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The Hydrogenation of Acetylene Catalyzed by Palladium: Hydrogen Pressure Dependence

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The kinetics of acetylene hydrogenation catalyzed by a clean palladium foil at high pressures are measured and yield an activation energy of 9.6 ± 0.1 kcal/mol when using hydrogen. The rate exhibits a deuterium isotope effect such that the reaction activation energy is 9.0 ± 0.2 kcal/mol for reaction with deuterium. The hydrogen pressure reaction order is 1.04 ± 0.02 at 300 K with an acetylene pressure of 100 Torr and the acetylene order is −0.66 at 300 K and with a hydrogen pressure of 100 Torr. These reaction kinetics closely mimic those of supported model catalysts. In addition, it is found that the rate of benzene formation is accelerated by the addition of hydrogen to the reaction mixture. This is rationalized by proposing that hydrogen enhances the coverage of acetylene under catalytic conditions. This notion can be used to successfully calculate the hydrogen pressure dependence for acetylene hydrogenation as a function of temperature, a value which varies between ∼1.05 and 1.3 as the temperature changes from 300 to 380 K. Possible origins for this effect are discussed.

Key Words: **acetylene; hydrogenation; benzene formation; kinetics; hydrogen pressure dependence; palladium; model catalyst; isotope effect.**

INTRODUCTION

Palladium has a unique ability to selectively hydrogenate alkynes since it is capable of hydrogenating small concentrations of alkynes to alkenes in the presence of a large excess of alkene and so, for example, it is used for preparing extremely pure ethylene feedstocks for subsequent polymerization reactions (1–4). The origin of this high selectivity is not well understood (5–7) but presumably arises either from differences between the relative heats of adsorption of ethylene and acetylene on palladium (4) or their relative subsequent reactivities with hydrogen. Studies in ultrahigh vacuum reveal that acetylene adsorbs much more strongly on palladium than does ethylene (8, 9). In addition, both ethylene and acetylene can undergo an array of other surface reactions. The most striking of these is the formation of benzene from acetylene on Pd(111) which has been demonstrated to form by reaction between acetylene and an intermediate metallocyclic C_4H_4 species (10, 11). In addition, adsorbed acetylene has been shown to convert into vinylidene on warming to ∼300 K (12). It has been demonstrated that vinylidene is very unreactive so that adsorbed acetylene is the precursor to benzene formation in ultrahigh vacuum and also reacts with hydrogen to yield ethylene. Thus, *under ultrahigh vacuum conditions*, vinylidene neither reacts with adsorbed hydrogen, nor does it react to form benzene. It has, however, recently been demonstrated that under high-pressure, catalytic conditions, acetylene and vinylidene can combine to yield a C_4H_4 intermediate that finally leads to benzene formation (13). The saturation coverage of vinylidene is unity (where coverages are referenced to the number density of palladium substrate atoms) (9) but it has been demonstrated in several cases that reactants can adsorb onto the metal surface even in the presence of such a carbonaceous layer. Thus ethylene can adsorb on an ethylidyne-covered surface (14, 15) and CO can adsorb onto a Mo(100) single crystal surface covered by a thick (∼8 monolayers) carbonaceous layer (16) as well as on a vinylidene-covered surface (17).

The kinetics of acetylene hydrogenation to ethylene, catalyzed by a model palladium metal catalyst, carried out at high pressures, are described below. This reaction catalyzed by supported palladium has been investigated previously where the activation energy has been shown to be ∼11.0 kcal/mol (18–20). The reaction kinetics are rather complicated and contradictory where, according to one report, the hydrogen pressure dependence is 1.0 at 273 and 303 K but changes to 1.4 at 400 K (18) but, according to another, displays no temperature dependence (19). The acetylene pressure dependence is negative and varies between −0.55 and −0.67, depending on temperature and hydrogen pressure (20).

