;  $^{13}\text{C}_4\text{H}_4\text{D}_4$ ) desorption spectra which exhibit small peaks at  $\sim 310$  K at low coverages. Both the peak temperature and intensity increase with deuterium coverage so that the maximum butene desorption rate is at 330 K following a 1 L deuterium exposure ( $\theta(\text{D}) = 0.8$  [23–25]).

Finally, Fig. 4 shows a series of benzene desorption spectra (84 amu;  $^{13}\text{C}_6\text{H}_6$ ) as a function of deuterium exposure (where the corresponding coverages are given in the figure caption). The low-temperature (280 K) benzene desorption state is not significantly affected, even by the presence of a monolayer of deuterium, indicating that the  $\text{C}_4$  for-

mation kinetics and their rate of reaction to form benzene are not drastically altered by the presence of deuterium. In contrast, however, the high temperature benzene state is *considerably* modified, even after dosing the surface with only 0.1 L of deuterium ( $\theta(\text{D}) = 0.18$  [23–25]). The 520 K state, which is predominant in the absence of deuterium, is substantially diminished in intensity and a new state grows in at  $\sim 410$  K. A further slow decrease in intensity of the 520 K peak is noted with the addition of more deuterium as well as a corresponding increase in intensity of the 410 K peak.

A similar growth of the 410 K state is also found by slowly heating an acetylene-covered surface to 300 K. In this experiment, Pd(111) is saturated with acetylene at 180 K (with no hydrogen addition, to give an acetylene coverage of 0.46) and slowly warmed to 300 K using a heating rate of  $\sim 1$  K/s. This heating rate is too low to allow any desorbing species to be detected. The sample is then allowed to cool to 180 K and a normal thermal desorption

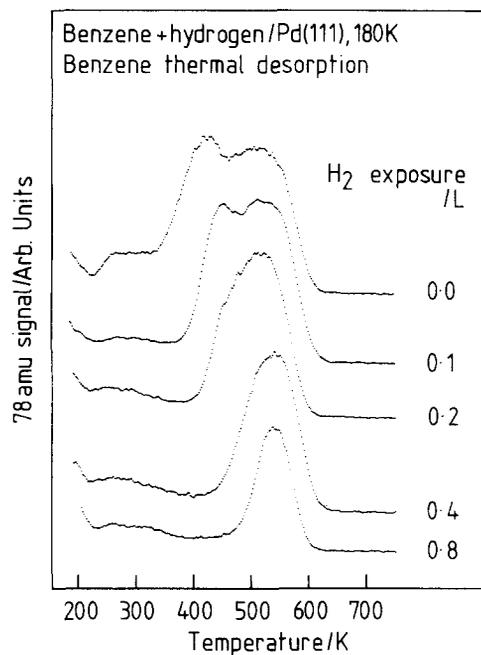


Fig. 5. 78 amu (benzene) thermal desorption spectra obtained by pre-dosing Pd(111) with hydrogen followed by 6 L exposure to benzene. Hydrogen exposures are marked adjacent to their corresponding spectra. The hydrogen coverages corresponding to the various exposures in order of increasing exposure are 0.18, 0.31, 0.50 and 0.74.

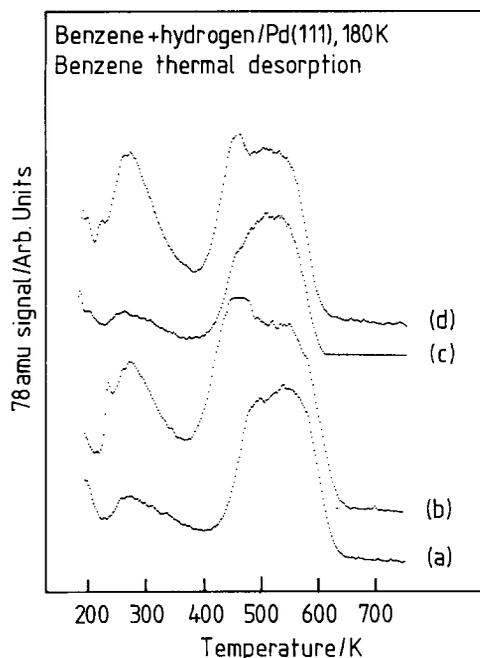


Fig. 6. 78 amu (benzene) thermal desorption spectra obtained following: (a) 0.4 L  $H_2$  ( $\theta(H) = 0.5$ ) then 6 L benzene; (b) 0.4 L  $H_2$  ( $\theta(H) = 0.5$ ) then 12 L benzene; (c) 0.8 L  $H_2$  ( $\theta(H) = 0.74$ ) then 6 L benzene; (d) 0.8 L  $H_2$  ( $\theta(H) = 0.74$ ) then 12 L benzene.

spectrum recorded using a heating rate of 8 K/s. The resulting trace is shown at the top of Fig. 4. Clearly, there is no desorption below the annealing temperature (300 K). Above 300 K, however, the usual 520 K state is present but an additional 410 K state appears in an identical position to that found when adding hydrogen. This result suggests that the yield of benzene is in some way kinetically limited and this will be discussed in greater detail below.

