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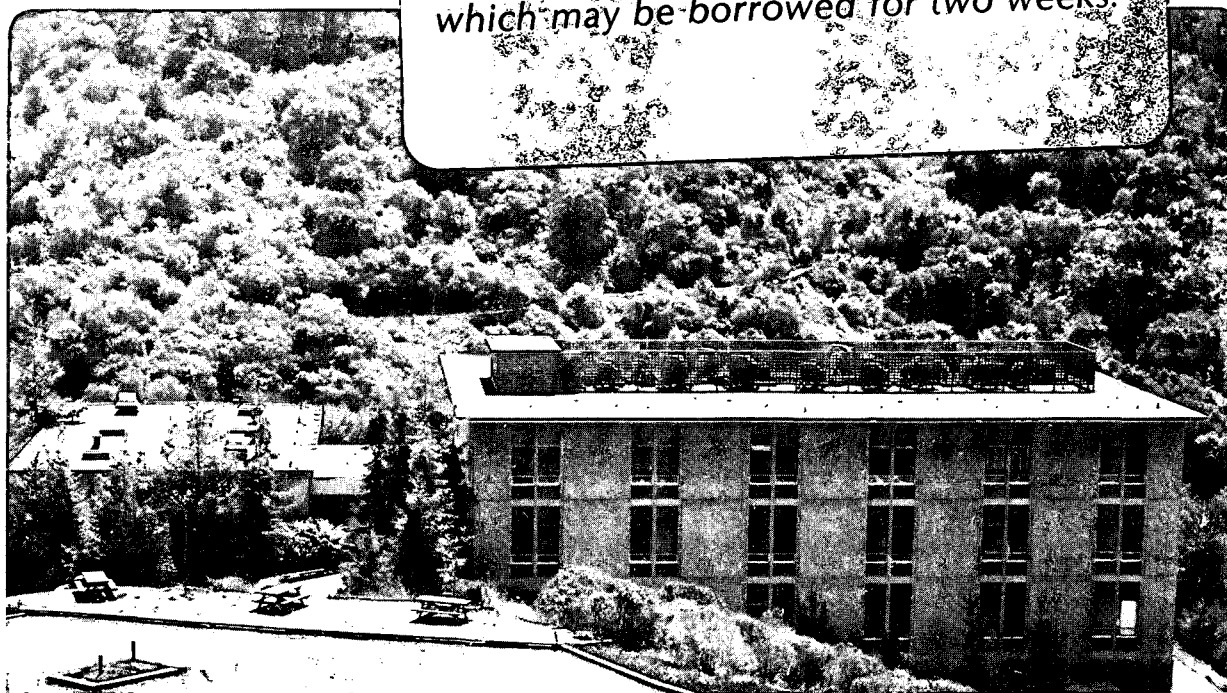
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BONDING AND THERMAL DECOMPOSITION OF PROPYLENE, PROPADIENE, AND METHYLACETYLENE
ON THE Rh(111) SINGLE CRYSTAL SURFACE

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Abstract

We have studied the reaction of propylene, propadiene and methylacetylene with Rh(111) crystal faces in ultra-high vacuum (UHV) from 80 to 800 K using low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS). All three hydrocarbons adsorb intact at 80 K, bonding with the surface through their unsaturated carbon-carbon bonds. At this temperature, methylacetylene forms a p(2x2) LEED pattern while propylene and propadiene adsorb as disordered monolayers. Above 200 K the first CH bonds are broken and all the C₃ hydrocarbons form p(2x2) LEED patterns which are stable up to 270 K. The propylene fragment in this temperature range is propylidyne ($\equiv\text{CCH}_2\text{CH}_3$), while propadiene isomerizes to methylacetylene. By room temperature all the C₃ hydrocarbons have decomposed to ethylidyne ($\equiv\text{CCH}_3$) and polymerized C_xH fragments. Surface hydrogen is instrumental in the C-C bond breaking, and partial deuteration studies were performed to determine which C-C bonds break first. The ethylidyne species are stable up to 400 K, above which they decompose to C_xH fragments. The bonding and the thermal decomposition pathways for these molecules on Rh(111) is discussed, in addition, a comparison is made to Pt(111) surface chemistry.

1. Introduction

Similar transition metal surfaces often perform quite differently in heterogeneous catalysis. For example, platinum and rhodium, neighbors in the periodic table, catalyze very different hydrocarbon synthesis and conversion reactions. Rhodium surfaces are much better catalysts for the synthesis of hydrocarbons from CO and H₂, while platinum surfaces are among the most active catalysts for the conversion of straight chain hydrocarbons like n-hexane into aromatics, saturated rings, and branched isomers [1].

These differences between platinum and rhodium in hydrocarbon catalysis must be the result of different bonding of the reactants, intermediates, and/or products to the metal surfaces. Consequently, we are studying in detail how hydrocarbons bond to and react on well-defined, platinum and rhodium single-crystal surfaces under ultra-high vacuum conditions in order to gain a molecular level understanding of why these metals do such different catalysis.

We have previously reported our findings on how ethylene [2-5] and benzene [6-9] bond and thermally decompose on the close-packed Rh(111) crystal surface. Interestingly, for these molecules, the thermal chemistry on Rh(111) is quite similar to that reported for Pt(111) [10-14] in that the same sequence of decomposition fragments are formed. However, the molecular adsorption geometries of ethylene and benzene on these isostructural surfaces are somewhat different. Further, the decomposition temperatures of these two adsorbates are 50-100 K lower on Rh(111) than on Pt(111), consistent with Rh surfaces being the more active catalysts for hydrocarbon

bond breaking reactions. However, Rh(111) and Pt(111) are equally good catalysts for the hydrogenation of ethylene to ethane [15-17], consistent with the similarities in ethylene chemistry in UHV on these surfaces.

In this paper we report our results on the bonding and thermal decomposition of propylene, propadiene and methylacetylene on Rh(111) in UHV. The chemistry of these C₃ hydrocarbons on Rh(111), unlike ethylene and benzene, is substantially different from their chemistry on Pt(111).

The main experimental techniques used in our studies were high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS). Partially deuterated compounds of propylene and methylacetylene have also been used to confirm the surface chemistry. We find that all the C₃ unsaturated hydrocarbons adsorb molecularly for temperatures below 200 K. Propylene decomposes above 200 K to form propylidyne ($\equiv\text{CCH}_2\text{CH}_3$) while propadiene isomerizes to methylacetylene, which remains adsorbed molecularly at temperatures up to 270 K. We also find that several of the previously reported LEED structures produced by large exposures of propylene and methylacetylene can be reproduced by smaller doses with the presence of coadsorbed CO. Above 270 K, all three C₃ hydrocarbons decompose on Rh(111) by C-C bond breaking to form ethylidyne and polymerized C_xH species, in contrast to Pt(111) chemistry where no ethylidyne is formed.