We have therefore measured the acetylene hydrogenation kinetics for a reaction catalyzed by palladium using a high-pressure reactor incorporated into an ultrahigh vacuum chamber, for two main reasons. The first is to determine whether a palladium foil model catalyst mimics the activity of the supported catalyst to establish whether it

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provides a suitable model system for the working catalyst. Despite the extensive surface science investigations that have been undertaken on palladium, this has not yet been established. Second, it is also found that the rate of benzene formation is accelerated by the addition of hydrogen to the reaction mixture, an effect that has been observed previously using alumina-supported palladium (21). It is therefore postulated in the following that hydrogen causes an increase in the coverage of acetylene on the surface. This postulate leads to a successful prediction of the variation in hydrogen pressure dependence of the hydrogenation reaction with temperature which can be related to the enhancement in benzene formation rate. Possible origins for this effect are also discussed below.

EXPERIMENTAL

The apparatus that was used for these experiments has been described in detail elsewhere (22, 23). Briefly, however, it consists of a bakeable, stainless-steel, ultrahigh vacuum chamber operating at a base pressure of 1×10^{-10} Torr following bakeout. It is equipped with a quadrupole mass analyzer for residual gas analysis, leak testing, and temperature-programmed desorption studies.

The apparatus also incorporates a co-axial, high-pressure reactor which can be sealed and filled to 1 atm while maintaining ultrahigh vacuum ($\sim 2 \times 10^{-10}$ Torr) in the rest of the apparatus. This is attached to a loop and the gas recirculated by a pump. The pressure is monitored by means of a capacitance manometer and the gas composition analyzed by diverting aliquots of the gas mixture to a gas chromatograph equipped with a 1-m-long column packed with Poropak-N and products were detected using a flame-ionization detector, where the resulting current is amplified by a Keithly picoammeter and collected using a computer for subsequent analysis. The reaction rate is measured directly from the product accumulation curve for low ($<1\%$) conversions. The low area of the model catalyst (~ 1 cm^2) means that, even at these low conversions, each site has catalyzed many reactions.

The palladium foil sample is attached to the end of the sample manipulator and can be resistively heated to $\sim$2000 K or cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir. A palladium foil is used as a model hydrogenation catalyst rather than an oriented single crystal since palladium adsorbs large amounts of hydrogen which can potentially destroy the crystallinity of the sample. The sample is cleaned using a standard procedure which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and the annealing at 1200 K *in vacuo* to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly in intensity. The complete absence of carbon is indicated by the desorption of only O_2.

The acetylene used for these experiments (Linde, Purified grade) was transferred from the cylinder to a glass bottle and further purified by repeated bulb-to-bulb distillations and its cleanliness monitored either mass spectroscopically or using the gas-chromatograph. The hydrogen, deuterium, and nitrogen (Linde, Ultrahigh Purity grade) were used without further purification. In all experiments, the high-pressure reactor was ballasted to 1 atm using nitrogen to ensure that the gas circulation rates were identical for all experiments.

RESULTS

A palladium foil sample catalyzes the hydrogenation of acetylene and reaction rates are calculated for low conversions (below $\sim$1%). As noted above, one of the rationales for studying acetylene hydrogenation catalyzed by palladium is its unique properties as a highly selective catalysts. Other products found in the reaction are C_4 compounds (primarily butene) and benzene and some ethane. Benzene is also formed following acetylene adsorption on Pd(111) in ultrahigh vacuum (8, 9) and this reaction is effectively catalyzed by the single crystal (24). This forms via the rapid initial formation of a C_4 metallocycle which then reacts with adsorbed acetylene to yield benzene (10, 11). The detection, therefore, of butene and benzene is entirely consistent with this surface chemistry. In addition, a small amount of ethane is detected due to further hydrogenation to ethylene. The selectivity to ethylene S is shown plotted as a function of hydrogen pressure when using 100 Torr of hydrogen at 300 K in Fig. 1. In this case, the selectivity is defined as

$$S = \frac{r(C_2H_4)}{\sum_{\text{products}} r(\text{products})},$$

where $r(C_2H_4)$ is the rate of ethylene formation and r(product) is the rate of formation of reaction products including ethylene so that $0 < S < 1$. As expected, the selectivity increases with increasing hydrogen pressure to attain a maximum for hydrogen pressure of 200 to 300 Torr and then remains constant or decreases slightly to a relatively low value of $\sim$32%. The other products are, as noted above, benzene and C_4 hydrocarbons. The corresponding data for the selectivity as a function of catalyst temperature when using 100 Torr of both ethylene and hydrogen are displayed in Fig. 2. Here the selectivity increases drastically with