In order to establish whether hydrogen affects the benzene formation or desorption kinetics, a series of benzene thermal desorption spectra were collected as a function of hydrogen coverage and the results are displayed in Fig. 5. These experiments were performed by predosing the surface with hydrogen (exposures are marked adjacent to each spectrum and the corresponding coverages given in the caption) and subsequently dosing with 6 L of benzene both at 180 K (corresponding to the formation of a saturated overlayer on the clean surface [17]; exposures are uncorrected for ionization gauge sensitivity). Shown for comparison is the corresponding spectrum for a

clean surface (0 L) which displays two principal desorption states at 520 and 410 K due to benzene desorption [17]. A smaller state is noted at  $\sim 280$  K and the origin of these peaks has been discussed in detail elsewhere [17,18]. Increasing the hydrogen exposure initially results in a diminution and slight shift in position of the benzene peak so that the spectrum obtained following a 0.4 L exposure to hydrogen ( $\theta(H) = 0.5$ ) consists of a single feature at  $\sim 550$  K. This peak decreases further in intensity with increasing hydrogen coverage. However, according to the results shown in Fig. 6, the original benzene desorption spectrum (consisting of peaks at 410 and 520 K) can be recovered merely by increasing the benzene exposure. Shown in Fig. 6a is the benzene desorption spectrum obtained by pre-dosing the surface with 0.4 L of hydrogen ( $\theta(H) = 0.5$ ) and then exposing to 6 L of benzene (reproducing the spectrum shown in Fig. 5). Fig. 6b shows the result of increasing the benzene exposure to 12 L; the original features are recovered. Similar results are obtained in Figs. 6c and 6d for an 0.8 L hydrogen exposure ( $\theta(H) = 0.75$ ). These results suggest that the effect of pre-adsorbed hydrogen is to decrease the benzene sticking probability but not modify the desorption kinetics from the surface.

#### 4. Discussion

The overall reaction pathway for acetylene cyclotrimerization is now well established. Initially, adsorbed acetylene dimerizes at  $\sim 200$  K to form a tilted metallocycle,  $C_4H_4$ , [16] which reacts with further acetylene [19] forming benzene. Reactively formed benzene cannot be accommodated on the surface in a flat-lying configuration so that sterically crowded benzene desorbs at  $\sim 280$  K. Remaining flat-lying benzene desorbs at  $\sim 520$  K. The formation of both ethylene (Figs. 1 and 2) and  $C_4$  hydrocarbons (Figs. 1 and 3) is consistent with the presence of both  $C_2$  and  $C_4$  species respectively on the surface.

A leading edge-plot of the thermal desorption data shown in Fig. 1 yields an activation energy for acetylene hydrogenation to ethylene of  $22.6 \pm 0.8$  kJ/mol. The activation energy of palladium-catalyzed acetylene hydrogenation is  $\sim 46$  kJ/mol [11–

13]; substantially larger than the activation energy for this process measured here in ultra-high vacuum. A similar effect is noted for Pt(111)-catalyzed ethylene hydrogenation where an activation energy of  $\sim 33$  kJ/mol is measured in UHV [20] compared to a value of 45 kJ/mol for the high-pressure reaction [21]. Since it has been shown above that vinylidene does not react with hydrogen under ultra-high vacuum conditions, it must be concluded that ethylene is formed by the reaction of hydrogen with flat-lying acetylene. The detection of predominantly  $d_2$ -ethylene is in accord with this view and implies almost no H–D exchange on the surface in this temperature range. The detection of butene is consistent with the presence of surface  $C_4H_4$  species although its desorption temperature is slightly higher than that of acetylene (320 K compared to 300 K). Curiously, however, no butadiene is detected in contrast to the results for reaction between low concentrations of hydrogen and acetylene catalyzed by supported palladium [5].

