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THE CHEMISOPTION OF ACETYLENE AND ETHYLENE ON Rh(111): A. LOW ENERGY ELECTRON DIFFRACTION (LEED), HIGH RESOLUTION ELECTRON ENERGY LOSS (ELS) AND THERMAL DESORPTION MASS SPECTRO-METRY (TDS) STUDY

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Author

Dubois, L.H.

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L. H. Dubois, D. G. Castner and G. A. Somorjai

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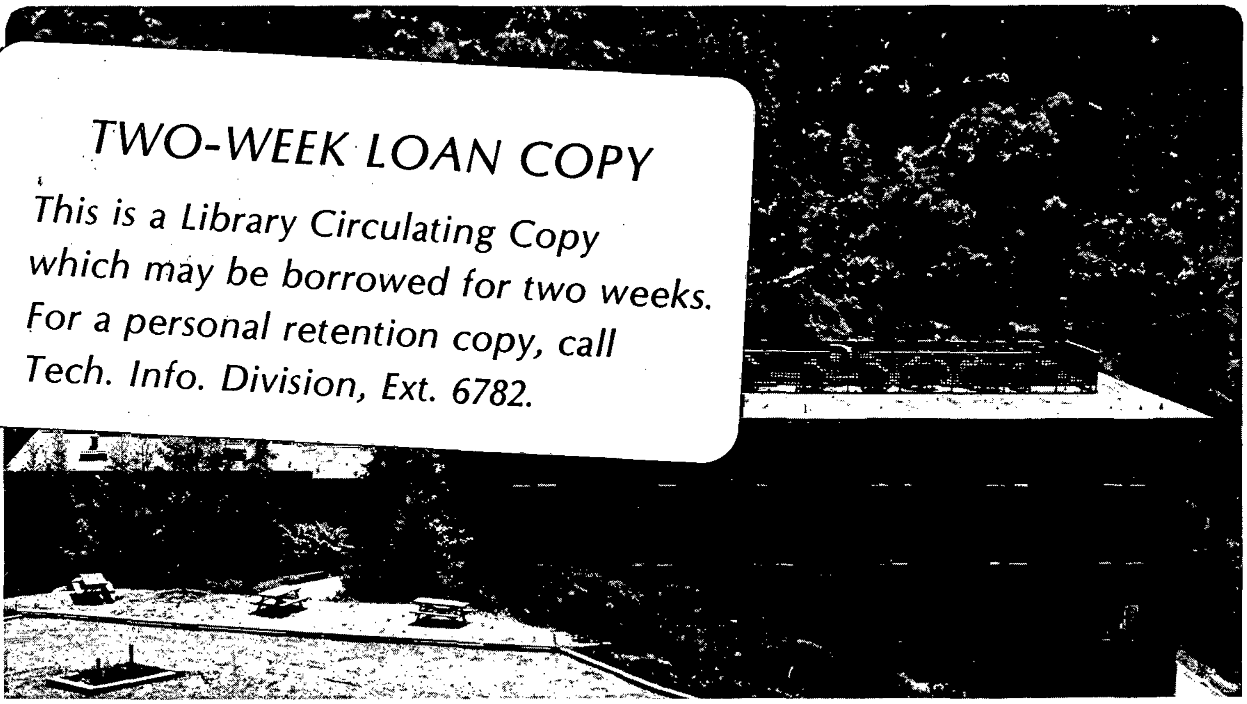

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THE CHEMISORPTION OF ACETYLENE AND ETHYLENE ON Rh(111): A LOW ENERGY ELECTRON DIFFRACTION (LEED), HIGH RESOLUTION ELECTRON ENERGY LOSS (ELS) AND THERMAL DESORPTION MASS SPECTROMETRY (TDS) STUDY

L.H. Dubois, D.G. Castner* and G.A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley
Laboratory, and Department of Chemistry, University of
California, Berkeley, California 94720

Abstract

We report the results of a detailed investigation of the chemisorption and reactivity of acetylene (C_2H_2) and ethylene (C_2H_4) on the Rh(111) single crystal surface. Below 270K ELS measurements indicate that acetylene chemisorbs on Rh(111) with its C-C bond oriented parallel to the surface forming an approximately sp^2 hybridized species. LEED investigations show that both C_2H_2 and C_2H_4 form metastable (2x2) surface structures on Rh(111) below 270K. An irreversible order-order transformation occurs between 270 and 300K to a stable c(4x2) hydrocarbon overlayer. The stable species formed from both molecules are identical. Hydrogen addition to chemisorbed acetylene is necessary to complete this conversion. The geometry of the adsorbed ethylene species does not change during this transformation although the overlayer structure does. This stable hydrocarbon fragment is identical to the hydrocarbon species formed from the chemisorption of either C_2H_4 or C_2H_2 and hydrogen on Pt(111) above 300 K. The addition of H_2 to chemisorbed C_2D_2 or C_2D_4 results in H-D exchange, but no change in the adsorbate geometry is detected by ELS. Decomposition of these molecules occurs on the Rh(111) surface above ∿420K.

*Present Address: Chevron Research Company, P.O. Box 1627, Richmond, CA 94802

Introduction

Determination of the molecular structure of adsorbed monolayers on metal surfaces is now possible by a variety of complementary techniques. Recently a combination of low energy electron diffraction (LEED) intensity analysis and high resolution electron energy loss spectroscopy (ELS) has been used to determine the structure of ethylene (C_2H_4) chemisorbed on Pt(111) at 300 K.[1] ELS is a particularly valuable technique for probing hydrocarbon interactions with metal surfaces since the observed inelastic losses correspond to the vibrational modes of the adsorbed species. Thus the orientation and geometry of chemisorbed molecules can be determined and monitored as a function of both surface coverage and substrate temperature. Hydrogen can also be detected through its vibration against either the substrate or other adsorbed atoms. Finally, ordered adsorbate overlayers are not needed to obtain intense ELS spectra. A dynamical LEED structure analysis provides bond lengths, bond angles and the position of the adsorbate on the surface if the overlayer is ordered. It is not very effective, however, in determining the location of hydrogen atoms —an important question in hydrocarbon surface chemistry. Changes in bonding with coverage and temperature can only be studied by LEED if the adsorbate layer remains well ordered.