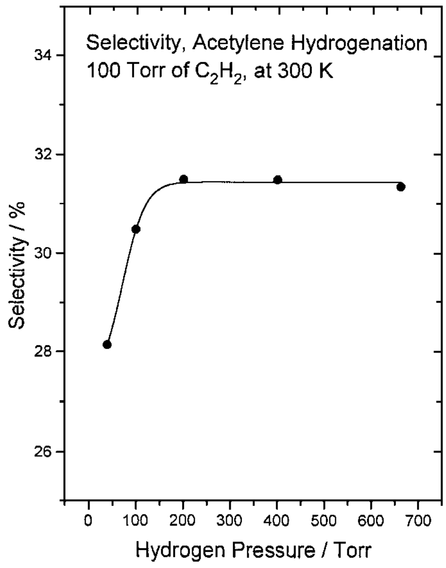

FIG. 1. The selectivity to ethylene as a function of hydrogen pressure when using 100 Torr of ethylene at 300 K for acetylene hydrogenation catalyzed by palladium.

increasing temperature from ~30% at 300 K to ~94% at 470 K.

The temperature dependence for acetylene hydrogenation measured both using hydrogen and deuterium is shown in Fig. 3. This reveals a normal isotope effect, where the ratio of the reaction rates with hydrogen and deuterium is 1.9 ± 0.3 at 300 K. This result indicates that hydrogen is involved in the rate-limiting step at the surface. The reaction activation energy when using hydrogen is 9.6 ± 0.2 kcal/mol

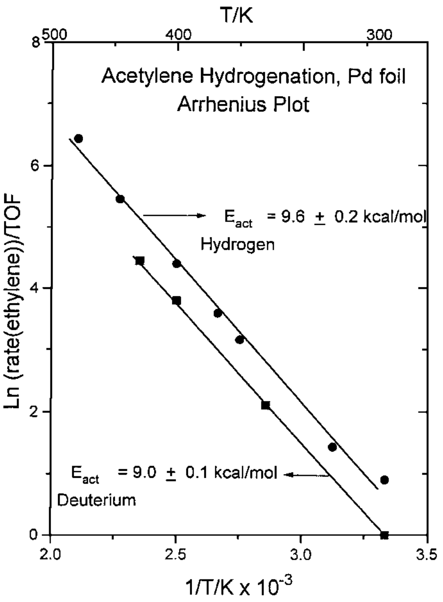

FIG. 3. Arrhenius plot of ln(rate) versus 1/T for the temperature dependence of the palladium-catalyzed hydrogenation of acetylene (100 Torr) when using hydrogen as a reactant (100 Torr) (●). The corresponding Arrhenius plot when using deuterium is also shown (■).

and the value when using deuterium is 9.0 ± 0.1 kcal/mol. These values of activation energy agree well with those obtained by previous workers (11.0 ± 0.5 (18), 10.6 ± 0.5 kcal/mol (19), and 11.0 ± 0.5 (20)).

The hydrogen pressure dependence is shown in Fig. 4 at a reaction temperature of 300 K using an acetylene pressure

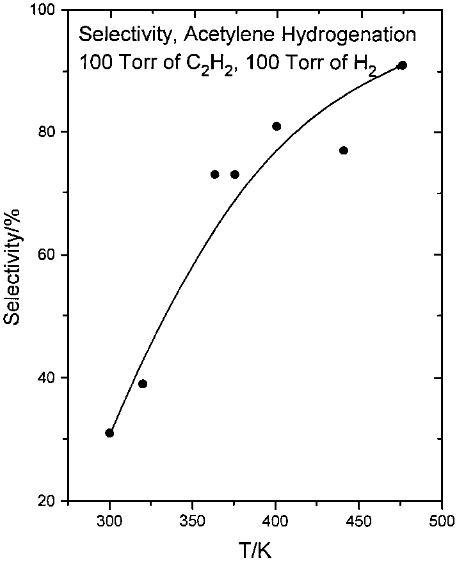

FIG. 2. The selectivity to ethylene as a function of temperature when using 100 Torr of acetylene and 100 Torr of hydrogen for acetylene hydrogenation catalyzed by palladium.