2. Experimental

Experiments were performed in two different ultra-high vacuum chambers with base pressures of 1×10^{-10} torr. Each chamber is equipped with LEED, Auger electron spectroscopy (AES), a mass spectrometer for TDS, and a HREEL spectrometer and both have been previously described [6,7,18]. Three different Rh(111) single crystal surfaces were used during the course of the experiments. All three were $0.5-1 \text{ cm}^2$ disks, $\sim 2 \text{ mm}$ thick, and cut from a single crystal rod of $>99.996\%$ purity obtained from the Materials Research Corporation. After polishing by standard methods [3], the crystals were mounted in UHV by spotwelding 0.020 inch Ta wire between the crystal edges and the manipulator. The crystals were resistively heated to temperatures $>1200 \text{ K}$ and cooled to 77 K by flowing liquid nitrogen through the manipulator. The single crystal surfaces were cleaned by a combination of heating in O_2 , Ar^+ sputtering, and annealing in UHV until free of C,S,O, and B [19] as detected by AES, LEED, and HREELS.

Gases were adsorbed on the Rh(111) surfaces using microcapillary array dosers. Dosages are reported in Langmuirs ($1 \text{ Langmuir (L)} = 10^{-6} \text{ torr} \cdot \text{sec}$) where the measured dose pressure has been corrected for $\times 5$ or $\times 20$ enhancements of the molecular flux at the crystal surface as a result of the array dosers in the two chambers, but are uncorrected for differing ion gauge sensitivities of the gases. The term saturation coverage is used to mean the highest attainable surface coverage of the hydrocarbons for the temperatures above multilayer desorption. Typically, exposures $>5 \text{ L}$ gave saturation coverages of about one hydrocarbon molecule per four surface Rh atoms.

Gases were checked for purity by gas chromatography (GC) or mass spectrometry and were used as obtained from the following sources: propylene (Matheson

Cp, 99%), methylacetylene (LBL, contains 7.5% C₂H₂), Propadiene (Matheson, 97%), propylene-d₆ (MSD isotopes, 99 atom %), propylene-3,3,3-d₃ (MSD isotopes, 98 atom %), methylacetylene-d₁ (MSD isotopes, 98 atom %), H₂ (Matheson, 99.9%), D₂ (Matheson, ~99.5 atom %). The C₃H₄ isomers (methylacetylene and allene) did not isomerize in the stainless steel gas handling lines as proven both by GC and by a chemical test to distinguish alkenes and alkynes [20].

For TDS, both sides of the single crystal disk were cleaned and exposed to gases using the array dosers. The crystal was heated at 10-30 K/sec with one side facing a UTI mass spectrometer with the ionizer ~5 cm from the surface. Multiple masses were recorded as a function of time and temperature using a Commodore PET 2001 computer interfaced to the mass spectrometer. Peak areas were determined by integration of the mass vs. time spectra. For overlapping peaks, perpendiculars were drawn from the baseline to the minimum in the overlap region.

The HREEL spectrometers are similar to designs commonly used and consist of 127° cylindrical monochromator and analyzer sectors. In one of the spectrometers [6] the total scattering angle is fixed at 120°, so for specular HREELS $\theta_{in} = -\theta_{out} = 60^\circ$ from the surface normal. The other HREEL spectrometer has a rotatable analyzer and was operated with $\theta_{in} = 65^\circ$ from the surface normal [7]. Both spectrometers were operated at an overall system resolution (FWHM) of 5-7.5 meV (40-60 cm⁻¹, 1 meV = 8.0655 cm⁻¹) and with incident beam energies of 2-5 eV. HREEL spectra were recorded either at room temperature or at 77 K after briefly annealing the adsorbed monolayer to the temperatures indicated on the spectra. All transformations with heating were irreversible.

3. Results and Interpretation

3.1 Thermal Desorption Spectroscopy (TDS)

Upon heating the rhodium crystal, H₂ gas is the primary desorption product from the (111) surface that has been covered with propylene, methylacetylene, or propadiene. Figure 1 shows the H₂ TD spectra for 10 Langmuir doses of methylacetylene, allene, and propylene adsorbed at 77 K on Rh(111). These are compared with the TD spectrum for ethylene adsorbed at 220 K. All four desorption profiles have similar H₂ desorption peaks at ~ 370, ~420, and 500-800 K.

There are several reasons for the similarities of the H₂ thermal desorption spectra for these four hydrocarbons. First, the work of Yates et al. [21] has shown that adsorbed hydrogen atoms desorb from a clean Rh(111) surface in the temperature range 250 to 400 K. Therefore, even though HREELS shows that ethylene, propylene, propadiene, and methylacetylene all decompose below room temperature, the adsorbed hydrogen atoms, which result from this decomposition, do not desorb until just above room temperature, resulting in the lowest temperature peak in the H₂ TD spectra shown in Figure 1. This desorption peak is absent when the hydrocarbons are adsorbed at room temperature.

Second, the similarity of the H₂ TD peaks above 400 K suggests that these hydrocarbons all decompose above 400 K to the same hydrocarbon fragment(s). This is supported by HREELS results, which we discuss in detail in separate publications [8,22]. We note here that the long H₂ desorption tail from 500 to 800 K is characteristic of hydrocarbon decomposition on Rh(111) [8,22]. This desorption feature has been previously discussed for benzene decomposition on Rh(111) and was attributed to polymerization of C_xH

fragments on the surface to form graphitic carbon [8].

Variation of the hydrocarbon coverage changed the appearance of the H_2 desorption spectra substantially. The coverage effects were studied for methylacetylene and propylene and are similar to those found for C_2H_4 adsorption on Rh(111) [4] and Pt(111) [23]. At low hydrocarbon coverages the H_2 TD peaks overlap and are poorly resolved, because the desorption of hydrogen bound directly to the metal surface occurs at higher temperature and the hydrocarbon fragments decompose at lower temperature. However, HREEL spectra show that the hydrocarbon fragments formed in the low coverage decompositions are the same as those for saturation coverages.

In the case of propylene and methylacetylene, we have also checked for desorption of products other than H_2 . For methylacetylene, masses 2, 16, 27, 40 and 78 were monitored and, at all coverages, no masses other than mass 2 were detected. For propylene, masses 2, 16, 27, 28 and 42 were monitored; besides mass 2, only molecular propylene desorption (mass 42) was observed (at 200 K), and then only for coverages above about 80% of saturation coverage. Analogous results have been found for ethylene on Rh(111) [4].