We report here the results of a detailed investigation of the chemisorption and reactivity of C_2H_2 and C_2H_4 on the Rh(111) single crystal surface. In the present study we have extended previous LEED and thermal desorption mass spectrometry (TDS)[2] investigations to lower temperatures ($T \sim 210$ K) and have complemented these results with data obtained by high resolution ELS and Auger electron spectroscopy (AES). This combination of techniques allows us to determine the structure of these hydrocarbons on the surface and follow their molecular rearrangements as a function of temperature between 210 and 420 K. We have also studied the vibrational spectra of chemisorbed C_2D_2 and C_2D_4 and the reactions of these molecules with hydrogen. Finally, the bonding of acetylene and ethylene on Rh(111) is compared to data previously obtained on the (111) single crystal faces of platinum and nickel.

Experimental

Experiments were carried out in two ion pumped ultrahigh vacuum chambers both having LEED, retarding field AES and TDS capabilities. One system was also equipped with a high resolution ELS spectrometer. The procedures for sample preparation, mounting and cleaning have been described previously.[2] Briefly, the Rh(111) crystal, oriented to $\pm\frac{1}{2}°$, was cleaned by a combination of argon ion bombardment (500-2000 eV) followed by annealling (800-1000 K) in vacuum and O_2 to remove carbon, sulfur and boron.

Acetylene and ethylene adsorption was studied at pressures between 5×10^{-9} and 1×10^{-6} torr and at temperatures between 210 and 420 K. Surface structures were observed both with increasing exposure and after the gas was pumped away. Gas exposures were not corrected for ion gauge sensitivity and differed slightly between the two chambers. TDS spectra were recorded at a heating rate of 40 K/sec. Blank desorption experiments were performed by replacing the crystal with tantalum foil to insure that all observed desorption peaks were from the rhodium surface.

The high resolution ELS spectrometer has been described elsewhere.[3] In the present series of experiments the angle of incidence was fixed at 65° to the surface normal and electrons were collected in the specular direction. The beam energy varied from 4.8 to 5.8 eV. The elastic scattering peak had a full width at half maximum between 70 and 90 cm^{-1} and maximum intensity of 1×10^{5} counts per second.

Results and Discussion

A. LEED studies of ethylene and acetylene adsorption on Rh(111).

Exposing the clean Rh(111) surface (Fig.1a) between 230 and 250 K to C_2H_4 results in the appearance of sharp half order diffraction spots in the LEED pattern (Fig.1b) from a (2x2) surface structure. If the cyrstal temperature is below ∿230 K, ethylene adsorption is disordered and the only change observed in the LEED pattern is an increased background intensity. This disordered hydrocarbon layer can be transformed into an ordered (2x2) surface structure by heating the crystal to between 230 and 250 K. Acetylene adsorption on the Rh(111) surface between 210 and 250 K also produces a (2x2) surface structure. The new diffraction spots from the ordered (2x2) hydrocarbon structures are sensitive to surface coverage. Although the spots are visible after a 1 L (1L= 1 Langmuir= $1x10^{-6}$ torr•sec) gas exposure, they do not become sharp and intense until 1.5 L and then immediately begin disordering above 1.5 L. A 15 sec exposure of $1x10^{-7}$ torr C_2H_4 or a 150 sec exposure of $1x10^{-8}$ torr C_2H_2 produce optimum (2x2) surface structures.

A diffraction pattern corresponding to a c(4x2) surface structure (Fig.1c) can be generated from the (2x2) surface structure without additional hydrocarbon exposure. For adsorbed C_2H_4 the transformation occurs in vacuum by slowly warming the crystal to 300 K over the course of several hours. Rapid heating results in the formation of a disorderd c(4x2) structure (broad, diffuse diffraction features and some streaking). For adsorbed C_2H_2 even this slow warm-up results in a disordered overlayer. To form a well ordered c(4x2) structure from adsorbed acetylene the crystal must be annealed for ∿4 minutes at 273 K in $1x10^{-8}$ torr of H_2 with the mass spectrometer filaments on. These filaments are located approximately 5 cm. from the crystal and provide the surface with a good source of atomic hydrogen.[4] Castner et al[2] previously observed the c(4x2) surface structures from the chemisorption of either acetylene or ethylene on Rh(111) near room temperature. The reported diffraction patterns were neither as sharp nor as intense as that shown in Fig.1c, however. The (2x2) hydrocarbon surface structures have not been seen previously.

In the transformation from the (2x2) to the c(4x2) structures the orientation and shape of the unit cell change,[5] but the areas of the primitive unit cells of these two structures are the same (25 Å^2 on Rh(111)). Thus, no variation in the surface coverage occurs. Furthermore, AES shows that the carbon coverage from the (2x2) structures produced during C_2H_2 and C_2H_4 chemisorption are the same and remain constant during the conversion to the c(4x2) structures. Thus, changes in binding site and adsorbate geometry are probably taking place without any change in the adsorbate coverage. Determination of the overlayer structure by LEED requires the analysis of the intensity vs. incident energy (I-V) beam profiles. We have not undertaken such calculations in the present study. The transformation from the (2x2) to the c(4x2) surface structures is irreversible; once the c(4x2) structure forms, the crystal can be cooled to 210 K with no visible changes in the diffraction pattern. The c(4x2) structures can only be altered by heating the crystal above 420 K which causes the surface to irreversibly disorder.