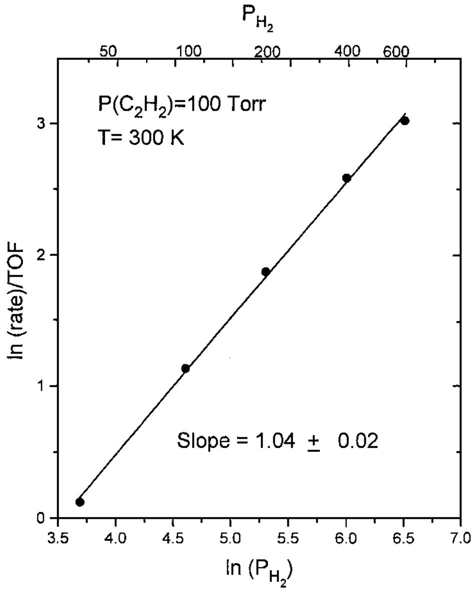

FIG. 4. The hydrogen pressure dependence of acetylene hydrogenation catalyzed by palladium plotted as ln(rate) versus ln(P(H_2)), where P(H_2) signifies hydrogen pressure for reaction at 300 K using 100 Torr of acetylene.

of 100 Torr over a wide hydrogen pressure range from 20 to 600 Torr and shows a very linear plot with a reaction order of 1.04 ± 0.02. This value is also in good agreement with that measured in other work (17–19) and the error limits imply that the reaction kinetics are slightly faster than first order and the difference from unity is greater than the experimental error. This will be discussed in greater detail below.

The corresponding acetylene pressure dependence measured using a hydrogen pressure of 100 Torr at 300 K, again over a wide acetylene pressure range from 5 to 300 Torr, also yields a good straight line corresponding to a reaction order of −0.66 ± 0.02. This is again within the range of values measured by others where between −0.55 and −0.67 have been measured by Bond (18), depending on temperature and pressure, between −0.4 and −0.6 by Yasunobu *et al.* (19) and −0.5 by Grignon-Dumoulin *et al.* (20).

As noted above, benzene is also found in the reaction products, consistent with previous observations that palladium is an effective acetylene cyclotrimerization catalyst. It has been shown previously using high-surface-area catalysts that the benzene formation rate on a freshly prepared catalysts is very large and diminishes to a low, steady-state rate with time on-stream (21). Interestingly, at least part of this initial high activity could be recovered by adding hydrogen (21). This effect is illustrated on this model system in Fig. 5 which displays the rate of benzene formation at 300 K using 100 Torr of acetylene as a function of hydrogen pressure. The rate with no added hydrogen present is in good agreement with that found elsewhere (24) and the rate increases linearly with hydrogen pressure and so it is well represented by

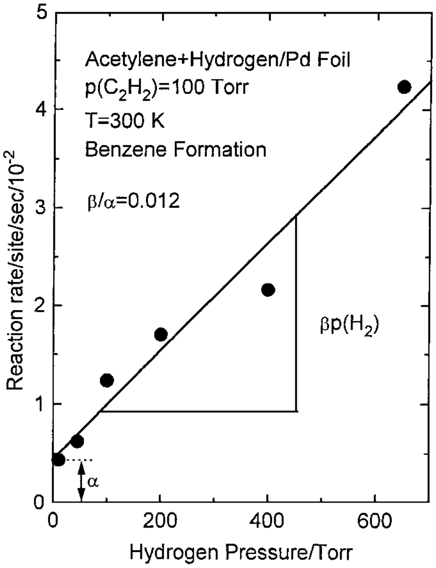

FIG. 5. The effect of hydrogen on the rate of benzene formation for a reaction catalyzed by a palladium foil. The reaction temperature is 300 K and the acetylene pressure is 100 Torr.