3.2 Low-Energy Electron Diffraction (LEED)

Low-energy electron diffraction was quite useful in determining the temperatures where the bonding of propylene, propadiene, and methylacetylene on the surface changed. In Figure 2 we summarize the LEED patterns observed for saturation coverages of the C_3 hydrocarbons and compare them with those observed previously for C_2H_4 [4,24] and C_2H_2 [2,25]. The vertical solid or dashed lines in Figure 2 indicate the temperatures at which there are changes in the surface vibrational spectrum. These are

the temperatures at which the hydrocarbons or hydrocarbon fragments decompose, and the decompositions are usually accompanied by a change in the LEED structure. The results in Figure 2 are consistent with those reported previously [24,26,27], except that the $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ and $c(4\times 2)$ LEED structures were produced here by coadsorption of CO. In Figure 2, the coadsorption of CO is indicated in Figure 1 by an "#".

By comparing the LEED patterns summarized in Figure 2, we can learn qualitatively how the decomposition pathways for these hydrocarbons are similar and different. Propylene and propadiene do not form ordered monolayers at 77 K, but methylacetylene, like acetylene, orders into a $p(2\times 2)$ overlayer. Above 200 K, the temperature at which ethylene decomposes to form a $p(2\times 2)$ ethylidyne overlayer [2-4], propylene and propadiene also form $p(2\times 2)$ structures. These $p(2\times 2)$ structures for all the C_3 hydrocarbons as well as for ethylidyne change to $c(4\times 2)$ structures at ~270 K in the presence of coadsorbed CO.

Above 420 K, all the C_3 hydrocarbons, like the C_2 hydrocarbons, form only (1×1) LEED patterns with some diffuse background intensity indicating that the hydrocarbon overlayer is disordered. This disordering temperature corresponds to the 420 K H_2 desorption peaks in the TD spectra of Figure 1, which are due to additional decomposition.

3.3 High-Resolution Electron Energy Loss Spectroscopy (HREELS)

Surface vibrational spectra were taken by HREELS for all the C_3 hydrocarbon, ordered monolayers listed in Figure 2. The spectra were taken after momentarily warming a saturation coverage of the hydrocarbon

to the temperature necessary to produce the hydrocarbon or hydrocarbon fragment monolayer. The temperature of the sample, when the spectra were taken, was either 77 K or room temperature.

3.3.1 Propylene Below 200 K

Figure 3 shows the vibrational spectra of a Rh(111) surface saturated with propylene at 77 K and after warming to the indicated temperatures. Also shown are the surface fragments responsible for these vibrational spectra which we now assign. The vibrational spectrum below 200 K has many poorly resolved and overlapping peaks, making assignment of this spectrum difficult. Upon deuteration, the overlap of the bending modes between 900 and 1400 cm^{-1} becomes even more severe and does not aid in the assignment. Also, most of the vibrational normal modes of molecularly adsorbed propylene are dipole active because of the low symmetry of propylene and, consequently, can be observed in the specular direction. Still, the spectrum in Figure 2A is consistent with molecularly adsorbed propylene, bonding with the surface through the carbon atoms originally involved in the π -bond.

Assuming that propylene is molecularly adsorbed, we can make an approximate assignment of the 100 K propylene spectrum by comparison to the frequencies of gas phase propylene [28] as follows: 2960 = $\nu(\text{CH}_3) + \nu(\text{CH}_2) + \nu(\text{CH})$; 1425 = $\delta_s(\text{CH}_3) + \text{CH}_2$ scissor; 1200 = CH_2 wag or CH deformation; 1050 = CH_3 rock; 925 = $\nu(\text{CC}) + \text{CH}_2$ twist, rock. The assumption that propylene adsorbs molecularly at 77 K is reasonable since chemisorbed ethylene on Rh(111) does not decompose until 200 K, and molecular propylene desorption is detected during TDS.

3.3.2 Propylene at 220 K

As indicated in Figure 2, chemisorbed propylene forms a (2x2) LEED structure on Rh(111) between 200 and 270 K. This structure has been previously studied by LEED by Koestner et al. [24]. These researchers proposed that this (2x2) structure consists of a propylidyne ($\equiv\text{C}_2\text{H}_2\text{CH}_3$) species, with the bottom two carbon atoms ordered in a (2x2) lattice, while the methyl groups are disordered. This proposal was based on the similarity of the LEED I-V curves for the (2x2) propylene/Rh(111) structure with those taken at the same temperature for the (2x2) ethylene/Rh(111) structure, which had been previously determined to be an ethylidyne ($\equiv\text{CCH}_3$) species. Further, Koestner et al. observed, for large propylene exposures (>100 L), a $(2\sqrt{3}\times 2\sqrt{3})$ R30° LEED structure, which they interpreted to result from the propylidyne methyl groups ordering into a $(2\sqrt{3}\times 2\sqrt{3})$ R30° superlattice. We were able to reproduce the $(2\sqrt{3}\times 2\sqrt{3})$ R30° LEED pattern more simply by coadsorbing CO with the (2x2) propylene/Rh(111) structure. The C-O stretching frequency of the CO in the $(2\sqrt{3}\times 2\sqrt{3})$ R30° structure is 1750 cm^{-1} , consistent with CO adsorption in the vacant hollow site present in the structure proposed by Koestner et al. for the $(2\sqrt{3}\times 2\sqrt{3})$ R30° propylidyne structure. The proposed propylidyne plus CO structure is shown in Figure 4.

Figure 3B shows the vibrational spectrum for a propylene monolayer annealed to 220 K in order to form the (2x2) monolayer. The vibrational spectrum for the $(2\sqrt{3}\times 2\sqrt{3})$ R30° CO + propylene structures is the same except for the added C-O stretching mode. We have also taken the surface vibrational spectrum for the (2x2) propylidyne overlayer on Pt(111) to compare with Rh(111). A similar spectrum for propylene decomposition on Pt(111) has also recently been reported and assigned by Avery and Sheppard [29]. Figure 5 shows the vibrational spectra for the propylene-

derived (2x2) monolayers on Pt(111) and Rh(111). The spectra are indeed quite similar. The extra modes between 500 and 700 cm^{-1} on Rh(111) are probably the result of coadsorbed atomic hydrogen [30]. Again, these vibrational spectra, because of their complexity cannot be definitively assigned. However, as we show in Table I, the vibrational spectra are consistent with propylidyne species.

