

Thermal Conversion of Chemisorbed Acetylene to Vinylidene and Hydrogenation to Ethylidyne on Rh{111}: A Laser Induced Desorption Study

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The kinetics of the conversion of acetylene (HCCH) to vinylidene (CCH₂) at the surface of Rh{111} has been studied using laser-induced thermal desorption (LITD). Acetylene is desorbed intact into the gas phase when the surface is rapidly ($\sim 10^{10}$ K s⁻¹) heated by a laser pulse, which provides a quantitative means of following the slow thermal conversion to vinylidene at the surface. This conversion is found to occur over the temperature range from 140 to 220 K. Temperature-jump isothermal studies of the conversion process were performed, and the results provide the basis for a one-step mechanism with a single activated complex involving the surface-assisted migration of one H atom across the C–C bond, with product inhibition of the reaction due to an activation energy barrier that increases strongly with the amount of vinylidene formed. With no surface vinylidene present the activation energy for the surface conversion is 39 kJ mol⁻¹, independent of acetylene coverage. If H₂ or D₂ are postdosed to the surface, ethylidyne (CCH₃) is efficiently formed by direct H (D) atom addition to CCH₂, and the product CCH₃ is found not to inhibit the HCCH to CCH₂ conversion.

Introduction

The reactivity of unsaturated hydrocarbons with transition metal surfaces is currently a topic of great interest.¹ The adsorption, bonding, and reactivity of acetylene, the prototype alkyne, have been studied on a variety of surfaces, with particular emphasis on the interaction of the triple bond with the surface. The decomposition of acetylene on Rh{111} has previously been studied with LEED, HREELS, and TDS.^{2–4} Experimental results indicate that acetylene adsorbs molecularly on the surface at low temperatures, with its C–C bond oriented approximately parallel to the surface. The stretching frequencies observed with HREELS for chemisorbed acetylene⁴ are dramatically shifted to lower frequency than those of gas phase acetylene, which is an indication of strong bonding to the surface, with rehybridization of the C–C triple bond from sp toward sp² and sp³. It is generally believed that bonding to the surface occurs through mixing of the filled acetylene π -orbital with an empty metal d-orbital, while the empty π^* -orbital overlaps a filled metal d-orbital.⁵ The geometrical structure of adsorbed acetylene has been characterized for several metal surfaces. A LEED analysis for HCCH on Pt{111}⁶ gives support to a flat-lying species in an atop position, with Pt–C and C–C distances of 2.5 and 1.3 Å, respectively. The flat-lying geometry has received confirmation from ARUPS,⁷ and a similar structure was suggested from an analysis of vibrational spectra.⁸ On Rh{111} an ordered (2×2) structure is formed at temperatures as low as 60 K,⁴ implying that the barrier to surface diffusion for chemisorbed acetylene at a quarter monolayer coverage is small, in agreement with an extended Hückel study.⁹

As identified by HREELS,^{3,4} acetylene thermally decomposes on Rh{111} predominantly to CCH₂ (vinylidene), with CCH and CCH₃ also being suggested as minor products of the reaction. The mechanism for the acetylene to vinylidene conversion is far from resolved. Two routes have been extensively discussed, a direct H “slippage” from one C to the next¹⁰ and a two-step conversion via an alkynyl intermediate.^{11,12} The conversion has been observed at between 220 and 270 K

on Pd{111}.^{13,14} Indirect evidence for the bonding geometry of CCH₂ on Rh comes from the theoretical work of Kang and Anderson,¹² who suggested that vinylidene sits preferentially on a μ/π site, with one carbon atom strongly bonded to the 2-fold bridge site and a π bond to the third Pt atom. The C–C bond length was calculated to be midway between a single and a double bond. In contrast to supported rhodium catalysts, where acetylene is stable at 300 K,¹⁵ acetylene decomposition occurs well below room temperature. Rh{111} does not form benzene from acetylene in UHV.^{4,16} Further dehydrogenation and polymerization occurs to C_xH species at higher temperatures. The hydrogenation of acetylene to ethylidyne has been observed on Rh{111} when acetylene and hydrogen are coadsorbed.³ However, the hydrogenation mechanism is unclear.

Laser-induced thermal desorption (LITD) has proved to be an effective tool in surface diffusion and reaction studies.^{17,18} The high heating rate induced on the surface by pulsed laser excitation ($\sim 10^{10}$ K s⁻¹) can often bypass reaction channels that are preferred under low heating rates and induce desorption of highly reactive species. This makes it possible to detect species on the surface and to follow the course of chemical reactions as they occur. By studying the isothermal time dependency of the reaction, valuable information is also obtained about the kinetics.

Here we use LITD to follow the loss of acetylene from the Rh{111} surface as it is converted to vinylidene. These kinetic measurements provide the basis for a product-inhibited reaction mechanism, the reaction rate depending critically on the extent of the surface covered with vinylidene. The adsorbed product causes an increase in the activation energy for the reaction. The deuteration of vinylidene to ethylidyne by adsorption of acetylene at low temperatures followed by D₂ postdosing has also been studied.