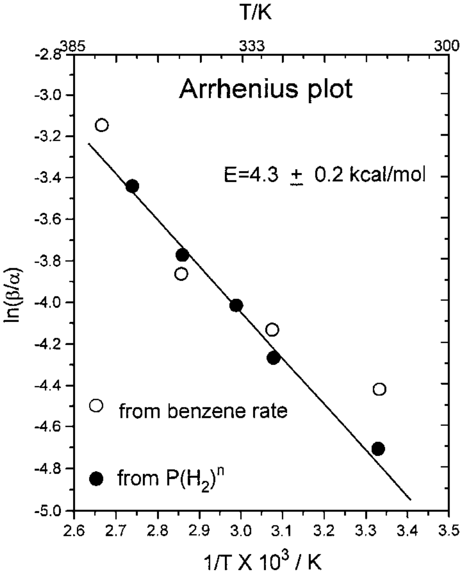

FIG. 6. An Arrhenius plot of ln(β/α) versus 1/T, where (β/α) is (a) measured directly from the variation in benzene formation rate as a function of hydrogen pressure at various temperatures (○) and (b) from the hydrogenation reaction order in hydrogen (see text) (●).

$$R(C_6H_6) \propto \alpha + \beta P(H_2) \qquad [1]$$

so that the rate increases linearly with hydrogen pressure, where α represents the rate without any hydrogen present (24) and β represents the effect of hydrogen and are illustrated in Fig. 5. This equation can be simply rewritten as

$$R(C_6H_6) \propto (1 + (\beta/\alpha)P(H_2)) \qquad [2]$$

and the data of Fig. 5 show that $(\beta/\alpha) = 1.2 \pm 0.1 \times 10^{-2}$ at 300 K using 100 Torr of acetylene. The value of (β/α) was also measured as a function of temperature from 300 to 365 K using 100 Torr of acetylene by repeating the experiment that resulted in the plot shown in Fig. 5 at several temperatures. The resulting Arrhenius plot (ln(β/α) versus 1/T) is displayed in Fig. 6 (○). The origin of the other data plotted on this curve (●) will be discussed below.

The corresponding temperature dependence of the reaction order was also measured using an acetylene pressure of 100 Torr over the temperature range 300 to 365 K and the results are displayed in Fig. 7, where the reaction order varies with temperature from ∼1.05 at 300 K (Fig. 4) to ∼1.25 at 365 K.

In general, an additional potential advantage to studying catalytic reactions using an isolatable high-pressure reactor is that the nature of the surface can be analyzed following reaction. Unfortunately, this was not possible in this case using the analytical tools available in this vacuum chamber since the carbon KLL Auger feature is effectively obscured by a palladium peak which renders this essentially

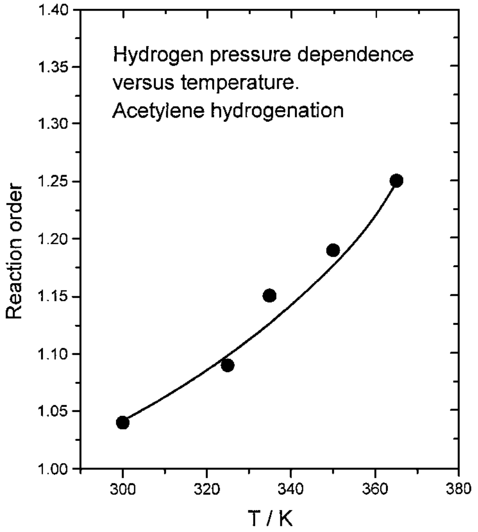

FIG. 7. The hydrogen pressure dependence plotted as a function of reaction temperature for palladium-catalyzed acetylene hydrogenation using 100 Torr of acetylene.

useless for monitoring the amount of carbon on the surface. In addition, since palladium can absorb a large amount of hydrogen into the bulk of the sample, hydrogen temperature-programmed desorption is also not a very sensitive measure of the nature of the species present on the surface.

DISCUSSION

Palladium provides an effective hydrogenation catalyst. The activation energy for the reaction is 9.6 ± 0.2 kcal/mol when using hydrogen and 9.1 ± 0.1 kcal/mol when using deuterium (Fig. 3) and the rates are proportional to $p(H_2)^{1.04\pm0.02}$ (Fig. 4) and $p(C_2H_2)^{-0.66\pm0.02}$. Note that all of the rates presented here are calculated as turnover frequencies by assuming that the palladium site density on the polycrystalline foil is equal to that on the (111) face of palladium. Since this is the lowest energy face, this is likely to be the predominant facet on an annealed foil. In addition, the integrated area of the infrared spectrum of CO adsorbed at 80 K on the foil and on a Pd(111) single crystal agree within 15% confirming the validity of this assumption. This allows a reaction rate to be given as

$$\text{rate} = 5 \pm 1 \times 10^6 p(H_2)^{1.04\pm0.02} p(C_2H_2)^{-0.66\pm0.02} \times \exp(-9600 \pm 200/RT) \text{ reactions/site/s.}$$