In Table I, the first two columns list the measured IR frequencies and approximate normal mode descriptions determined by a normal mode analysis for 1,1,1-trichloropropane [31], a propylidyne species bonded to three chlorine atoms. Only frequencies for modes of A' symmetry are listed, since only these modes will show dipole activity for a surface propylidyne species having C_s symmetry. The vibrational frequencies of 1,1,1-trichloropropane were chosen to predict the surface vibrational frequencies of propylidyne, since an analogous comparison between the vibrational spectra of gas phase 1,1,1-tribromoethane and surface ethylidyne showed good agreement [10]. Columns 3 and 4 of Table I list the frequencies we have observed by HREELS for the (2x2) propylene-derived monolayers on Pt(111) and Rh(111). Column 5 tabulates the frequencies for propylene adsorbed on Pt(111) at 300 K observed and assigned by Avery and Sheppard to propylidyne. Column 6 lists the IR frequencies attributed to a propylidyne ligand in an organometallic tricobalt cluster: $\text{Co}_3(\text{CO})_9(\text{C}_2\text{H}_5)$ [32].

Qualitatively, the Rh(111) frequencies are consistent with propylidyne. Also, the relative intensities are similar to those for propylidyne on Pt(111) and to those for analogous modes in 1,1,1-trichloropropane. We conclude, in agreement with Koestner et al. [24], that propylene decomposes above 200 K on Rh(111) to form propylidyne which bonds in a 3-fold hollow site like a

methyl-substituted ethylidyne.

Further chemical evidence supports the conclusion of a propylidyne species. The chemical evidence for propylidyne is based on a comparison of propylene chemistry on Rh(111) to ethylene chemistry on Rh(111) and to propylene chemistry on Pt(111). C_2H_4 adsorbed on Rh(111) forms an ethylidyne species ($\equiv CCH_3$) above 200 K which "stands up" on the surface in a 3-fold hollow site with the C-C bond perpendicular to the surface, and forms a (2x2) LEED pattern like propylene adsorbed at this temperature [3]. Analogous bond breaking and bond formation for propylene produces propylidyne. On Pt(111), TDS [33] and secondary ion mass spectrometry [34] results indicate that propylene forms propylidyne at the same temperature at which ethylene decomposes to ethylidyne. Also, on Pt(111), propylidyne and ethylidyne both form (2x2) LEED patterns.

3.3.3 Propylene at 300 K

Figure 3C shows that by annealing to 300 K, propylidyne decomposes leaving a much simpler vibrational spectrum. Several aspects of this vibrational spectrum suggest that C-C bonds have broken in the decomposition of propylidyne to form ethylidyne plus C_xH fragments.

First, the peak frequencies and relative intensities in the 300 K vibrational spectrum are quite similar to ethylidyne on Rh(111) [4], Pt(111) [11], and Pd(111) [35]. The only differences are extra peaks at 730 and 3005 cm^{-1} . This suggests that two species are produced from propylidyne by C-C bond breaking: ethylidyne and another hydrocarbon fragment.

Figures 6A and 6B compare the vibrational spectra of C_2D_4 and C_3D_6

adsorbed on Rh(111) at 300 K. The C_3D_6 derived spectrum has all the peaks in the the C_2D_4 spectrum along with extra peaks 575, 1455, and 2185 cm^{-1} . The 575 and 2185 cm^{-1} peaks are due to C-D vibrations, since they correspond to the 730 and 3005 cm^{-1} peaks in the undeuterated spectrum shifted in frequency by about $\sqrt{2}$. The 1452 cm^{-1} peak is probably a C-C stretching mode, unshifted upon deuteration, and obscured by the C-H bends in Figure 3C. So, these spectra are consistent with the interpretation of propylene decomposing at 300 K into ethynidyne and another hydrogen fragment.

We propose that the other hydrocarbon fragments for decomposed propylene are C_xH species. Such species, with similar vibrational frequencies, were reported for decomposed benzene on Rh(111) [8]. In this case, the vibrational spectrum was assigned, by comparison to organometallic clusters, as $\delta(CH) \approx 800$, $\nu(CH) \approx 3000$, and $\nu(CC) \approx 1400$ cm^{-1} . These C_xH species probably result from the polymerization of some of the CH fragments which are initially formed in the decomposition. Consistent with this polymerization interpretation, we have observed that the relative intensity and position of the 730 cm^{-1} (575 cm^{-1}) modes varies some, depending on whether the monolayer is formed by annealing from 77 to 300 K or by dosing propylene at 300 K.

For two reasons, we rule out the presence of a C_3 hydrocarbon species on Rh(111) at 300 K having a vibrational spectrum resembling that of ethynidyne. First, the C-C stretching frequencies at 1130 cm^{-1} in Figure 3C and at 1155 cm^{-1} in Figure 6B are the same as for $\equiv CCH_3$ and $\equiv CCD_3$; it is highly unlikely that a three carbon species would have the same C-C stretching frequency.

Second, the intense 1340 cm^{-1} peak and weak shoulder at 1430 cm^{-1}

are characteristic of δ_s and δ_{as} CH_3 vibrations excited by dipole scattering for a methyl group with its symmetry axis close to the surface normal. Such a geometry would be highly unlikely for a C_3 hydrocarbon chain with nearly tetrahedral bond angles. Therefore, we conclude that propylidyne decomposes at room temperature on $\text{Rh}(111)$ by both C-H and C-C bond breaking to form ethylidyne and C_xH species.

3.3.4 Propylene Above 450 K

Annealing to 450 K, all vibrational features due to ethylidyne disappear, indicating that the ethylidyne species decomposes at this temperature. From 450 to 800 K, the surface vibrational spectrum undergoes subtle, gradual changes, consistent with the broad H_2 desorption tail in the TDS over this temperature range. This behavior of the HREELS and TDS above 450 K is characteristic for the thermal decomposition on $\text{Rh}(111)$ of all the C_2 , C_3 , C_4 hydrocarbons, and benzene [8,22]. In our previous reports for benzene above 450 K on $\text{Rh}(111)$, we proposed that, from 450 to 800 K, C_xH species are present on the surface [8]. As the temperature increases above 450 K, these fragments dehydrogenate and polymerize to form longer chains and, eventually, a graphitic overlayer. The spectrum of decomposed propylene at 500 K, as shown in Figure 3D, illustrates the general features in the vibrational spectra of these C_xH polymer species: intense C-H bending modes at $750\text{--}850\text{ cm}^{-1}$, weak and broad C-C stretching modes at $1300\text{--}1500\text{ cm}^{-1}$, and C-H stretching modes at $2950\text{--}3050\text{ cm}^{-1}$.