B. ELS studies of acetylene and ethylene adsorption on Rh(111)

The vibrational spectrum of the (2x2) hydrocarbon surface structure formed from the chemisorption of C_2H_2 on Rh(111) between 210 and 270 K is shown in Fig.2a The peak positions and their relative intensities[6] are listed in Table I.

Analysis of the low frequency region in this spectrum is hampered by a spurious background peak near 800 cm^{-1}. This apparent loss, first observed by Froitzheim et al, may be caused by electron reflection from the outer half of the analyzer.[8] The dashed lines in Figs. 2 and 3 indicate the approximate location and magnitude of this peak. As a result of this experimental artifact, both the position and intensity of all loss features between 650 and 900 cm^{-1} are rather uncertain. Isotopic substitution is of some help in assigning the observed vibrational frequencies to normal modes of the adsorbed species. The ELS spectrum of the (2x2) C_2D_2 surface structure is shown in Fig.2b.

The vibrational spectra of the (2x2) acetylene overlayer in Figs.2a and 2b do change up to 270 K in vacuum. Furthermore, the positions and relative intensities of the observed energy loss peaks are independent of the acetylene exposure (from >0.2 L to <50 L) and, more importantly, are independent of surface order (as determined by observation of the LEED pattern). Thus, using high resolution ELS we conclude that the bonding of the adsorbed molecules do not change upon disordering.

The frequencies of the carbon-hydrogen (carbon-deuterium) stretching vibrations can be used to characterize the state of hybridization of the adsorbed species. Acetylene, C_2H_2 (C_2D_2), is sp hybridized in the gas phase and has C-H (C-D) stretching vibrations between 3289 and 3374 (2439 and 2701) cm^{-1};[9] ethylene, C_2H_4 (C_2D_4), is sp^2 hybridized and has C-H (C-D) stretching vibrations between 2989 and 3106 (2200 and 2345) cm^{-1};[9] while ethane, C_2H_6 (C_2D_6), is sp^3 hybridized and has C-H (C-D) stretching vibrations between 2896 and 2985 (2083 and 2235) cm^{-1}.[9] Thus, the losses at 2980 (2230) and 3085 (∿2320) cm^{-1} in Figs. 2a and 2b and Table I correspond to the C-H (C-D) stretching vibrations of a molecule near sp^2 hybridization. This indicates that the C-C-H (C-C-D) bond in adsorbed acetylene is no longer linear. Thus, the adsorbed C_2H_2 molecule is more " ethylene-like" in its C-H bonding and one might conclude that the C-C-H (C-C-D) bond angle is near 120° (as found in gas phase ethylene). The low frequency mode at 323 cm^{-1} does not shift significantly upon deuteration (∿20 cm^{-1}) and most likely corresponds to the entire molecule vibrating against the surface. The two largest peaks in the spectrum at 706 and 887 cm^{-1} shift by almost 200 cm^{-1} (to 565 and 686 cm^{-1}, respectively) when C_2D_2 is chemisorbed and can be assigned to C-H (C-D) bending modes. The adsorbate must be oriented with its carbon-carbon axis approximately parallel to the surface since only small, broad peaks (1300 - 1400 cm^{-1}) are seen in the C-C stretching region. Observation of such a mode is prohibited by the normal dipole selection rule[10] if the C-C bond is parallel to the surface. The vibrational mode assignments are summarized in Table I.

Bond lengths, bond angles and the position of adsorbed C_2H_2 on the surface cannot be accurately determined without a complete dynamical LEED intensity analysis. Nevertheless, the high resolution ELS results indicate that acetylene chemisorbs on Rh(111) below 270 K with its C-C axis oriented approximately parallel to the surface. The molecule is near sp^2 hybridization and therefore the C-C-H bond angle is no longer linear. A similar C_2H_2 geometry is seen in numerous organometallic cluster compounds.[11,12]

Both LEED and ELS indicate that the (2x2) acetylene overlayer is stable on the surface in vacuum between 210 and 270 K. The addition of H_2 to adsorbed C_2H_2 below ∿260 K causes no changes in the observed ELS spectra, although this surface species is still quite reactive. The addition of H_2 to chemisorbed C_2D_2 below 260 K results in a complex vibrational spectrum with peaks in both the C-H (C-D) stretching and bending regions. Although the deuterium and hydrogen readily exchange, no change in the adsorbate geometry is detected by high resolution ELS. The vibrational spectra of adsorbed acetylene only begin to change when the crystal is heated above 270 K in vacuum. The (2x2) C_2H_2 surface structure also disorders at this temperature.

The vibrational spectrum from the c(4x2) acetylene overlayer is shown in Fig.2c. This spectrum can either be obtained by warming the (2x2) acetylene overlayer to ∿270 K in the presence of 1×10^{-8} torr of hydrogen or by chemisorbing C_2H_2 on Rh(111) above 300 K. Hydrogen addition to the surface species above 270 K is necessary to obtain good quality, intense ELS spectra, however. Hydrogen addition was also required to complete this conversion in the LEED studies. This species is stable on the surface up to ∿420 K. The structure of this hydrocarbon overlayer will be discussed in the next section.