These kinetics are typical for transition-metal catalyzed hydrogenation reactions which have reaction activation energies ~10 kcal/mol, a zero or negative order in hydrocarbon pressure and some positive order between ~1.0 and ~1.5 in hydrogen pressure. These values are also in very good agreement with kinetic data collected for other supported palladium catalysts (18–20) and therefore suggest that a palladium foil provides a good model for a supported acetylene hydrogenation catalyst. The data of Fig. 1 show that the selectivity *S* increases with hydrogen pressure for low pressure and then reaches a plateau and the data of Fig. 2 show that the selectivity also increases with temperature so that, at the very highest temperatures, palladium provides a reasonably selective catalyst.

The other products that are found from the reaction are C_4 hydrocarbons and benzene as well as some ethane. The amount of ethane formed in the reaction is in fact rather small, particularly for low conversions suggesting that ethylene rapidly desorbs from the surface immediately after it is formed and has little chance to hydrogenate further. Certainly ultrahigh vacuum experiments show that ethylene adsorbs only weakly on palladium (111) and thermally desorbs below 300 K (9). The low conversions used for the kinetic measurements means that the chance of subsequent product reaction is very low. The formation of C_4 and C_6 species is also in accord with the surface chemistry found in ultrahigh vacuum since palladium catalyzes the cyclotrimerization of acetylene to benzene via a C_4H_4 metallocyclic intermediate (10, 11). The gas-phase C_4 product presumably arises from the hydrogenation of this intermediate and C_4 hydrocarbons are also detected in temperature-programmed desorption when acetylene is adsorbed on a hydrogen precovered surface (12). The increase in selectivity as the hydrogen pressure increases can be explained in terms of this model since increasing the hydrogen pressure increases the rate of acetylene hydrogenation relative to the rate of dimerization so that less C_4 hydrocarbons are formed.

Note, however, that the benzene formation rate *increases* with increasing hydrogen pressure (Fig. 5). In fact, the opposite would be expected based on the above assertion that the selectivity increases due to loss of acetylene from the surface. The surface chemistry of acetylene has been studied extensively on Pd(111). Two forms of adsorbed acetylene have been detected, one a flat-lying acetylene which is the precursor to benzene formation (11) which can also react with adsorbed atomic hydrogen to form ethylene (25). The other is a vinylidene species ($CH_2{=}C{=}$) that forms when an acetylene-covered surface is heated to ~300 K (12). This species binds more strongly to the palladium surface and is unreactive in ultrahigh vacuum. The activation energy measured for acetylene hydrogenation by temperature-programmed desorption is 5.4 ± 0.2 kcal/mol (25), compared with 9.6 ± 0.2 kcal/mol for the catalytic reaction measured here. It has also been demonstrated that acetylene hydrogenation is first order in hydrogen coverage in ultrahigh vacuum (25). This would be expected to lead to an approximately zero to half-order hydrogen pressure dependence assuming dissociative adsorption, whereas an order close to unity is found experimentally (see above). Note that recent molecular beam studies of *ethylene* hydrogenation catalyzed by platinum also show a reaction rate proportional to $\Theta(C_2H_4)^{1.2}\Theta(H)^{0.8}$ on Pt(111) in accord with this view (26). Clearly, then, there are large disparities between the reaction kinetics measured in ultrahigh vacuum and at high pressures. One obvious difference between the nature of the sample in ultrahigh vacuum and under high external pressures is the presence of a strongly bound, relatively unreactive hydrocarbon species present on the surface in the latter case. Such hydrocarbons are found on the surface of model catalysts after reaction both on platinum (27) and molybdenum (28) and recent sum-frequency generation (SFG) (14, 15) and reflection– absorption infrared spectroscopy (RAIRS) (29) experiments have confirmed the presence of such strongly bound hydrocarbons *during* reaction at high pressures. It is likely that the vinylidene species referred to above (12) are also present on the catalyst surface during acetylene hydrogenation. It has been suggested, based on SFG data, that ethylene can adsorb on the surface in spite of the presence of an ethylidyne layer (14, 15). Line broadening found in the infrared spectrum of an ethylidyne on Pd(111) is in accord with this view (29) and it has recently been shown that CO can adsorb onto molybdenum even when it is covered by a thick (several monolayers) carbonaceous layer (16) and on a vinylidene-covered Pd(111) surface (17). Acetylene must also adsorb on vinylidene-covered palladium, since it is capable of catalyzing acetylene cyclotrimerization at high pressures. Recent results have suggested that the reaction proceeds at high pressures by reaction between adsorbed acetylene and vinylidene to form a C_4 precursor to benzene formation (13). There are precedents for this reaction in the organometallic literature (30–32).