3.3.5 Methylacetylene and Propadiene Below 270 K

By taking HREEL spectra as a function of temperature, we find that propadiene, like propylene and ethylene, begins to decompose on Rh(111) at ~200 K. Methylacetylene, like acetylene, however, does not decompose until 270 K. Figures 7A and 7C show the vibrational spectra of molecularly adsorbed propadiene at 100 K and methylacetylene at 240 K. Figure 7B shows the HREEL spectrum of a propadiene monolayer annealed to 240 K to initiate decomposition.

To interpret the surface vibrational spectrum of propadiene adsorbed on Rh(111) at 100 K shown in Figure 7A, we have compared it to the IR spectra of gas phase propadiene [36] and 1,2,2,3-tetrachloropropane [37], which was chosen to mimic di- σ bonding of molecular propadiene to the surface. It appears that all three carbon atoms of propadiene interact with the surface, since the CH₂ stretching frequencies are centered at 2950 cm⁻¹, with no evidence for a peak near the gas phase propadiene ν CH₂ frequency of 3015 cm⁻¹. The peak frequencies below 1500 cm⁻¹ are reasonable for scissor, wag, rock, and/or twist vibrations of the CH₂ groups.

After annealing to 240 K, the most significant changes in the propadiene vibrational spectrum (Figure 7B) are that (1) the peaks near 1400 cm⁻¹ increase in the relative intensity, (2) the CH stretches shift to slightly lower frequency and (3) the modes near 950 cm⁻¹ shift to higher frequency. These changes suggest formation of a methyl group; in the gas phase, the characteristic CH₃ bending vibrations are at ~1380 and ~1470 cm⁻¹, a rocking vibration is at ~1115 cm⁻¹ and a symmetric stretching vibration is at ~2910 cm⁻¹. Further, the vibrational spectrum

of the (2x2) propadiene-derived overlayer at 240 K begins to resemble that for the (2x2) overlayer of methylacetylene at 240 K (Figure 7C). We therefore propose that at least part of the monolayer of propadiene isomerizes to methylacetylene species above 200 K. A similar isomerization has been proposed to occur on Pt surfaces based on calorimetrically determined heats of adsorption [38]. Next, we interpret the spectrum of chemisorbed methylacetylene on Rh(111).

We have already noted that the bonding of methylacetylene to Rh(111) is the same at 77 as at 240 K. Figure 7C shows the vibrational spectrum at 240 K. We find that this spectrum is consistent with molecular bonding to the surface through the carbon atoms originally involved in the C-C triple bond. The peak at 1370 cm^{-1} is characteristic of a symmetric bending mode of the methyl group ($\delta_s\text{CH}_3$). Since CH and CH_2 vibrations are unlikely at this frequency, the 1370 cm^{-1} is spectroscopic evidence for molecular adsorption. Presumably, the 1005 and 1115 cm^{-1} peaks are the two rocking modes of the CH_3 group, the 1445 cm^{-1} peak a $\delta_{as}(\text{CH}_3)$ mode, and the 2930 cm^{-1} peak a symmetric CH_3 stretch; although, these peaks may also have contributions from the CH vibrations at the other end of the molecule. By analogy to acetylene [25], methylacetylene most likely bonds in a 3-fold hollow site on Rh(111) with di- $\sigma + \pi$ [39] coordination to three metal atoms.

3.3.5 Methylacetylene and Propadiene Above 270 K

Above 270 K, the hydrocarbon monolayers formed by methylacetylene and propadiene adsorption are virtually identical as that formed by propylene adsorption. Figure 8 shows the vibrational spectra at 310 K for these hydrocarbon monolayers as well the one for an ethylidyne monolayer formed

from ethylene adsorption. As noted in the interpretation of the propylene decomposition spectra (section 3.3.3), these spectra at 310 K are characteristic of ethylidyne and C_xH species. The ethylidyne species has modes at 440, 1120, 1345, and 2865 cm^{-1} . The C_xH species have modes at ~ 750 , ~ 1350 , and $\sim 3010\text{ cm}^{-1}$. By heating above 430 K, the ethylidyne species decompose to C_xH species, which dehydrogenate and polymerize to form graphitic carbon by 800 K.

3.3.6 Partially Deuterated Propylene and Methylacetylene

In order to gain more insight into which bonds break during the decomposition of propylene and methylacetylene, we have studied partially deuterated propylene (CH_2CHCD_3) and methylacetylene ($DCCCH_3$) by TDS and HREELS. First, we discuss the thermal desorption studies.

The integrated area for the total TD spectrum and for the individual peaks for 2, 3, and 4 amu are given in Table II. The absolute areas are normalized to the mass spectrometer sensitivity for H_2 using the sensitivity factors $S_H/S_D = 2.0$ and $S_H/S_{HD} = 1.5$. The S_H/S_D factor was determined experimentally using H_2 and D_2 and the S_H/S_{HD} factor was calculated by using the S_H/S_D factor and comparing the total desorption yields of H_2 , HD, and D_2 from saturation doses of CH_3CHCH_2 and CD_3CHCH_2 .

The individual peaks in the TDS show distributions far from those expected for rapid scrambling. For example, the random recombination distribution for H and D atoms in a 1:1 ratio is $H_2:HD:D_2 = 25\%:50\%:25\%$; this ratio will be found for all the peaks in $C_3H_3D_3$ TDS if rapid H,D exchange occurs and there are no large isotope effects in the decomposition or desorption steps. For $C_3H_3D_3$, the first peak has more H_2 and the

second and third peaks more D_2 than for random scrambling. Since the second and third TDS peaks result from decomposition of hydrocarbon fragments, we can estimate the H:D ratio in these fragments [40]. By comparison of the H_2 , HD, and D_2 ratios for these peaks with those expected for random recombination of various H:D ratios, we conclude that the fragments decomposing in peak 2 for $C_3H_3D_3$ have a H:D stoichiometry of $\sim 1:2$ and those decomposing in peak 3 have an H:D stoichiometry of $\sim 1:3$.

For C_3H_3D , the random recombination distribution for the 3:1 ratio of H and D atoms in C_3H_3D is $H_2:HD:D_2 = 56\%:38\%:6\%$. The H_2 , HD, and D_2 ratios for the first TDS peak correspond to an H:D ratio on the surface of 6:1. This clearly implies that C-H bond breaking below room temperature occurs predominantly in the methyl group. The hydrocarbon fragments that dehydrogenate to produce peak 2 have a stoichiometry H:D $\cong 3:1$, and the fragments responsible for peak 3 have an H:D stoichiometry of about 2:1. These results will be interpreted further after the assignment of the vibrational spectra.