The vibrational spectra from the (2x2) and c(4x2) ethylene surface structures are shown in Figs. 3a and 3b. The ELS spectrum in Fig.3a is obtained by chemisorbing C_2H_4 on the crystal below 270 K. Spectrum 3b can either be observed by slowly warming the (2x2) overlayer structure (3a) to room temperature or by simply adsorbing ethylene on the Rh(111) surface above 290 K. The measured peak positions are listed in Table II. Once again the observed vibrational frequencies are independent of surface order and hydrocarbon exposure (>0.2 to <50 L). Note that these ELS spectra are almost identical to the vibrational spectrum from the stable c(4x2) acetylene overlayer shown in Fig.2c. The hydrocarbon species derived from ethylene chemisorption is also stable on the surface up to ∿420 K. Degradation of both the c(4x2) LEED pattern and of the vibrational spectrum occur at this temperature. The ELS spectrum resulting from the chemisorption of either C_2H_4 or C_2H_2 and H_2 on Pt(111)[4,13] above room temperature are quite similar and their stretching frequencies are also listed in Table II. The vibrational spectrum from the chemisorption of C_2D_4 on either Rh(111) (Fig.3c and Table II) or Pt(111)[4] (Table II) are also quite similar. Although the chemisorption of ethylene on Pt(111) has been studied by numerous techniques,[1,4,13,14] there is still debate over the precise geometry of the stable surface species. We simply point out that the stable hydrocarbon overlayer formed from the chemisorption of either ethylene or acetylene and hydrogen on both Pt(111) and Rh(111) yield identical vibrational spectra. A more complete discussion of the similarities between the chemisorption of ethylene on Rh(111) and Pt(111) will be presented in the next section.

It is interesting to note that the geometry of the adsorbed ethylene species on Rh(111) remains the same (as indicated by the ELS spectra) while the overlayer structure changes from a (2x2) to a c(4x2). This chemisorbed hydrocarbon should be an excellent candidate for a LEED structural analysis since the I-V beam profiles should change while the molecular geometry does not. The order-order transformation observed by LEED is irreversible at the low pressures employed in our experiments, and again no intermediate species are observed. Although this conversion is not affected by the presence of hydrogen, H-D exchange will occur in the hydrocarbon overlayer when H_2 is added to chemisorbed C_2D_4. No change in the adsorbate geometry is detected by high resolution ELS. The stable ethylene or acetylene plus hydrogen overlayer on Rh(111) can be decomposed to surface CH and CH_2 species above ∿420 K. The LEED pattern disorders at this temperature as well. These decomposition products will be discussed in a subsequent publication.[15]

C. TDS studies of ethylene and acetylene adsorption on Rh(111)

Castner et al[2,15] have previously shown that both C_2H_2 and C_2H_4 decompose on the Rh(111) single crystal surface upon heating to yield gas phase molecular hydrogen and surface carbon. The H_2 thermal desorption traces from the room temperature adsorption of these hydrocarbons have one major peak near 500 K followed by continuous hydrogen evolution up to approximately 825 K. The position of this desorption maximum was found to be independent of gas exposure.

Hydrogen desorption spectra from the ordered hydrocarbon overlayers chemisorbed on Rh(111) are shown in Fig.4. Traces 4a and 4d are from the (2x2) structures formed at 240 K from the adsorption of 1.5 L of acetylene and ethylene, respectively. Spectra 4b and 4c are from the c(4x2) surface structures formed from the metastable (2x2) C_2H_2 and C_2H_4 structures, respectively. After forming the c(4x2) structures, the crystal is cooled to 240 K before initiating the desorption experiments. Molecuar C_2H_2 and C_2H_4 desorption near 375 K is also observed.[16] The amount of hydrocarbon that is detected desorbing is less than 1°/o of the amount of hydrogen desorbed indicating that most of the adsorbed hydrocarbons decompose on the surface upon heating. — — — — — — — — — — — — — — — — → The hydrogen desorption spectrum from the c(4x2) ethylene species (Fig.4c) has a single desorption peak at 440 K followed by continuous hydrogen evolution until 750 K. This suggests that the desorption peak at 440 K in Fig.4d is from the stable hydrocarbon species which can be formed as the crystal is heated during the TDS experiments. The desorption peak at 350 K in Fig.4d is due to chemisorbed hydrogen on the Rh(111) surface. This desorption peak has been observed from hydrogen adsorption on clean Rh(111)[2,16,17] and after annealing the Rh(111)-(2x2)-C_2H_2 structure in hydrogen (Fig.4b). A similar peak is seen in H_2 TDS spectra from ethylene chemisorbed on Pt(111) at 320 K.[14] The origin of the desorption peak at 395 K in Fig.4d remains in question. Possible assignments include an unstable low temperature ethylene species or a transient intermediate hydrocarbon fragment present during the conversion of the metastable adsorbate to the stable surface phase.

Desorption traces b and c in Fig.4 from the c(4x2) hydrocarbon surface structures are identical above ∿400 K. The low temperature peak in 4b is from the hydrogen added in order to form a well ordered c(4x2) overlayer structure. This is in agreement with both the LEED and ELS results. ELS spectra taken before and after heating the crystal to 350 K show no major differences. Finally, the amount of H_2 desorbed from the surface in 4c is significantly less than the amount desorbed in 4d, indicating that the stable ethylene phase on Rh(111) is partially dehydrogenated.