Experimental Section

All experiments were carried out in a diffusion and titanium-sublimation-pumped ultrahigh-vacuum chamber described previously,¹⁹ equipped with a rotatable hemispherical electrostatic

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analyser, Masssorr DX-200 quadrupole mass spectrometer, and Varian four-grid LEED optics. The system was operated at a base pressure of 2×10^{-10} mbar, the main component of the residual gas being hydrogen. The rhodium crystal had been cut to within 0.5° of the respective plane, mechanically polished to a mirror finish, and bulk cleaned with a procedure described elsewhere.¹⁹ The cleanliness of the sample was checked with AES. The crystal was mounted on a low-temperature probe capable of resistive heating to approximately 1300 K and cooling to 80 K; the temperature was measured by a chromel-alumel thermocouple spot welded to the backside of the crystal.

Acetylene (MG Distillers, purity 99.5%) was used without further purification and dosed through a capillary doser at a distance of about 1 mm from the sample. Hydrogen TPD was used to characterize acetylene coverages. Unless stated, TPD spectra were collected at a heating rate of 3.5 K s^{-1} . The values are normalized to the hydrogen TPD at the acetylene saturation coverage. Cleaning treatments with oxygen were regularly carried out between TPD and/or LITD runs to remove residual carbon.

The laser pulses for the LITD experiments were provided by a Lambda Physik excimer laser operated at 308 nm (XeCl gas filling) coupled to a pulse extender/beam profiling system.¹⁹ This provided "top hat" light pulses with a temporal width of 120 ns focused down to a $413 \mu\text{m}$ spot. The laser beam intensity was measured with an energy meter (C-25, Coherent). The laser peak temperature was calculated from the measured intensity using the surface heating model developed by Bechtel.²⁰ A laser intensity of 84 MW/cm^2 gives a temperature rise of 1018 K within the irradiated spot. For this temperature increase, less than 5% of damaged sites are produced on the surface, and the surface was annealed after each experiment to repair the damage done by laser-induced heating.²¹ The laser was scanned across the surface so that no area of the surface was revisited during a run. Laser-induced-desorption species were measured using the mass spectrometer in time-of-flight (TOF) mode.

The LITD data were fitted using a modified Maxwell-Boltzmann velocity distribution to the maximum regions of the spectra collected, and the net area under these curves was measured. The mass spectrometer is interfaced to a multichannel scaling board synchronized with a scanning unit that controls the position of the beam on the sample.

Results and Discussion

Temperature-Programmed-Desorption Spectra. Acetylene, as is the general case for unsaturated hydrocarbons on transition metal surfaces, adsorbs irreversibly on Rh{111}. No molecular acetylene desorption is observed in the TPD spectra above 120 K. The only gaseous product is hydrogen. Figure 1 shows the hydrogen TPD spectra after exposing Rh{111} to acetylene for various exposures. Hydrogen evolves over a wide temperature range, from 350 to 700 K. The main desorption peak at 410 K is reaction limited since the desorption-limited peaks from adsorbed hydrogen come at lower temperatures, both from a clean surface and from a surface with C-C species as shown below. This 410 K peak is attributed to the liberation of hydrogen from the decomposition of CCH_2 species, formed by rearrangement from C_2H_2 . The mixture of CCH and CH species left on the surface decompose at higher temperatures, producing the broad feature in the desorption spectra at $\sim 650 \text{ K}$, which has also been observed for C_2H_4 ²² and C_6H_6 ;¹⁶ it is followed by carbon polymerization to form a graphitic overlayer at $T > 800 \text{ K}$.¹⁶ The absence of desorption-limited hydrogen might imply that adsorbed vinylidene forms as a result of an intramolecular 1,2 hydrogen shift in adsorbed acetylene. Kang and Anderson¹² from a theoretical study of the $\text{C}_2\text{H}_2/\text{Pt}\{111\}$

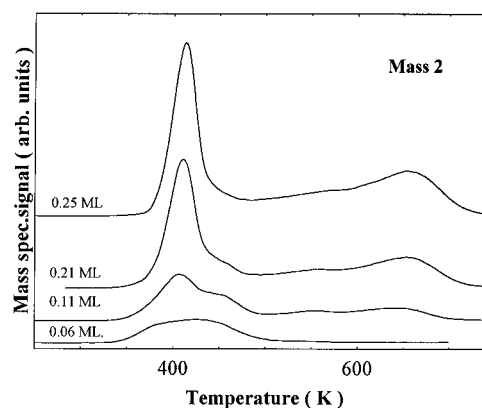


Figure 1. H_2 temperature-programmed-desorption spectra at a heating rate of 3.5 K s^{-1} , after various acetylene exposures at 130 K, leading to the coverages, in monolayers, indicated.