Next, we discuss our results from vibrational spectroscopy. The thermal desorption studies on CH_2CHCD_3 and $DCCCH_3$ show that some exchange of the H and D atoms occurs in these molecules below room temperature. As a result of this exchange and the inherently large number of vibrational frequencies for these polyatomics, the vibrational spectra below 270 K are too complex to assign and to determine whether the alkane, alkene, or alkyne C-H bonds break first. However, we can assign the simpler room temperature vibrational spectra of these decomposed molecules. These spectra are due to partially deuterated ethylidyne and $C_xH(D)$ species and give further insight into which C-C bonds break first.

Figure 9 shows the vibrational spectra for saturation coverages of H_2CCHCD_3 and DCCCH_3 adsorbed on $\text{Rh}(111)$ at 310 K. We assign these spectra by comparison to published spectra of partially deuterated ethylidyne [5] and of C_xH and C_xD species [8] on $\text{Rh}(111)$. For the methylacetylene decomposition (Fig. 9A), the peaks at 1330 ($\delta_s\text{CH}_3$) and 1110 (νCC) are characteristic of a CCH_3 species, while those at 1230 (CH_2 wag), and 1395 (CH_2 scissor) suggest a CCH_2D species. The 580 cm^{-1} peak (δCD) characterizes a C_xD fragment. There may be a δCH peak of a C_xH fragment in the $735\text{--}815\text{ cm}^{-1}$ feature, but this region also contains vibrations of the CCH_2D species. We conclude that the predominant ethylidyne species are CCH_3 and CCH_2D and the other predominant fragment is C_xD . This interpretation of the vibrational spectra is consistent with the TDS H:D stoichiometry of 3:1 in the 420 K ethylidyne decomposition peak (Table II). The presence of CCH_3 species implies that the gas phase carbon-carbon triple bond is the C-C bond that breaks first on the surface.

In the room temperature HREEL spectrum of decomposed propylene-3,3,3- d_3 , shown in Figure 9B, the absence of the intense 1330 cm^{-1} ($\delta_s\text{CH}_3$) indicates that no detectable CCH_3 is formed. The presence of the 1240 cm^{-1} (δCH) peak and absence of a CH_2 scissor at $\sim 1400\text{ cm}^{-1}$ means that the predominate species here is CCD_2H , consistent with the 1:2 = H:D TDS ratio for the 420 K decomposition peak (Table II). There may also be a small amount of CCD_3 ($\delta_s\text{CD}_3 = 990\text{ cm}^{-1}$). This spectrum with an expanded intensity scale shows that the 805 cm^{-1} (δCH) peak predominates over the 595 cm^{-1} (δCD) peak, so the other fragment predominately is C_xH . The lack of CCH_3 and CCH_2D species suggests that it is the C-C bond closest to the surface that breaks when propylidyne decomposes. This assumes that the propylidyne still has most of the deuterium in its methyl group when

it decomposes.

4. Discussion

In the previous sections we have presented and interpreted our results on propylene, methylacetylene, and propadiene bonding and thermal decomposition on a Rh(111) single crystal surface. In this section, we first summarize and comment on the bonding and decomposition pathways, then compare our results on Rh(111) to those published for Pt(111), and finally comment on the important role of surface hydrogen atoms in the decomposition pathways.

4.1 Propylene, Methylacetylene, and Propadiene Bonding and Thermal Decomposition Pathways on Rh(111)

In figure 10 we summarize our structural results on the thermal decomposition pathways for propylene, propadiene, and methylacetylene on Rh(111) and compare them to previous results for C_2H_4 . Nearly 100% of the C_3 hydrocarbons molecularly adsorbed at 77 K on Rh(111) dehydrogenate by these pathways. The only competing thermal chemistry is a small percentage of molecular desorption at high coverages.

Below 200 K, the C_3 hydrocarbons are adsorbed molecularly, but only methylacetylene forms an ordered (2x2) monolayer on the surface. We have proposed that all these unsaturated hydrocarbons bond with the surface through carbon atoms originally involved in the π -bonds. Consistent with this interpretation and with rehybridization of the carbons in forming the chemisorption bond, the C-C and C-H stretching frequencies are substantially lower than their gas phase values.

Propylene and propadiene begin to decompose by C-H bond breaking

at 200 K. Propylene, like ethylene [3], "stands up" on the surface to make propylidyne ($\equiv\text{CCH}_2\text{CH}_3$), which has a (2x2) LEED pattern and probably bonds in a threefold hollow site analogous to ethylidyne ($\equiv\text{CCH}_3$). Propadiene isomerizes at 200 K to make methylacetylene and forms a (2x2) LEED structure. We propose that chemisorbed methylacetylene bonds to the surface in a 3-fold hollow site with di- $\sigma + \pi$ coordination [39], analogous to acetylene bonding at low temperature on Rh(111) [25].

Carbon-carbon bond breaking occurs at 270 K for these C_3 hydrocarbon fragments, and they all form ethylidyne and C_xH species. Our partial deuteration studies suggest that the carbon-carbon bonds nearest the surface break first. These C_xH fragments and ethylidyne, like CO and ethylidyne [4], form a c(4x2) LEED ordered structure in the presence of coadsorbed CO. The ethylidyne species in these monolayers decompose at 400 K to C_xH fragments which further dehydrogenate and polymerize to graphite as the temperature is raised to 800 K.

4.2 Comparison of Propylene Decomposition on Pt(111) and Rh(111)

As mentioned in the introduction, Pt and Rh surfaces produce very different product distributions in heterogeneous hydrocarbon catalysis, and yet the thermal chemistry of ethylene and benzene on the (111) crystal faces of these metals in UHV is quite similar. In this section we compare the thermal chemistry we have determined for propylene on Rh(111) to published LEED [24,27], TDS [33], HREELS [29] and theoretical [41] results for propylene on Pt(111).

Propylene adsorbs molecularly on both Pt(111) and Rh(111) below 200 K. The vibrational spectra are, however, actually quite different and

indicate different degrees of rehybridization and possibly different bonding sites. Judging from the frequency of the CH stretching modes [2925 cm^{-1} on Pt(111) [29] and 2960 cm^{-1} on Rh(111)], the gas phase propylene C-C double bond is more rehybridized towards sp^3 on Pt(111). Analogous differences in the bonding of ethylene to Rh(111) and Pt(111) at low temperature have also been noted [4]. Also, analogous to ethylene chemistry, more propylene desorbs molecularly from Pt(111) than from Rh(111).