It is also evident from the data shown in Fig. 5 that the addition of hydrogen to the reaction mixture causes an increase in the rate at which benzene is formed. This effect has ben noted previously (21). Based on arguments made above, it is proposed that this means that the acetylene coverage increases with hydrogen pressure. Possible origins of this effect will be discussed below. As noted above, hydrogen adsorbs dissociatively on the metal surface to form atomic hydrogen which, according to the Horiuti–Polanyi model (33, 34), are proposed to add sequentially to adsorbed acetylene to form ethylene. The observed isotope effect (Fig. 3) is consistent with this pathway. A simple semi-classical treatment suggests that $r_H/r_D \approx \Delta E/RT$, where ΔE is the difference in zero-point energy between the deuterated and hydrogenated transition state and where the normal mode leading to reaction is assumed to be localized on the hydrogen (deuterium) (35). The activation energy difference (ΔE) can be measured from Fig. 3 (0.6 ± 0.2 kcal/mol) and directly yields a vibrational frequency of the transition state of 1400 ± 400 cm^{-1}. This value is consistent with reaction via the transfer of an adsorbed hydrogen atom to a hydrocarbon fragment bonded to the surface (36). This simple analysis also predicts that the ratio of the rates for hydrogenation and deuteration at 300 K should be 2.7 ± 0.1 in reasonable agreement with the value measured experimentally (1.9 ± 0.3, Fig. 3).

In addition, the reaction rate measured in ultrahigh vacuum which is proportional to $\Theta(\text{hydrocarbon}) \times \Theta(\text{hydrogen})$ (11, 25) is consistent with this pathway which implies therefore that the catalytic reaction rate depends on hydrogen pressure as

$$Rate \propto \left(1 + \left(\frac{\beta}{\alpha}\right) P(H_2)\right) \times \sqrt{P(H_2)}, \qquad [3]$$

where the first term represents the acetylene coverage determined empirically from the benzene formation kinetics above (Eq. [2]), and the second term represents the hydrogen coverage assuming that this adsorbs dissociatively on the vinylidene-covered surface. Note that it has been suggested that adsorbed hydrocarbon species contribute to the source of hydrogen in addition to adsorbed hydrogen (37–41). First, there is no thermodynamic driving force for this reaction and second catalysts covered by thicker carbonaceous layers such as molybdenum (42) would be expected to be very active, whereas they are not. Equation [3] predicts that the hydrogen pressure dependence is a function of (β/α) and that reaction orders can vary between 0.5 and 1.5. The value of (β/α) measured at 300 K with 100 Torr of acetylene can be taken directly from the data of Fig. 5 and is shown marked on the theoretic plot of Fig. 8 derived from the function shown in Eq. [3]. This predicts a hydrogen pressure dependence of 1.04 ± 0.04, in extremely good agreement with the value measured experimentally under exactly identical experimental conditions.