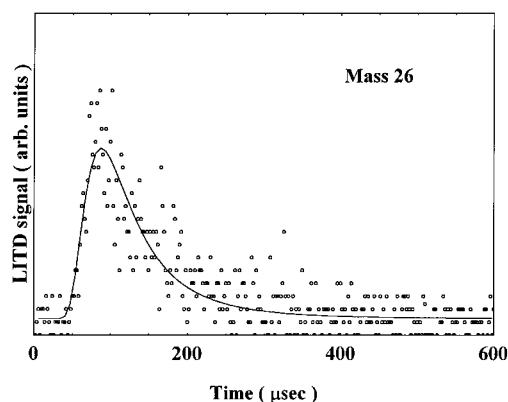


Figure 2. Time-of-flight spectrum for acetylene desorption (mass 26) using a 120 ns laser pulse after adsorption of 0.15 ML at 130 K. The line through the data is a fit with a modified Maxwell-Boltzmann velocity distribution.

system found the surface to interfere with this shift, proposing that most rearrangement reactions in adsorbed C_2 species involve surface hydrogen intermediates. The present spectra are in good agreement with previous spectra reported for C_2H_2 on Rh{111}.²⁻⁴ No benzene was detected in the TPD spectra, showing that, in contrast to Pd^{23,24} and Cu²⁵ surfaces, C_2H_2 cyclization does not occur on Rh{111}.

Laser-Induced Thermal Desorption: The Acetylene to Vinylidene Conversion. Laser-induced thermal desorption takes place at heating rates of $\sim 10^{10} \text{ K s}^{-1}$, many orders of magnitude higher than in standard TPD. At these heating rates entropically favored desorption channels may be preferred to the lower energy channels accessed at slow heating rates, when the activated complex for the latter process is associated with a lower entropy. An example is the LITD product CH_3 , the methyl radical, from acetate on Rh{111} where standard TPD produces only H_2 and CO_2 .²⁶ In the present work we found that after acetylene adsorption at substrate temperatures below $\sim 135 \text{ K}$ exposing the surface to 120 ns laser pulses produced molecular acetylene intact in the gas phase. No H_2 was detected, and we conclude that at these high heating rates the low activation barrier surface reaction path that leads to vinylidene and, at higher temperatures, dehydrogenation, which is accessed under normal TPD conditions, is completely bypassed. The time-of-flight spectrum for the acetylene LITD signal is shown in Figure 2. Attempts were also made by LITD to find possible intermediates formed on the surface during the acetylene to vinylidene conversion on the surface as the temperature was slowly raised to 300 K, but none were found. We note that no benzene was detected all the way up to 450 K.

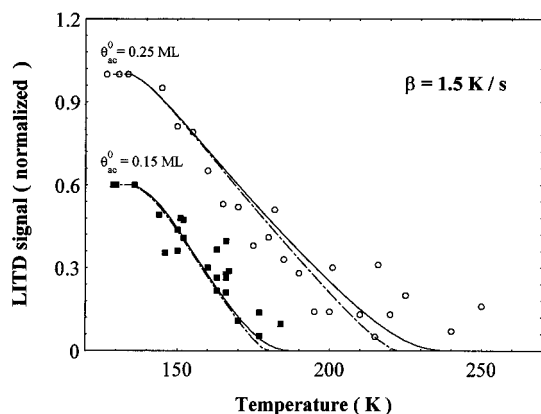


Figure 3. 3. LITD analysis of the acetylene to vinylidene conversion on Rh{111} as the crystal temperature is ramped at 1.5 K s^{-1} from 130 to 250 K, for two different starting coverages of acetylene. The LITD signal for acetylene (mass 26) is shown. The solid and dotted lines are theoretical best fits to the data based on eqs 1 and 2, with, respectively, $n = 1$ and $n = 1/2$.

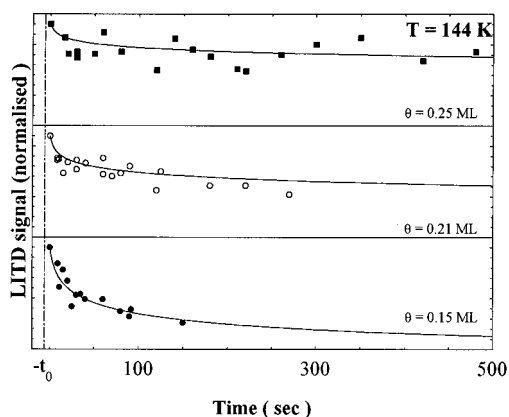


Figure 4. Isothermal LITD studies of the acetylene to vinylidene conversion, showing the fall in acetylene signal, for different starting coverages of acetylene, at a temperature of 144 K. Adsorption is carried out at 130 K, and at $t = -t_0$, the temperature is rapidly increased to 144 K, reaching this temperature at $t = 0$. The solid lines are the fit to the data with eqs 1 and 2, with $n = 1$.