The data of Fig. 2 show that the ethylene yield increases with increasing deuterium coverage. Since ethylene arises from a reaction between adsorbed hydrogen and acetylene (as opposed to vinylidene), the total ethylene desorption yield  $Y$  from the surface reaction is given by:

$$Y = \int \theta_{\text{hyd}}(T)^n \theta_{\text{acety}}(T) \exp(-E_{\text{act}}/RT) dT/\beta, \quad (1)$$

where  $\theta_{\text{hyd}}(T)$  is the hydrogen coverage and  $\theta_{\text{acety}}(T)$  the acetylene coverage respectively as a function of temperature,  $E_{\text{act}}$  is the reaction activation energy ( $\sim 22.6$  kJ/mol) and  $\beta$  the heating rate.  $n$  is the order of reaction with respect to hydrogen coverage and the reaction is assumed to be first order in acetylene coverage. Fig. 7 shows an ethylene temperature-programmed desorption profile for a 1 L  $D_2$  ( $\theta(D) = 0.8$ ) exposure followed by a saturation exposure to acetylene ( $\theta(C_2H_2) = 0.46$ ; taken from Fig. 2) compared with a plot of hydrogen coverage as a function of temperature using parameters for the desorption of hydrogen from Pd(111) established using molecular beam experiments [22]. It is clear that the hydrogen coverage remains constant throughout most of the ethylene desorption trace and only decreases when the ethylene desorption rate has

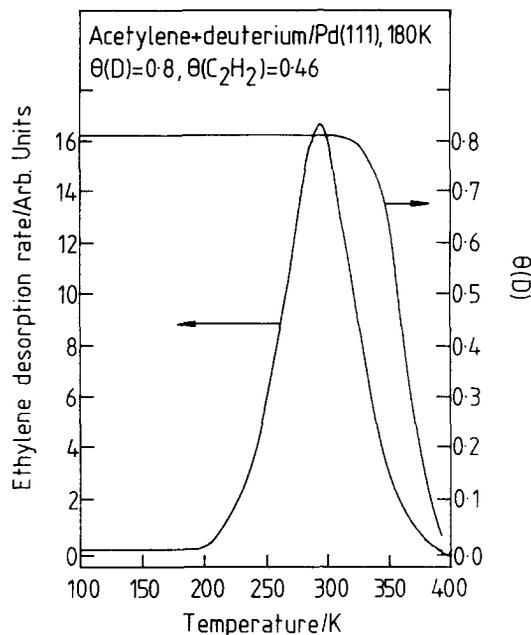


Fig. 7. The thermal desorption trace obtained following an exposure of 1 L of deuterium ( $\theta(D) = 1.0$ ) and then saturating the surface with acetylene, compared with the coverage of deuterium on the surface as a function of temperature during the desorption sweep.

more or less diminished to zero. If the total yield  $Y$  is measured only up to a temperature at which the hydrogen coverage remains constant (in this case  $\sim 320$  K), then Eq. (1) for this value, designated  $Y_{320}$ , becomes:

$$Y_{320} = \theta_{\text{hyd}}(T)^n \int_{200}^{320} \theta_{\text{acety}}(T) \times \exp(-E_{\text{act}}/RT) dT/\beta, \quad (2)$$

since the constant hydrogen coverage can now be factored out of the integral. In addition, since the initial acetylene coverage is constant for all experiments, the integral in Eq. (2) is also constant for all of the experiments displayed in Fig. 2. Thus, Eq. (2) can be rewritten as:

$$Y_{320} = A \theta_{\text{hyd}}(T)^n, \quad (3)$$

where  $A$  is a constant. The slope of a plot of  $\ln(Y_{320})$  versus  $\ln \theta_D$ , where  $\theta_D$  is the deuterium coverage, yields the reaction order  $n$  directly. Such a plot is shown in Fig. 8. In this case, exposures have been converted to coverages using literature data [23–25].

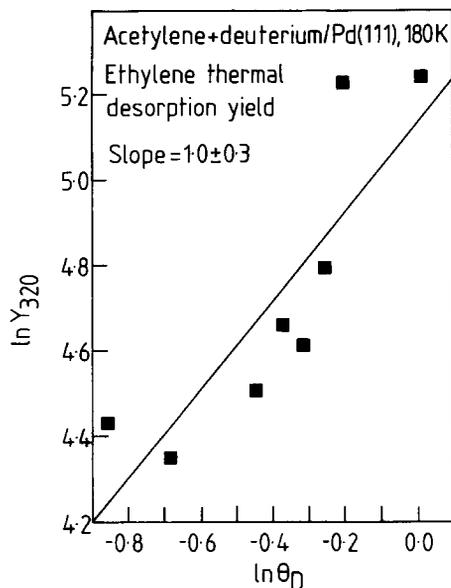


Fig. 8. Plot of  $\ln(Y_{320})$  versus  $\ln\theta_D$ , where  $Y_{320}$  is the ethylene thermal desorption yields for the reaction of acetylene and hydrogen up to a surface temperature of 320 K and  $\theta_D$  is the deuterium coverage.