Correlations with C_2H_4 Chemisorption on Pt(111) and Ni(111)

Below room temperature C_2H_2 and C_2H_4 associatively adsorb on Pt(111) with their C-C bond oriented approximately parallel to the surface.[4,13,18] Both molecules form (2x2) surface structures[19] and are significantly rehybridized.[4,13,18] These species are only metastable and can be transformed into a single stable phase by gently heating the crystal.[4,13,18,19] Addition of hydrogen and heating to ∿350K are necessary for acetylene to complete this conversion.[4] Although the stable species remains in a (2x2) surface structure, the LEED intensity vs. incident energy beam profiles change significantly.[18,19] This transformation has been detected by LEED,[18,19] ultraviolet photoelectron spectroscopy (UPS)[14] and high resolution ELS,[4,13] but there is still disagreement as to the geometry of the stable surface state, Proposed structures include ethylidyne ($\rightarrow$ C-CH$_3$)[1], ethylidene (>CH-CH$_3$)[4,13] and a vinyl species (>CH-CH$_2$).[14] Finally, the partial dehydrogenation of the surface ethylene species during the metastable to stable transition was observed by a combination of TDS and UPS.[14]

The chemisorption behavior of these two simple hydrocarbons on Rh(111) and Pt(111) are summarized in Table III. The similarities are quite striking. The rhodium substrate appears to be more reactive, however, since the conversion to the stable state occurs at a lower temperature. This can be correlated with the realtive posistions of these two metals in the periodic table; in general the bonding of small molecules to transition metal surfaces becomes stronger as one moves to the left in the periodic table.[20] By analogy with Pt(111) one might expect a weakly parallel bonded ethylene phase to form on Rh(111) at low temperatures. Such a species is not detected under our experimental conditions.

By comparison, the chemisorption of acetylene and ethylene on Ni(111) is quite different from that on either Rh(111) or Pt(111). Both molecules are associatively adsorbed at low temperatures,[7,21-25] but upon heating, the C-C bond of chemisorbed C_2H_2 is broken.[21] The remaining CH fragments undergo either carbon-hydrogen bond cleavage to leave carbon atoms on the surface or self-hydrogenation to form CH_2 species.[21] Alternatively, at high gas exposures acetylene can cyclotrimerize on the Ni(111) surface to form chemisorbed benzene.[22] Upon heating, chemisorbed ethylene first dehydrogenates to adsorbed acetylene[7,22,25] and then can undergo a similar C-C and C-H bond breaking sequence. The formation of CH and CH_2 species on Rh(111) at elevated temperatures is also observed.[15] High temperature studies have not been performed on Pt(111) as yet. We conclude that the species formed from the chemisorption of acetylene and ethylene on the Rh(111) and Pt(111) are quite similar and that analogous hydrocarbon fragments are not formed on Ni(111). Extension of these studies to Pd(111) would be most interesting.

Conclusions

These investigations lead to the following conclusions:

1. The chemisorption of acetylene and ethylene on Rh(111) yields a series of ordered structures:

$$Rh(111) + C_2H_2 \longrightarrow \underset{210-270\ K}{Rh(111)-(2x2)-C_2H_2} \xrightarrow{+H} \underset{270-420\ K}{Rh(111)-c(4x2)-C_2H_n}$$

$$Rh(111) + C_2H_4 \longrightarrow \underset{230-270K}{Rh(111)-(2x2)-C_2H_n} \longrightarrow \underset{270-420K}{Rh(111)-c(4x2)-C_2H_n}$$

where C_2H_n stands for the stable hydrocarbon species with undetermined hydrogen content. These order-order transformations are irreversible.

2. Below 270 K acetylene chemisorbs on Rh(111) with its C-C bond oriented parallel to the surface forming an approximately sp^2 hybridized species.

3. The chemisorption of C_2H_4 or C_2H_2 and hydrogen on Rh(111) and Pt(111) produce an identical stable surface species. This species has a stoichiometry of C_2H_n where n is less than 4.

4. The geometry of the adsorbed ethylene species on Rh(111), as determined by ELS, does not change during the conversion from the metastable to the stable species although the overlayer structure changes from a (2x2) to a c(4x2).

5. The addition of H_2 to chemisorbed C_2D_2 or C_2D_4 results in H-D exchange, but no change in the adsorbate geometry is detected by ELS.

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5. On the (111) crystal face of an fcc metal the (2x2) unit cell is a rhombohedron while the c(4x2) primitive unit cell is a rectangle.
6. The loss intensities are a strong function of the incident electron energy and only average values are reported here. This could be due to resonance or short-range scattering as discussed by Lehwald and Ibach for the case of acetylene chemisorption on Ni(111).[7]
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TABLE I: Vibrational modes for the metastable (2x2) - C_2H_2 (C_2D_2) species observed on Rh(111) at T < 270K (all frequencies in cm^{-1})

$C_2H_2(C_2D_2)$/Rh(111)	Assignments
3085 (∿2320) w	C-H(C-D) stretch
2984 (2230) m	
a	C-C stretch
887 (686) m	C-H (C-D) bend
706 (565) m	
323 (∿300) w	M-C stretch

Intensity: s=strong m=medium w=weak

a. Small broad peak in the 1300-1400 cm^{-1} region is observed in several spectra

TABLE II: VIBRATIONAL MODES FOR THE STABLE SPECIES OBSERVED ON Rh(111) AND Pt(111) UPON ADSORPTION OF EITHER C_2H_4 OR C_2H_2 AND H ABOVE 300 K.

(all frequencies in cm^{-1})

Chemisorption of C_2H_4 or C_2H_2+H		Chemisorption of C_2D_4	
Rh(111)	Pt(111)	Rh(111)	Pt(111)
∿3000 w	3025 - 3105 w	2180 w	broad unresolved band
∿2900 w	2900 - 2940 m	2080 m	
shoulder	1420 m	1150 s	1150 s
1350 s	1350 - 1360 s	990	1010 w
1130 s	1130 s	860 m	850 w
880 m	900 m	403 w	430 m
450 w	435 m		

Intensity: s=strong m=medium w=weak

TABLE III: Summary of LEED, ELS and TDS data for the chemisorption of C_2H_2 and C_2H_4 on Rh(111) and Pt(111).