On both Pt(111) and Rh(111), propylene decomposes to propylidyne. The temperatures at which $\equiv\text{CCH}_2\text{CH}_3$ forms [200 K on Rh(111) and 270 K on Pt(111)] are the same as the temperatures for C_2H_4 decomposition to $\equiv\text{CCH}_3$ on these surfaces. The HREEL spectra for $\equiv\text{CCH}_2\text{CH}_3$ on Pt(111) and Rh(111) are very similar, indicating similar bonding at 3-fold hollow sites. By contrast, molecular orbital calculations for propylene adsorption and decomposition on Pt(111) [41] have suggested that the first stable decomposition fragment would be a surface allyl (CH_2CHCH_2). Probably, this specie does not form because, as is discussed in the next section, surface hydrogen influences the decomposition kinetics. We have noted elsewhere [4] how surface hydrogen in C_2H_4 decomposition could lead to formation of CCH_3 rather than the CCH_2 predicted by similar calculations.

The propylidyne decomposition products on Rh(111) and Pt(111) are entirely different -- the first major difference reported in the UHV chemistry of hydrocarbons on well-defined Pt and Rh surfaces. On Rh(111), propylidyne decomposes at 270 K by C-C bond breaking to give ethylidyne and C_xH species. On Pt(111), propylidyne decomposes above 400 K produces an as yet unassigned HREEL spectrum [29]; however, no peaks in this spectrum can be attributed to ethylidyne.

Interestingly, above 500 K the propylene decomposition products on Pt(111) and Rh(111) are again the same. On both surfaces a mixture of CH and C₂H species forms at this temperature. These species polymerize on both surfaces to graphitic carbon.

We find that methylacetylene decomposition shows similar differences on Pt and Rh(111): methylacetylene bonds molecularly to both surfaces below 270 K, decomposes to very different fragments at room temperature, but forms C_xH fragments on both surfaces above 500 K [42].

4.3 Role of Surface Hydrogen in Propylidyne Decomposition

An important question is "Why does propylidyne decompose by different pathways on Pt(111) and Rh(111)?" In comparing the two decompositions, the most obvious difference, at the decomposition temperature, is the presence of surface hydrogen on Rh(111) and its absence on Pt(111). We propose that surface hydrogen is required in order for propylidyne to decompose to ethylidyne. Surface hydrogen may actually enhance propylidyne decomposition; on Rh(111), in the presence of surface hydrogen, propylidyne decomposes at 140 K lower temperature than ethylidyne, while on Pt(111), in the absence of surface hydrogen, propylidyne decomposes only 70 K lower than ethylidyne.

To test the effect of surface hydrogen on propylidyne decomposition, we decomposed propylidyne on Pt(111) in the presence of 5×10^{-4} torr H₂ [43]. The experiments were carried out in a chamber without HREEL spectroscopy, so the results were monitored by TDS and are shown in Fig. 11. Figs. 11A and 11E show the TD spectra of saturation coverages of propylene and ethylene. The 440 K peak in the propylene spectrum is due to propylidyne decomposition, and the 520 K peak in the ethylene spectrum is due to ethylidyne decomposition.

Heating propylene to 470 K in the presence of H₂ would enable ethylidyne to form since it is still stable at this temperature. As shown in Figs. 11B and 11C, heating a propylidyne monolayer to 470 K or 480 K in 5x10⁻⁴ torr H₂ decreases the size of the propylidyne decomposition peak, and a new peak begins to form at the ethylidyne decomposition temperature. Both of these peaks are absent when a propylene monolayer is heated to 470 K in UHV as shown in Fig. 11D. This series of experiments supports our proposal that the decomposition of propylidyne to ethylidyne requires surface hydrogen.

Further, we propose that the role of surface hydrogen in propylidyne decomposition is to force propylidyne to fall over and bond to the surface in a geometry where the C-C bond can be broken. Evidence for this comes from the experiments with partial deuterated methylacetylene, which indicate that at least one of the methyl group C-H bonds of methylacetylene is broken in the formation of ethylidyne. The C-H bond breaking in the methyl group of methylacetylene enroute to C-C bond breaking suggests that the undetected intermediate in the decomposition of propylidyne and methylacetylene to ethylidyne is a 3-carbon species in which all three carbon atoms bond to the surface. That surface hydrogen is necessary for propylidyne decomposition to ethylidyne and yet methylacetylene, with two less hydrogens, also decomposes to ethylidyne suggests that surface hydrogen forces propylidyne to bond flat on the surface like methylacetylene. This may occur by bonding of the surface hydrogen to the propylidyne α carbon to form a bridge-bonded propylidene ($=CHCH_2CH_3$) species which can then fall over on the surface and dehydrogenate to form the C-C bond breaking intermediate. Such a mechanism is analogous to the proposed formation of a

bridge-bonded ethylidene ($=\text{CHCH}_3$) intermediate in ethylidyne H,D exchange [5]. In support of this proposal, we have found that H,D exchange in ethylidyne is facile on Rh(111) at room temperature [5], but, on Pt(111), this exchange, like propylidyne decomposition, is immeasurably slow [44] until temperatures above the hydrogen desorption temperature.

Finally, we note a similarity between the reaction of methylacetylene with Rh(111) and with a cobalt complex in solution [45]. The analogous reactions are shown in Fig. 12. Both in solution and on the surface the C-C triple bond in the alkyne is broken and two alkylidyne fragments are formed. In solution the two resulting alkylidynes bridge opposite faces of the trinuclear cobalt cluster, and on the surface the alkylidynes bond in two 3-fold hollow sites. Such an analogy between organometallic and surface chemistry is intriguing, since many similarities in the bonding of organic fragments in metal clusters and on metal surfaces have been previously noted.

5. Conclusions

The major findings from our studies of the thermal decomposition of propylene, propadiene, and methylacetylene on Rh(111) are summarized in Figure 10. Propylene decomposes to propylidyne ($\equiv\text{CCH}_2\text{CH}_3$) above 200 K, propadiene isomerizes to methylacetylene above 200 K, and these adsorbates all decompose at 270 K by C-C bond breaking to produce ethylidyne ($\equiv\text{CCH}_3$) and C_xH species. Between 200 and 400 K, the decomposition fragments form ordered LEED patterns.