The intact desorption of molecular acetylene with laser-induced heating enables us to probe the presence of adsorbed acetylene and hence to follow the kinetics of the surface transformation to vinylidene as it occurs. Figure 3 displays the decrease of the mass 26 LITD signal from adsorbed acetylene after dosing at $T = 128 \text{ K}$ and then ramping the substrate temperature upward at a rate of 1.5 K s^{-1} . (The solid lines represent theoretical fits to the data, which are discussed later.) The results show that for the two different initial coverages acetylene is stable on Rh{111} up to $\sim 140 \text{ K}$. Above this temperature C_2H_2 conversion is initiated, as shown by the drop in the LITD signal. For the lower initial coverage the decomposition is complete at about 180 K since no acetylene is detected above this temperature, whereas at higher coverage the acetylene to vinylidene conversion is slowed down and is only completed at $\sim 240 \text{ K}$.

For a quantitative analysis of the kinetics of surface processes isothermal data are necessary. The rate of conversion of acetylene was monitored by following the decrease of the C_2H_2 LITD signal as a function of time at a given temperature for a given initial coverage. The surface was ramped quickly to the desired temperature in less than 10 s. Figure 4 shows the isothermal decrease of the acetylene coverage at 144 K for three initial coverages, from 0.15 to 0.25 ML, the saturation coverage achievable at 140 K. The time t_0 represents the time it takes to

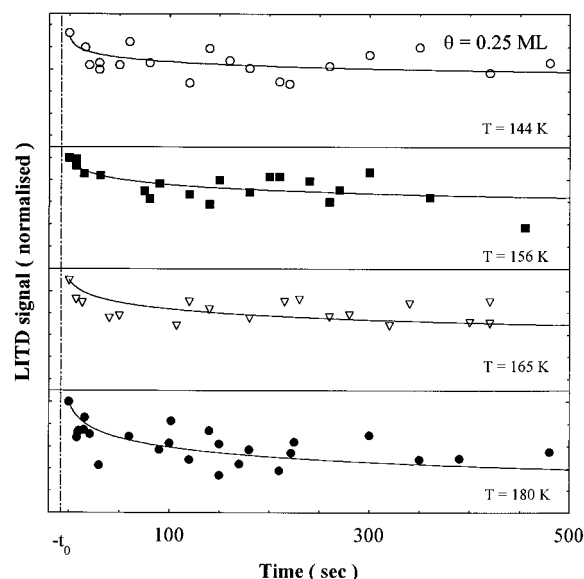


Figure 5. Time dependence for the acetylene conversion to vinylidene for an initial coverage of 0.25 ML, at various temperatures. The lines represent the model fits to the data, with $n = 1$.

reach the desired temperature, while $t = 0 \text{ s}$ is the starting time at the desired temperature. The data were normalized to the LITD signal at time $t = 0 \text{ s}$. The results are clearly unusual. At an initial coverage 0.15 ML the half-life of the C_2H_2 LITD signal is about 120 s. However, when the initial coverage is increased to 0.21 ML, the reaction only reaches 40% completion at 300 s, and for an initial coverage of 0.25 ML the rate of the surface process is close to zero after 500 s, at only $\sim 25\%$ completion. Subsequent heating to 250 K drives the reaction to completion in each case. Comparison of the data for $\theta_{\text{ac}}^0 = 0.15$ and 0.21 ML shows that the *initial* rate of the surface conversion is not significantly altered by the change in initial coverage: the reaction is not self-inhibited by excess reactant, for example by blocking empty sites required in the conversion process. The behavior of these kinetic plots demonstrates that the progress of the reaction is strongly inhibited by the product, vinylidene, on the surface. This conclusion is confirmed by an examination of the further isothermal kinetic data shown in Figures 5 and 6, corresponding, respectively, to initial coverages of 0.25 and 0.15 ML, at temperatures between 144 and 180 K.

A range of kinetic models were tested for applicability to the rate data for the surface conversion of acetylene to vinylidene, including those accounting for the availability of free sites. A fit could only be obtained with an expression that included a strong dependence in the activation energy term on the presence of the vinylidene product; the rate of loss of acetylene is given by

$$\frac{d\theta_{\text{ac}}}{dt} = k\theta_{\text{ac}}^n \quad (1)$$

with

$$k = \nu \exp \frac{-(E_0 + \alpha\theta_{\text{ac}}^0\theta_{\text{vin}})}{RT} \quad (2)$$

Here θ_{ac} and θ_{vin} are the surface fractional coverages of acetylene and vinylidene in ML, respectively, at time t , θ_{ac}^0 is the initial acetylene coverage before ramping ($t = t_0$), $\theta_{\text{vin}} = \theta_{\text{ac}}^0 - \theta_{\text{ac}}$, α is a constant, ν is a rate constant pre-exponential, E_0 is the activation energy barrier when $\theta_{\text{vin}} = 0$, and n is the order of the reaction in the acetylene coverage. The solid lines through the data in Figure 3, 4, 5, and 6 represent the best fit