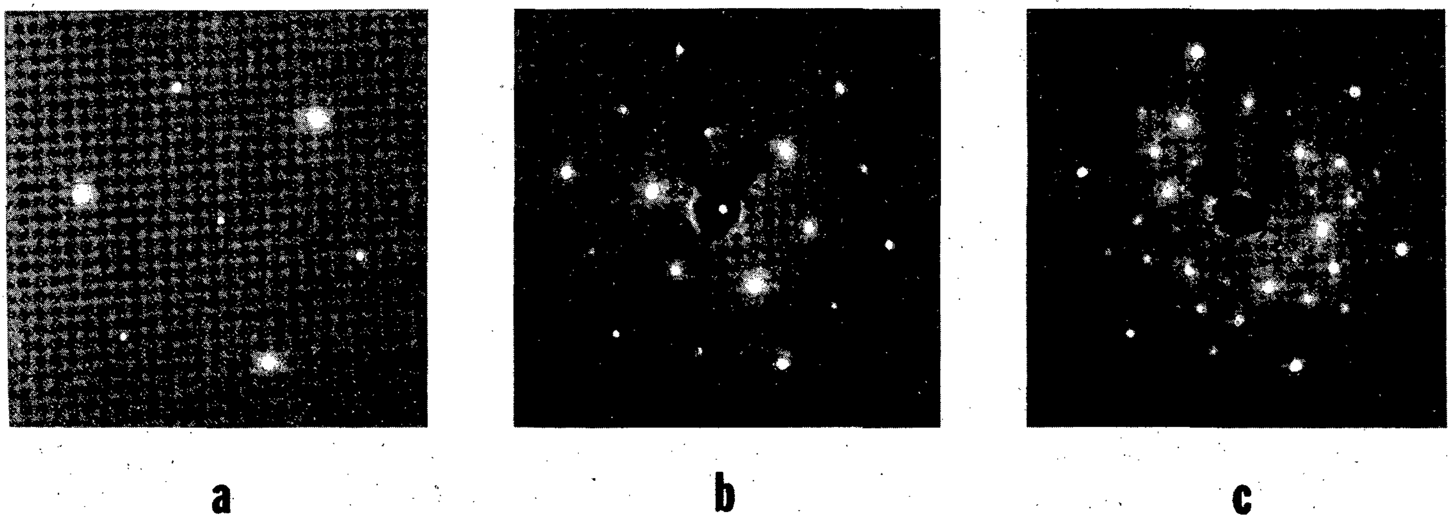
	Rh(111) C_2H_2	 C_2H_4	Pt(111) C_2H_2	 C_2H_4
Metastable species:				
LEED	(2x2)	(2x2)	(2x2)	(2x2)
ELS	parallel bonded ($\sim sp^2$)	C_2H_n[a]	parallel bonded ($\sim sp^2$)	parallel bonded ($\sim sp^3$)
Conversion to stable species:[b]				
Temperature	∼270K	∼270K	∼350K	∼300K
Addition of hydrogen?	yes	no	yes	no
Stable species:				
LEED	c(4x2)	c(4x2)	(2x2)	(2x2)
ELS	C_2H_n	C_2H_n	C_2H_n	C_2H_n
Partial dehydrogenation (TDS)	no	yes	no	yes
Decomposition temperature	420K	420K	450K	450K

a. Vibrational spectrum previously assigned as ethylidyne ($\geqslant$C-CH_3), ethylidene (>CH-CH_3) and a vinyl species (>CH-CH_2), see text.

b. Conditions for complete conversion.