Since α in the data in Eq. (1) is taken to represent the amount of acetylene adsorbed onto a vinylidene-covered surface, this will vary with temperature, the temperature variation presumably depending on the heat of adsorption of acetylene on this surface. The value of β is also likely to be temperature dependent although the interpretation of any temperature dependence that it does have will rely on identifying the origin of the variation in benzene formation rate as a function of hydrogen pressure (Fig. 5). This proposal is borne out experimentally by the data of Fig. 6 which reveal that the value of (β/α) measured directly from the variation in benzene formation rate with hydrogen pressure indeed varies in an Arrhenius fashion with temperature (○). The data of Figs. 5 and 6 taken together therefore also imply that the hydrogen reaction order should depend on temperature. Previous experiments on supported palladium model catalysts have suggested that it does and this is confirmed by the data of Fig. 7 which reveal that the hydrogen pressure dependence varies between 1.04 and 1.25 as the temperature changes from 300 to 365 K. The

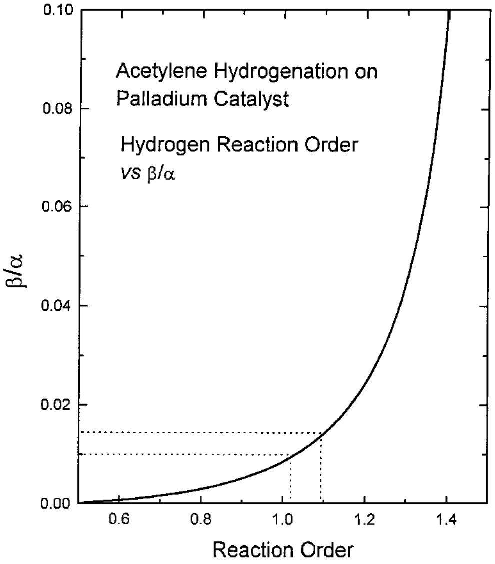

FIG. 8. Theoretical plot of (β/α) versus the hydrogen pressure dependence for acetylene hydrogenation. Plotted also on this graph is the value of (β/α) taken from Fig. 6, yielding a predicted hydrogen pressure dependence of 1.04 ± 0.04, in good agreement with experiment (Fig. 4).

corresponding values of (β/α) as a function of temperature can also be calculated from the data displayed in Fig. 7 using the theoretical relationship between (β/α) and hydrogen reaction order plotted in Fig. 8 and shown in Eq. [3]. The resulting Arrhenius plot of $\ln(\beta/\alpha)$ versus 1/T measured using hydrogen pressure dependences is also shown in Fig. 6 (●). This yields a good straight line so that the values of (β/α) measured directly from the benzene formation rate and those obtained from the kinetic model described above are in excellent agreement. The slope of the Arrhenius plot yields an energy of 4.3 ± 0.2 kcal/mol. The significance of this value remains to be established and, as noted above, will rely on successfully identifying the processes involved in increasing the rate of benzene formation as a function of hydrogen pressure.

Note that the range of hydrogen pressure dependence predicted by the model (between 0.5 and 1.5, Fig. 8) is consistent with values measured for a range of acetylene and ethylene hydrogenation reactions so that these ideas may be generally applicable to other model systems. There are several possible explanations for the observed apparent increase in surface acetylene coverage with increasing hydrogen pressure. First, adsorbed hydrogen may modify the surface in some way to increase the reactivity of the acetylene that is adsorbed on the surface so that increasing the hydrogen pressure does not actually increase the acetylene coverage but merely modifies its activity. Another possible explanation for the observed increase in rate may be that adsorbed vinylidene reacts with hydrogen to form some other surface species, perhaps adsorbed vinyls or ethylidyne, which less effectively block the surface.

A final possibility, in view of the fact that, as noted above, these strongly bound species can be titrated from the surface at high hydrogen pressures, is that vinylidene is reactively removed from the surface to reveal active metal sites below thereby leading to an increase in reaction rate where several acetylenic species hydrogenate to ethylene before the site is once again blocked by the formation of a vinylidene species. Note that, on molybdenum where the carbonaceous layer is much thicker and so can easily be monitored using Auger spectroscopy, a decrease in the amount of carbon on the surface correlates with a corresponding increase in the rate of olefin metathesis (43).

CONCLUSIONS

Palladium foils provide good model acetylene hydrogenation catalysts since they exhibit identical pressure and temperature dependences as do supported palladium catalysts. It is found that the rate of benzene formation is enhanced by the addition of hydrogen to the reaction mixture and this is taken to mean that hydrogen increases the coverage of acetylene on the surface. This simple model successfully predicts the variation in hydrogen pressure dependence of acetylene hydrogenation as a function of temperature. Possible origins for this effect are discussed.

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