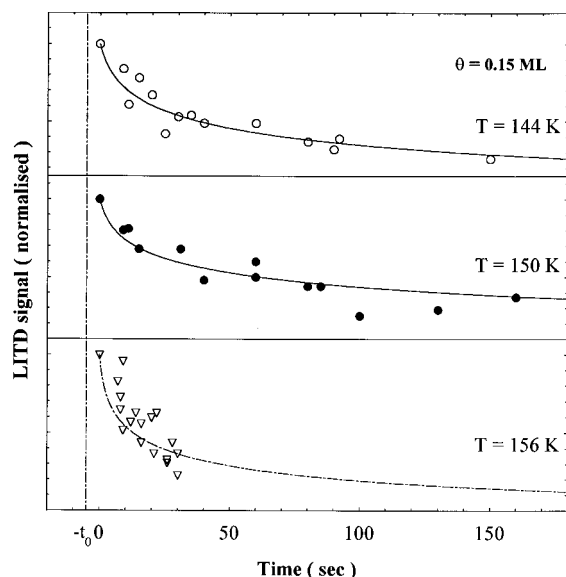


Figure 6. Time dependence for the acetylene conversion to vinylidene for an initial coverage of 0.15 ML at different temperatures. The lines are the model fits to the data.

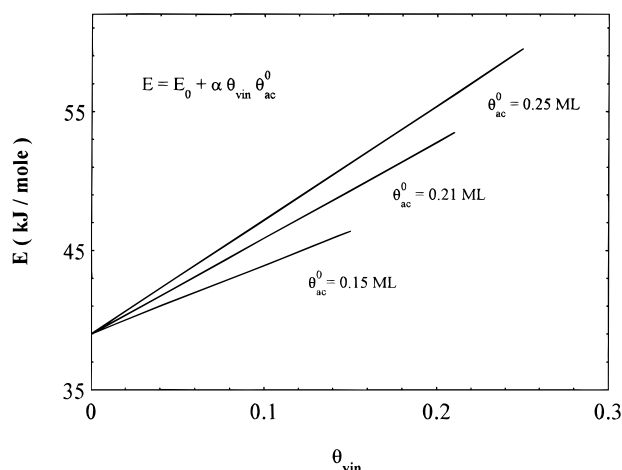


Figure 7. Dependence of the activation energy barrier for acetylene to vinylidene conversion on the product fractional coverage, θ_{vin} , for different initial acetylene coverages, θ_{ac}^0 .

with $\alpha = 328 \text{ kJ mol}^{-1} \text{ ML}^{-2}$, $E_0 = 39 \text{ kJ mol}^{-1}$, and $\nu = 10^{13} \text{ s}^{-1}$. The loss of reactant during ramping to the desired T was taken into account each time. Dependence on n is swamped by the exponential dependence on coverage; good fits were obtained with $n = 1$ or $n = 0.5$.

We note that according to eq 2, the activation barrier for the surface conversion process is independent of the initial acetylene coverage at $t = t_0$, when $\theta_{\text{vin}} = 0$. The reaction barrier is not affected by the number of empty sites, which may indicate that acetylene forms islands on the surface. However, the barrier height is not simply dependent on the coverage of the vinylidene product; the slope of the surface reaction barrier E dependence on θ_{vin} is strongly dependent on θ_{ac}^0 , as shown in Figure 7. The more crowded the surface, the greater the effect of vinylidene on E .

As shown in the following section, acetylene adsorption followed by postdosing the surface at low temperatures with H_2 or D_2 leads to the formation of ethylidyne from vinylidene. The influence of postdosed deuterium on the rate of acetylene conversion was followed isothermally, at 150 K, by LITD. In Figure 8 the drop in the LITD HCCH signal is compared to that of a nondeuterated surface. The initial rate of HCCH conversion is unaffected by the presence of deuterium, but the

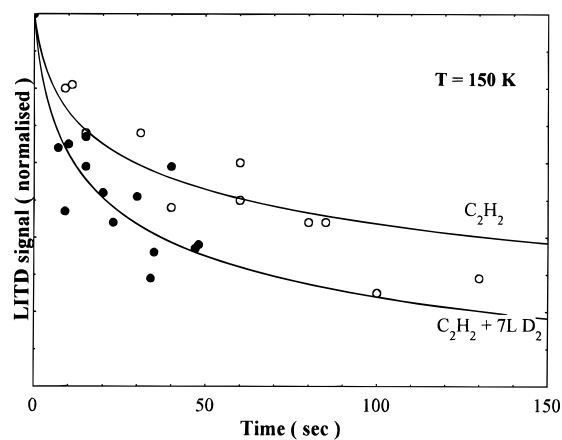


Figure 8. Acetylene to vinylidene conversion studied by LITD, at a crystal temperature of 150 K, showing a comparison between the conversion in the absence of coadsorbed D_2 (or H_2), open circles, and the conversion in the presence of coadsorbed D atoms introduced by postdosing the surface with D_2 subsequent to the adsorption of 0.15 ML of acetylene at 130 K, filled circles. The theoretical fits are described in the text.