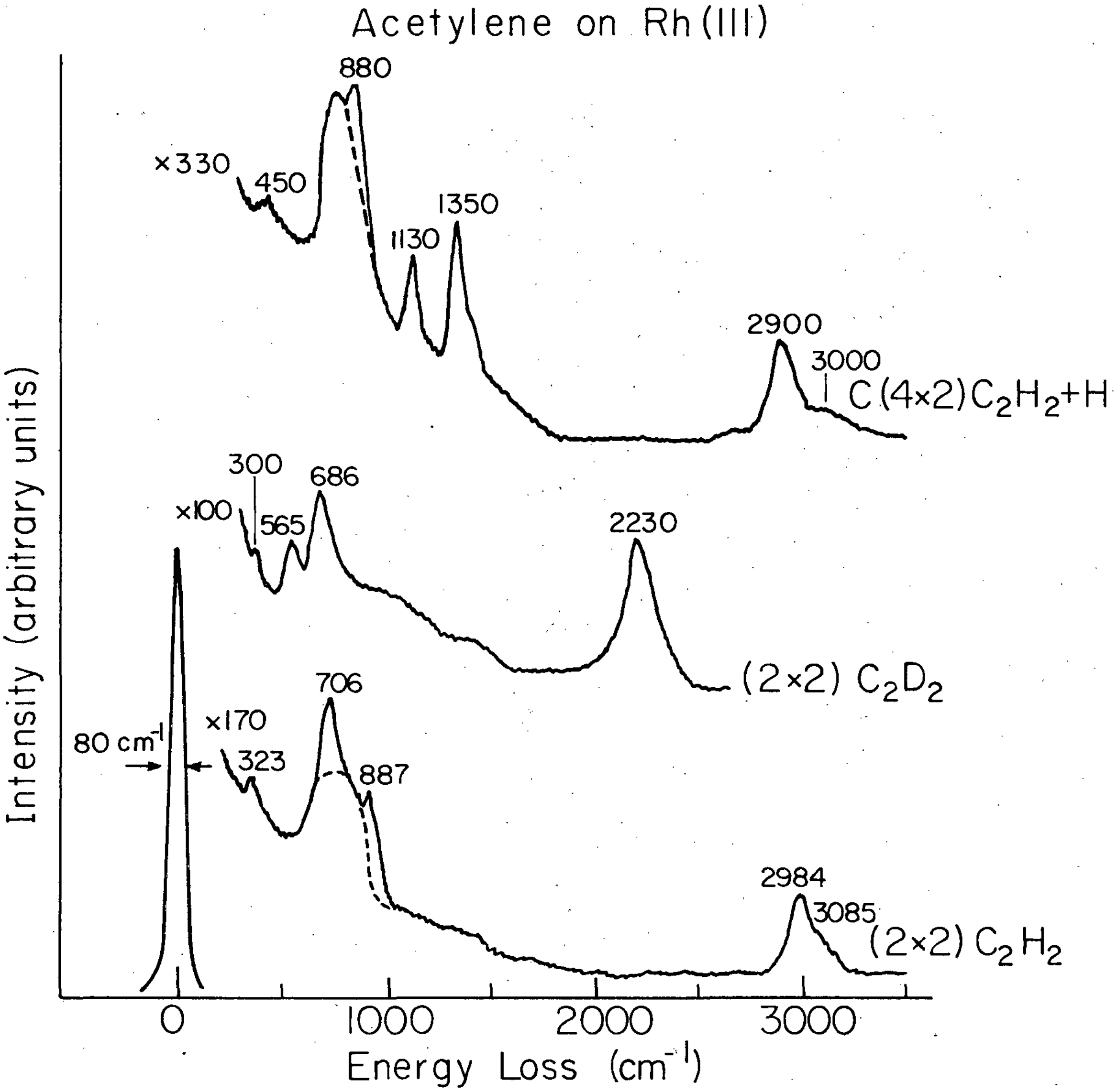
Figure Captions

1. LEED patterns from surface structures produced by either C_2H_2 or C_2H_4 adsotption on Rh(111). (a) clean Rh(111) at 92.5 eV, (b) Rh(111)-(2x2) from C_2H_4 chemisorption at 74 eV, and (c) Rh(111)-c(4x2)-C_2H_2+H at 67.5 eV.
2. High resolution ELS spectra of chemisorbed acetylene on Rh(111). (a) (2x2)-C_2H_2, (b) (2x2)-C_2D_2, and (c) c(4x2)-C_2H_2+H. The vibrational frequencies are listed in Tables I (spectra a and b) and II (spectrum c). The broad peak (dotted line) centered near 800 cm^{-1} may be caused by a reflection inside the spectrometer (see text).[8]
3. High resolution ELS spectra of chemisorbed ethylene on Rh(111). (a) (2x2) from C_2H_4 chemisorption, (b) c(4x2) from C_2H_4 chemisorption and (c) (2x2) from C_2D_4 chemisorption. The vibrational frequencies are listed in Table II.
4. Hydrogen desorption from the (a) (2x2) and (b) c(4x2) overlayer structures formed during C_2H_2 adsorption on Rh(111) and from the (c) c(4x2) and (d) (2x2) structures from C_2H_4 adsorption on Rh(111). After forming the c(4x2) surface structures, the crystal is cooled to 240K before initiating the desorption experiments. The heating rate is 40K/sec.