The slope of this curve is  $1.0 \pm 0.3$  so that the reaction between acetylene and hydrogen on the surface is first order in hydrogen coverage. The activation energy of the reaction has been measured above as 22.6 kJ/mol and this suggests that this is the activation energy of addition of a single hydrogen atom from the surface.

The leading edge portion of the ethylene thermal desorption trace reflects the temperature dependence of the reaction rate constant. Conventionally in thermal desorption, the trailing edge of the trace is due to depletion of the reactant because of its desorption. However, in this case, the results of Fig. 7 demonstrate that loss of hydrogen is not responsible for the decrease in ethylene desorption rate at higher temperatures and this must therefore be due to the loss of acetylene from the surface. Acetylene converts to vinylidene between 200 and 300 K and the experiments described above demonstrate that vinylidene does not react with hydrogen under ultra-high vacuum conditions. The rate of ethylene formation is given by:

$$d\theta(\text{ethylene})/dt = A\theta_D(T)\theta_A(T)\exp(-E_{\text{act}}/RT), \quad (4)$$

where  $\theta_D$  and  $\theta_A$  are the temperature-dependent deuterium and acetylene coverages respectively and  $E_{\text{act}}$  is the reaction activation energy (measured at 22.6 kJ/mol). The temperature dependence of the deuterium coverage  $\theta_D(T)$  can be found using literature data [22–25] and this is displayed in Fig. 9 along with the corresponding ethylene desorption trace (and reproduce the data of Fig. 7 for clarity). The kinetic parameters for the conversion of acetylene to vinylidene are completely unknown except that, from photoelectron spectroscopic data, the transformation occurs between  $\sim 200$  and 300 K [1,10]. It is assumed that the conversion of acetylene to vinylidene is first order in acetylene coverage, and the temperature dependence of the acetylene coverage  $\theta_A(T)$  is varied to yield the best fit to the experimental thermal desorption data (Fig. 9). The activation energy and pre-exponential factor for acetylene-to-vinylidene conversion are adjusted to yield the best fit to the experimental ethylene desorption profile using a non-linear least-squares program

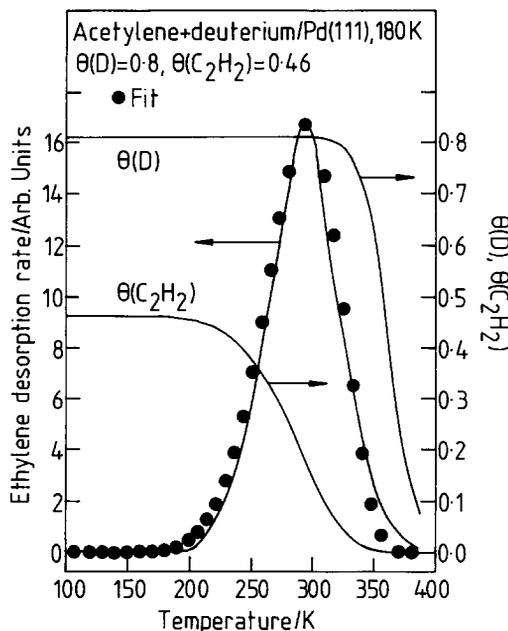


Fig. 9. The thermal desorption trace obtained following an exposure of Pd(111) to 1 L of deuterium and the saturating the surface with acetylene, compared with the coverage of deuterium on the surface during the desorption sweep. Shown also is the acetylene coverage during the sweep calculated to give the best fit to the thermal desorption data (●).

using both Monte Carlo and thermal-annealing algorithms. The result of the fit to the ethylene desorption trace is shown in Fig. 9 (●) and agrees well with the experimental profile (—). The calculated activation energy for the conversion is  $16 \pm 2$  kJ/mol and the pre-exponential factor is  $600 \pm 200$  s<sup>-1</sup>. The resulting variation in acetylene coverage calculated using these parameters as a function of temperature is also displayed in Fig. 9 (—). Note that the range over which the adsorbed acetylene disappears and vinylidene is formed (between 200 and 350 K) is consistent with that found by analyzing the surface using photoelectron spectroscopy [1,10]. The low value of the pre-exponential factor for the conversion indicates that this does not occur as a single step.