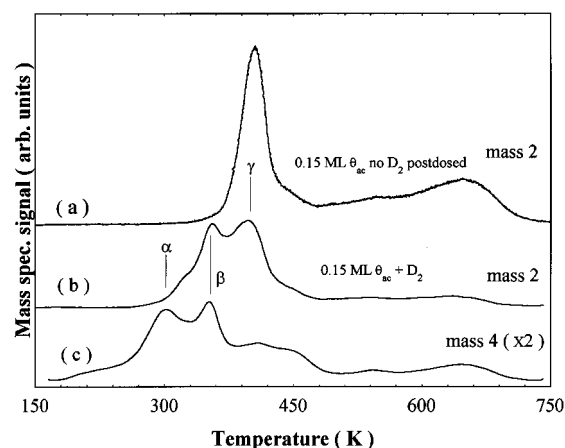


Figure 9. The influence of D_2 postdosing on the H_2 and D_2 desorption spectra from 0.15 ML acetylene adsorbed on $\text{Rh}\{111\}$ at 130 K. (a) H_2 TPD spectrum after dosing acetylene alone. (b) H_2 TPD spectrum after dosing acetylene and postdosing D_2 for 7 langmuirs. (c) D_2 TPD spectrum from the mixed acetylene and D_2 adlayer. The assignment of the three peaks, α , β , and γ , is discussed in the text.

inhibiting effect of the product CCH_2 is now considerably less. The solid line through the data obtained in the presence of deuterium is obtained using eqs 1 and 2, but with the assumption that only two-thirds of the vinylidene formed in the conversion from acetylene remains as vinylidene, the remainder being converted to ethylidyne, which accordingly has no influence on the reaction. The factor of 2/3 is justified in the following section. We conclude that ethylidyne, CCH_3 , does not have an inhibiting effect on the reaction and that at 150 K the vinylidene produced in the surface conversion process is efficiently deuterated to ethylidyne.

The Vinylidene to Ethylidyne Conversion. The adsorption of acetylene and hydrogen on $\text{Rh}\{111\}$ at temperatures above 300 K leads to the conversion to surface ethylidyne, CCH_3 .² This process was studied in the present work by adsorbing C_2H_2 at 130 K and postdosing the surface with D_2 before obtaining H_2 and D_2 desorption spectra. Typical results are shown in Figure 9, where a comparison is made with data for H_2 desorption in the absence of D_2 postdosing. The peak labeled γ at 400 K has already been attributed to the decomposition of vinylidene on the surface. After D_2 postdosing this peak is reduced in size and a new peak β (Figure 9) appears at 350 K,

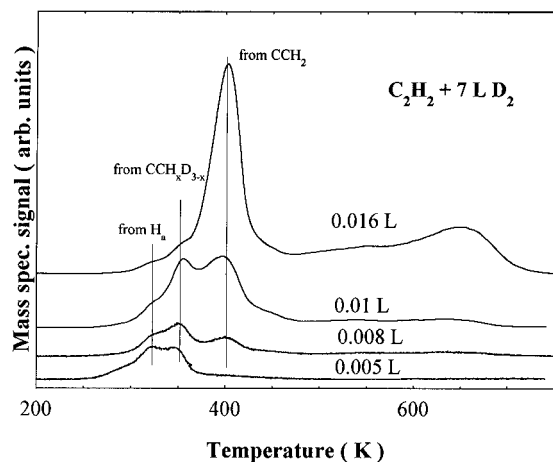


Figure 10. H_2 TPD spectra following the adsorption of varying amounts of acetylene and postdosing with 7 langmuirs of D_2 at 130 K.

which we now attribute to the decomposition of the deuterated ethylidyne species, $\text{CCH}_x\text{D}_{3-x}$. This is further justified below. A γ -peak at 400 K is attributed to decomposition of unreacted vinylidene.

Figure 9 also shows a comparison of the H_2 and D_2 desorption peaks observed after postdosing C_2H_2 with D_2 . In addition to γ and β peaks, a new desorption peak, more intense than the others, is observed at 300 K, which we assign as α - D_2 and attribute to a recombination of unreacted D adatoms. The γ - H_2 peak, from unreacted CCH_2 , is considerably larger than the γ - D_2 peak, which demonstrates that the exchange



is a minority process. The dominant peak in the D_2 desorption spectrum is the α -peak, from the recombination process



from unreacted postdosed D_2 , while the α - H_2 peak is negligible by comparison. The dominant ethylidyne formation occurs, as expected, via

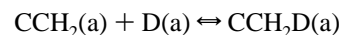


A separate experiment was performed in which the adsorption temperature was raised to 250 K so that the acetylene was converted to vinylidene before the addition of D_2 , and similar results were obtained, confirming that ethylidyne is a direct product of vinylidene hydrogenation. This is in agreement with Dubois et al.,³ who had to anneal the acetylene adlayer for several minutes in a hydrogen environment at 275 K to get a well-ordered $c(4 \times 2)$ structure associated with CCH_3 .

The H_2 desorption spectrum from vinylidene alone shows, in addition to the major γ -peak at 400 K, higher temperature peaks at 450, 550, and 650 K attributed to the successive cracking of CCH species produced at 400 K. We note that the D_2 desorption spectrum from vinylidene postdosed with D_2 also shows peaks at these temperatures; we attribute these peaks to the cracking of CCD formed at 350 K from the initial decomposition of the mixed isotope ethylidyne species, CCH_2D .