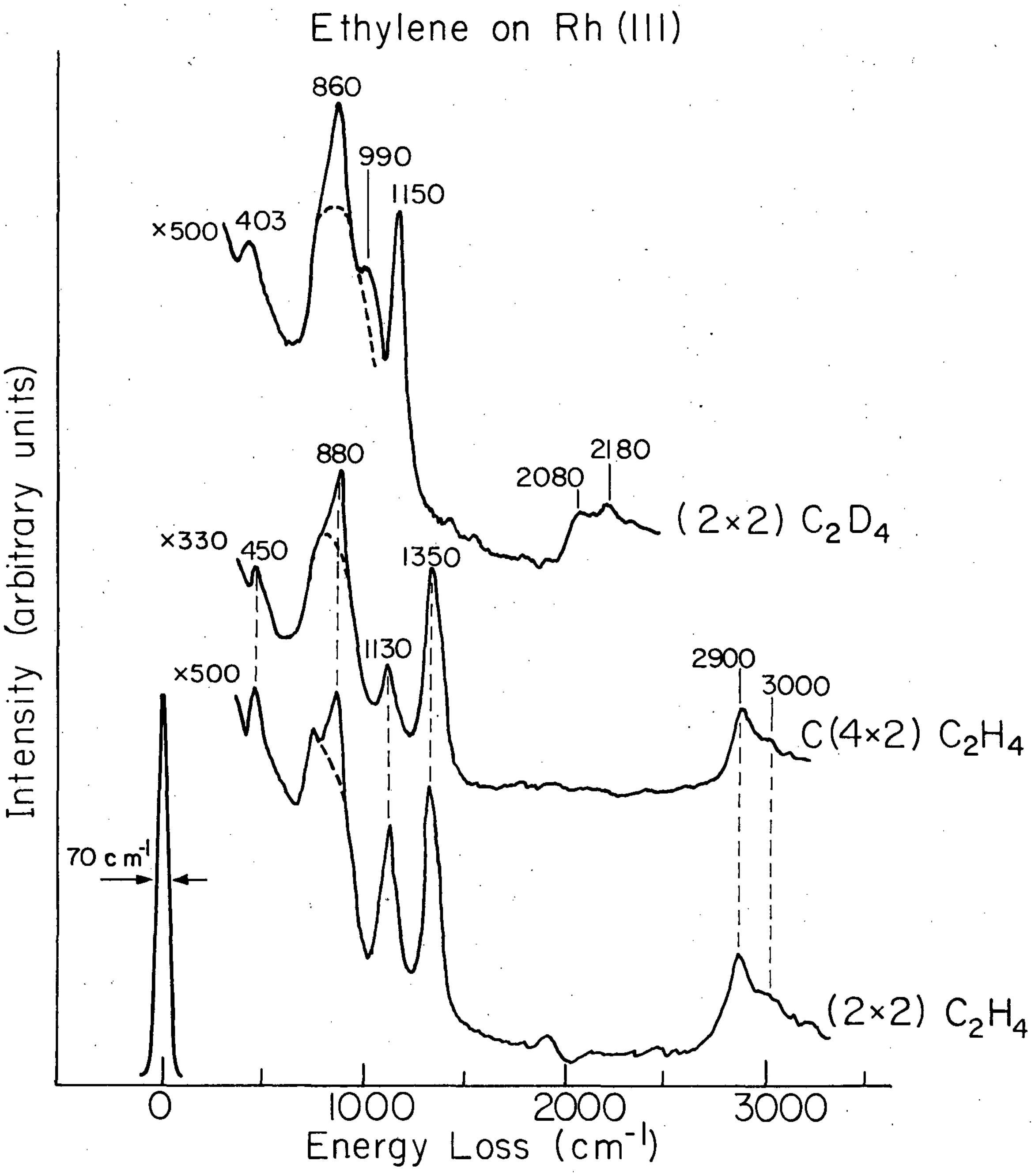
XBB788 10161

Fig. 1



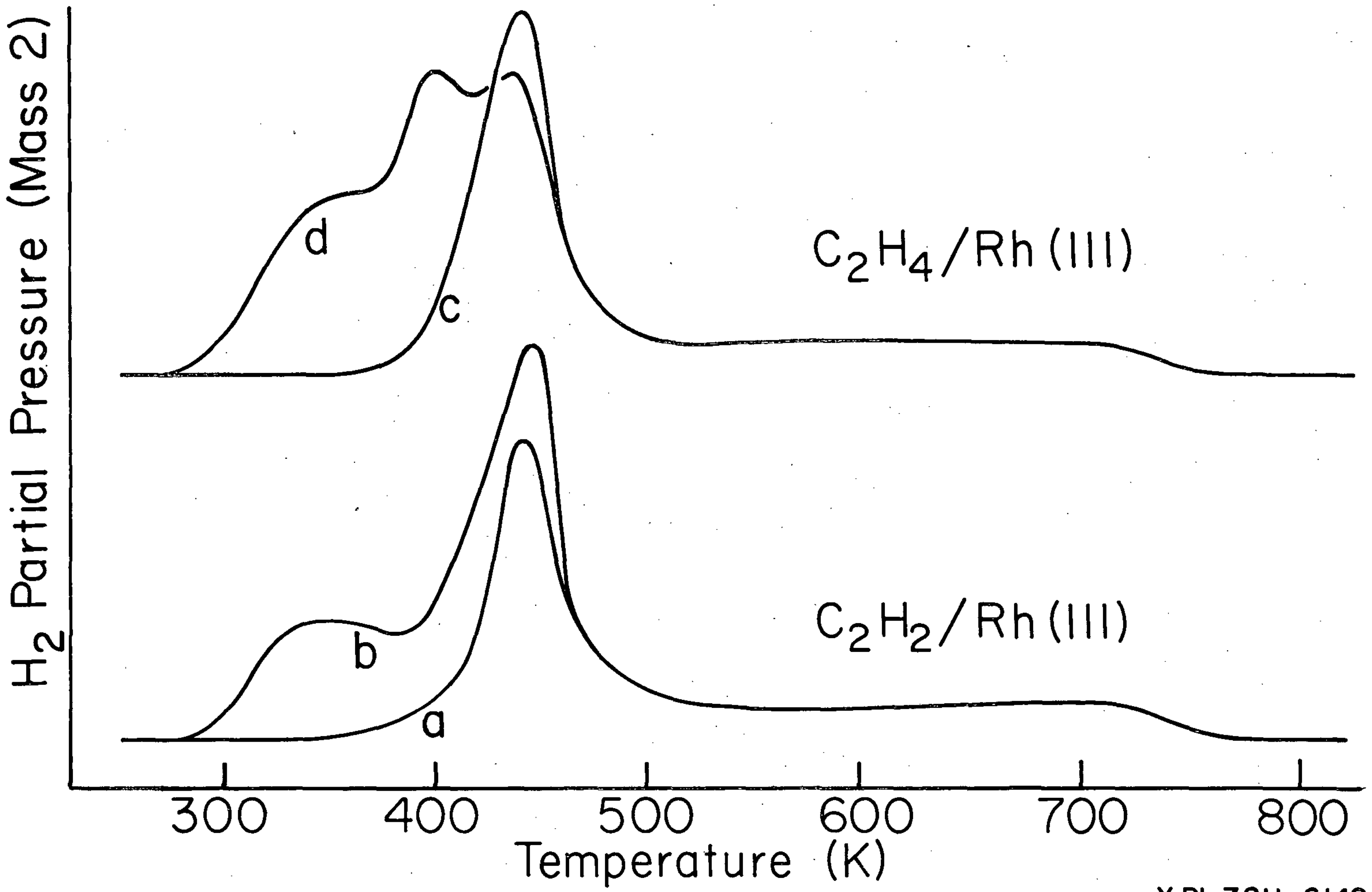
XBL 798-6968

Fig.2



XBL798-6969

Fig.3



XBL 7811-6149A

Fig.4

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720