It should be noted that the conversion of acetylene to vinylidene also potentially provides a route by which the surface crowding of reactively formed benzene can be relieved to allow it to adopt a flat-lying configuration and the temperature interval over which this occurs (200–350 K) is within the range that benzene desorbs from the surface in the low-temperature state (with a peak centered at  $\sim 280$  K).

The C<sub>4</sub> hydrocarbon yield also increases with increasing hydrogen exposure (Fig. 3). In this case, adsorbed acetylene must first react forming surface C<sub>4</sub>H<sub>4</sub> species which then hydrogenates. The complexity of this reaction precludes a similarly simple analysis of these data.

The shape of the benzene desorption spectra (Figs. 1 and 4) is significantly modified by hydrogen addition. Here, the 520 K desorption peak is attenuated to be replaced by a peak at 410 K; the onset of this process occurring at hydrogen exposures of  $< 0.1$  L corresponding to  $\theta(\text{H}) \approx 0.2$ . The yields of hydrogenation products are negligible at this coverage so that such an effect cannot be attributed to the removal of reactants. Note also that the total benzene yield is not substantially affected by co-adsorbed hydrogen. Indeed, the low-temperature (280 K) desorption peak remains essentially unaffected by the presence of hydrogen although some attenuation in this peak may be observed at higher hydrogen exposures ( $\sim 1.0$  L;  $\theta(\text{H}) \approx 0.8$ ). It has been shown that adsorbed benzene completely thermally decomposes on clean Pd(111) at low coverages ( $\theta(\text{benzene}) <$

0.05)) yielding hydrogen and leaving carbon on the surface [17]. Such a decomposition pathway is not observed for benzene reactively formed from acetylene. A possible explanation for this effect is that surface carbon formed by vinylidene decomposition inhibits benzene decomposition. Such an inhibition has been observed previously in the chemistry of benzene itself on Pd(111) where benzene desorbs molecularly from Pd(111) at coverages above 0.05 because intermolecular repulsive interactions between adjacent benzene molecules facilitates desorption and the occupation of neighboring sites also inhibits decomposition [17,18]. It is possible that a similar role is played by co-adsorbed carbon. Hydrogen co-adsorbed with acetylene may influence the kinetics of carbon formation on the surface and hence the desorption kinetics of reactively formed benzene. This view is given credence by the results displayed in Fig. 4 which also show the effect on the benzene thermal desorption spectrum of slowly annealing an acetylene-covered surface to 300 K prior to thermal desorption at a heating rate of 8 K/s. The desorption trace in this case bears a striking resemblance to that obtained in the presence of pre-adsorbed hydrogen (Figs. 1 and 4). A possible explanation for the effect, in this case, may be that the branching ratio for competing vinylidene and benzene formation reactions from flat-lying acetylene and C<sub>4</sub>H<sub>4</sub> precursors is also likely to be effected by the heating rate since both of these reactions occur between 200 and 300 K. Since adsorbed vinylidene decomposes at  $\sim 450$  K to yield surface carbon and desorb hydrogen, differences in the rate at which the sample is annealed to 300 K may also result in differing amounts of surface carbon. If this effect is true, it should be noted that the acetylene-to-vinylidene conversion kinetics measured here for a surface covered by hydrogen and those for a hydrogen-free surface may be different.

## 5. Conclusions

Both ethylene and butene are formed by reaction of hydrogen with acetylene on Pd(111) confirming the presence of surface acetylene monomers (C<sub>2</sub>H<sub>2</sub>) and dimers (C<sub>4</sub>H<sub>4</sub>) in accord with previous spectroscopic results. The activation energy for ethylene

formation is measured at  $22.6 \pm 0.8$  kJ/mol and the reaction is shown to be first order in hydrogen coverage. The high-temperature ( $> 300$  K), reactively formed benzene desorption kinetics are substantially modified by hydrogen pre-dosing, a phenomenon that is ascribed to the effect of hydrogen on the relative vinylidene and benzene formation rates rather being due to any effect that hydrogen has on the benzene that has been formed. The kinetics parameters for the conversion of acetylene to vinylidene *in the presence of co-adsorbed hydrogen* are measured from the thermal desorption trace and yield and activation energy of  $16 \pm 2$  kJ/mol and a pre-exponential factor of  $\sim 600$  s<sup>-1</sup>.

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