The H_2 desorption spectra are shown in Figure 10 for increasing exposures to acetylene prior to D_2 postdosing. At low acetylene coverages the γ - H_2 peak is completely absent, showing complete conversion to ethylidyne via step c above, whereas at saturation exposures the α - and β - H_2 peaks are almost completely absent and vinylidene is the dominant species: D_2 adsorption is almost completely blocked. At

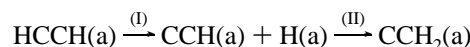
intermediate acetylene coverages, however, we note that α -, β -, and γ -peaks are all present, implying that even with excess D adatoms present there is incomplete conversion of CCH_2 to CCH_2D . There are several possible explanations for this result. If acetylene has a tendency to form islands, the smaller islands formed at low coverages would be completely deuterated to ethylidyne at low initial coverage, but for higher coverages the acetylene at the island center may remain undeuterated. Alternatively, the activation energy barrier to vinylidene deuteration to ethylidyne may increase as the reaction proceeds. And finally, it is possible that the D_2 desorption spectra indicate that the equilibrium



is established with measurable quantities of each species at intermediate coverages.

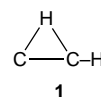
After postdosing with D_2 the proportion of the 0.15 ML acetylene dose that is converted to CCH_2D compared with CCH_2 can be estimated from the relative heights of the H_2 β and γ desorption peaks. For a 0.15 ML acetylene coverage, from Figure 9 we estimated that one-third of the acetylene is converted to ethylidyne. This is the proportion used in the calculation performed to fit the data presented in Figure 8.

General Discussion. It is widely believed that the conversion of acetylene to vinylidene on transition metal surfaces occurs via a two-step process, as described by Kang and Anderson:¹²



There are, however, several results from the current work that do not support this model. At the high heating rates induced by a laser pulse, adsorbed acetylene is converted directly to gaseous acetylene with no detectable H_2 formation. This implies that the phase space for any activated complex *en route* to surface CCH_2 production is very small compared to that for thermal desorption, so that the higher energy barrier process to HCCH(g) production nevertheless becomes the preferred route at high heating rates. In turn, this would imply that the activation entropy for step I, if there is a two-step process, is considerably smaller than that for HCCH desorption. This result does not necessarily contradict the two-step model. However, when D_2 is postdosed after HCCH adsorption, some undeuterated vinylidene remains on the surface, and when this is heated, it decomposes to produce gaseous H_2 at 400 K and very little D_2 (Figure 9), implying that D atoms are not picked up in vinylidene formation. More importantly, no C_2HD was detected ($<5\%$) in the LITD from the mixed HCCH/D adlayer. This result is clearly inconsistent with the two-step mechanism. Finally, we note that in the absence of H_2 or D_2 postdosing we could find no evidence for CCH_3 formation on the surface. The β - H_2 TPD peak (Figure 9) at 350 K, derived from CCH_3 decomposition, is completely absent in the TPD data (Figure 1) obtained from a pure acetylene adlayer. Given the facile reaction step $\text{CCH}_2 + \text{H} \rightarrow \text{CCH}_3$, this result is again inconsistent with the two-step mechanism.

We therefore propose that the acetylene to vinylidene process occurs via a single activated complex involving a surface-assisted migration of one H atom across the C–C bond in adsorbed acetylene, shown as **1**. Of direct relevance are the



results from both full CI and many-body expansion calcula-

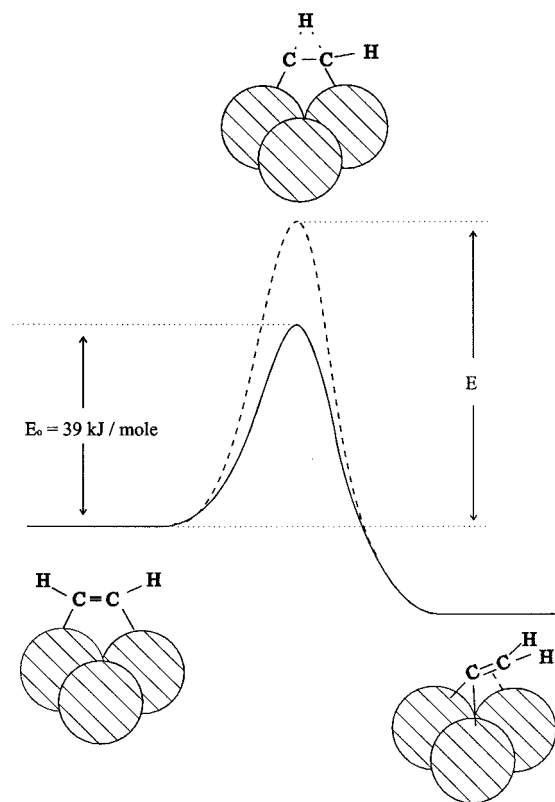


Figure 11. Schematic figure of the potential energy along the reaction coordinate for the surface conversion of acetylene to vinylidene, showing the barrier (E_0) with no product present (full line) and the barrier (E) in the presence of the product (dashed line). The structures for HCCH, a flat-lying species, and for CCH₂, a μ/π -bonded species, are consistent with theoretical studies.^{10,12}

tions.^{27,28} These show that the potential for acetylene has a secondary minimum corresponding to the structure of vinylidene, with a saddle point for the HCCH to CCH₂ rearrangement which is 2.53 eV above the acetylene minimum, corresponding to a C–C bridging H at $r(\text{C–H}) = 1.3 \text{ \AA}$, compared with $r(\text{C–H}) = 1.06 \text{ \AA}$ for the singly bonded H atom. Chen et. al. have also experimentally observed the vinylidene to acetylene isomerization in the gas phase by using stimulated emission pumping spectra (SEP).²⁹ Since the minimum activation energy barrier determined from the present work for the HCCH to CCH₂ rearrangement on Rh{111} is only 0.4 eV (39 kJ mol^{−1}), we conclude that the metal surface provides a considerably lower saddle point for the process, which is schematically illustrated in Figure 11. This is in full agreement with the earlier conclusions of Silvestre and Hoffmann.¹⁰ We note that, in contrast to the gas phase, vinylidene is more stable than acetylene chemisorbed on Rh{111}.

We have shown that the saddle point energy associated with the activated complex **1** on Rh{111} is strongly affected by the product vinylidene, but not by ethynyl (Figure 8). When the surface is saturated with acetylene at low temperatures, the barrier height increases from an initial 39 kJ mol^{−1} to 60 kJ mol^{−1} as the process nears complete conversion to CCH₂. This implies either strong repulsive interactions between product CCH₂ and activated complex, which would destabilize the complex, or attractive interactions between product and reactant HCCH, causing adsorbed acetylene to be stabilized. We also note a considerably larger influence of the product on the activation barrier if the initial coverage is high (Figure 7), which can be explained as follows. At low coverages the product is able to diffuse away from the reactant (and the complex), whereas this cannot occur when the surface is crowded. Even

if acetylene is initially adsorbed into islands, this mechanism therefore indicates that the islands break up as vinylidene is formed. This could not occur if there was a strong pairwise attraction between CCH₂ and HCCH; the results are therefore consistent with a small repulsion between CCH₂ and HCCH that keeps them apart at low coverages and a large repulsion between CCH₂ and the activated complex, which destabilizes the latter. Given a (2×2) adlayer structure, the increase in barrier height from 39 to 60 kJ mol^{−1} is consistent with a pairwise nearest neighbour repulsive interaction between CCH₂ and the complex of 5 kJ mol^{−1}. This is not inconsistent with interaction energies determined for other molecular species by single crystal adsorption calorimetry.³⁰ Conversely, however, there is no comparative interaction between ethynyl or the reactant acetylene and the activated complex. It remains for future work to determine the nature of the interactions involved.

We note that Hall and co-workers³¹ attributed product inhibition of methanol decomposition on Ni{100} to electronic interactions with the methoxy product, which increase the barrier to the reaction. On the other hand, for the tricyclization of acetylene to benzene on Pd{111}, Abdelrehim et al.³² reported that the activation energy for the process increases with increasing acetylene coverage, suggesting an attractive interaction between adsorbed acetylene molecules leading to a strengthening of C–Pd bond energies at higher coverages. In the present work no evidence was found for an influence of acetylene coverage on activation energy, which would imply either negligible interaction between acetylene molecules on Rh{111} or attractive interactions leading to island formation. Clearly, there is a major contrast between the behavior of the acetylene on these two surfaces; on Rh{111} the preferred pathway leads to vinylidene, which does not undergo tricyclization, whereas on Pd{111} the preferred pathway leads to benzene. The facile deuteration or hydrogenation of CCH₂ to CCH₃/CCH₂D on Rh{111} is to be expected, given the nature of the μ/π CCH₂ species proposed by Kang and Anderson, which is strongly supported by early studies of metal cluster complexes.³³

Conclusions

The kinetics of the thermal conversion of acetylene to vinylidene on Rh{111} has been studied using LITD. In contrast to a previous study⁴ from which acetylene was thought to be stable up to 270 K, the LITD results show that the decomposition of acetylene starts at temperatures as low as 140 K and is completed at a fast rate at temperatures above 220 K.

A one-step kinetic model is strongly supported by the data, which demonstrate a significant increase in the reaction barrier due to the presence of the product, vinylidene. This is attributed to a repulsive interaction between CCH₂ and the activated complex, **1**.

The hydrogenation of acetylene to ethynyl, CCH₃, is found to be facile, proceeding efficiently at 150 K. It is formed from acetylene through vinylidene. This hydrogenated product, unlike vinylidene, does not have an inhibiting effect on the acetylene to vinylidene conversion. The decomposition of adsorbed ethynyl is found to occur at a lower temperature than for vinylidene; at a heating rate of 3.5 K s^{−1} this occurs at 350 K, compared with 400 K for vinylidene.

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