Thermal decomposition of these C_3 hydrocarbons shows both similarities and differences from ethylene and acetylene chemistry on Rh(111) and propylene chemistry on Pt(111). Propylene decomposition to propylidyne on Rh(111)

occurs at the same temperature that ethylene decomposes to ethylidyne, and both ethylidyne and propylidyne form (2x2) LEED patterns. However, propylidyne decomposes at 270 K by C-C bond breaking, while ethylidyne is stable up to 400 K. Surface hydrogen appears to drive the decomposition of propylidyne to ethylidyne at 270 K, while for ethylidyne at this temperature surface deuterium has been shown to cause H,D exchange in ethylidyne [5]. Propylidyne is also produced in propylene decomposition on Pt(111), but surface hydrogen is absent at the propylidyne decomposition temperature and ethylidyne is not produced in the decomposition.

Methylacetylene, like C_2H_2 , forms a (2x2) LEED pattern on Rh(111) at 77 K and does not decompose until 270 K. Unlike C_2H_2 whose C-C bond is intact up to 400 K, methylacetylene breaks its C-C bonds at 270 K. We have proposed that the intermediate in both propylidyne and methylacetylene C-C bond breaking is a 3-carbon species that bonds flat on the Rh(111) surface. Lastly, the C_3 hydrocarbons, like all hydrocarbons we have studied on Rh(111), produce C_xH polymers above 500 K which dehydrogenate and condense to graphitic carbon.

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Footnotes

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Figure Captions

Figure 1 H₂ thermal desorption spectra for ethylene, propylene, propadiene and methylacetylene decomposition on Rh(111). Propylene, propadiene and methylacetylene were adsorbed at 77 K, and ethylene was adsorbed at 220 K. The heating rate was 20 K/sec.

Figure 2 LEED patterns observed for the adsorption and thermal decomposition of the C₂ and C₃ unsaturated hydrocarbons on Rh(111). Solid dividing lines indicate temperatures at which the HREEL spectrum changes. The dashed line indicates a change in LEED pattern as the surface hydrogen desorbs as H₂.

* LEED pattern for $\theta_{\text{C}_2\text{H}_4} = 1/3$. 25 % of the C₂H₄ in this overlayer desorbs at 210 K to give $\theta_{\text{C}_2\text{H}_4} = 1/4$.

LEED pattern formed by coadsorption of CO.

Figure 3 Surface vibrational spectra by HREELS in the specular direction of a saturation coverage of propylene adsorbed on Rh(111) at 100 K and warmed momentarily to the indicated temperatures.

Figure 4. An atop view of the proposed (2/3x2/3) R30° propylidyne + CO structure. In the upper portion of the figure, the slashed circles represent hydrogen atoms and the solid circles represent CO molecules; Van der Waals dimensions are shown. In the lower portion of the figure, the hydrogen atoms are represented by small solid circles in order to make more visible the Rh surface atoms and the carbon skeleton of the propylidyne.

Figure 5 Specular HREEL spectra of propylene adsorbed on Pt(111) at 310 K and on Rh(111) at 220 K to produce (2x2) LEED patterns. These vibrational spectra are attributed to propylidyne ($\equiv\text{CCH}_2\text{CH}_3$) species on these surfaces and are assigned in Table II.

Figure 6 Comparison of the specular HREEL spectra for room temperature decomposition of ethylene- d_4 and propylene- d_6 on Rh(111). The vertical lines indicate the spectral differences. The C_2D_4 fragment is ethylidyne (CCD_3) and the C_3D_6 fragments are CCD_3 and C_xD species.

Figure 7 Specular HREEL spectra for 10 L exposures of (A) propadiene at 77 K, (B) propadiene at 240 K, and (C) methylacetylene at 240 K on Rh(111). Propadiene begins to decompose at 210 K while methylacetylene does not decompose until 270 K on Rh(111).

Figure 8 Comparison of the specular HREEL spectra for ethylene, propylene, propadiene, and methylacetylene adsorbed on Rh(111) at 310 K. The deuterated analogue of the propylene spectrum is shown in figure 6B. At 310 K, all the C_3 hydrocarbons have decomposed to the same fragments (CCH_3 and C_xH) on Rh(111).

Figure 9 HREEL spectra for 10 L of DCCCH_3 and 10 L of CH_2CHCD_3 decomposed on Rh(111) at 310 K. The spectra are due to partially deuterated ethylidyne, C_xH and C_xD species.

Figure 10 Pathways for the thermal decomposition of ethylene, propylene, methylacetylene, and propadiene on Rh(111). These decomposition intermediates, determined by surface vibrational spectroscopy and thermal desorption studies, are stable in the indicated temperature ranges. Bonding geometries of these species are discussed in the text.

Figure 11 H₂ thermal desorption spectra from Pt(111) for (A)propylene adsorbed at 200 K, (B)propylene adsorbed at 200 K and flashed to 470 K in 5×10^{-4} torr H₂, (C)propylene adsorbed at 200 K and flashed to 480 K in 5×10^{-4} torr H₂, (D)propylene adsorbed at 200 K and flashed to 470 K in UHV and (E)ethylene adsorbed at 200 K. Vertical lines indicate the decomposition temperatures of propylidyne (440 K) and ethylidyne (520 K). These spectra suggest that propylidyne may decompose to ethylidyne on Pt(111) when surface hydrogen is present.

Figure 12 The formal similarity between the reaction of methylacetylene with a Rh(111) single crystal surface in UHV and with a cobalt complex in solution. In both cases two alkylidyne species are produced, and each alkylidyne bonds to three metal atoms.

Table I

Vibrational Frequencies of A' Normal Modes in CCH₂CH₃ Species

Approximate Normal Mode Description	^a Cl ₃ CCH ₂ CH ₃	^b Rh(111)/C ₃ H ₆ , 240 K	^b Pt(111)/C ₃ H ₆ , 310 K	^c Pt(111)/C ₃ H ₆ , 300 K	^d Co ₃ (CO) ₉ (C ₃ H ₅)
$\nu_s \text{CH}_3$	2989		2930	2980	
$\nu_s \text{CH}_2$	2944		2870	2920	
$\nu_s \text{CH}_3$	2933				
$\delta_s \text{CH}_3 + \delta_s \text{CH}_2$	1455	1445	1435	1465	1450
$\delta_s \text{CH}_2$	1430				1420
$\delta_s \text{CH}_3$	1382	1385	1370		1370
$\delta_w \text{CH}_2 + \nu \text{CC}$	1323	1290	1240	1295	
ρCH_3	1107	1120	1105	1115	1155
	1066	1055	1045	1055	1050
$\nu \text{CC} + \rho \text{CH}_3 + \delta_w \text{CH}_2$	929	950	925	940	1040

^a A. Goursot-Leray, M. Carles-Lorjou, G. Pouzard, and H. Bodot, ref. 31.

^b This work

^c D. Seyferth, C.N. Rudie, and J.S. Merola, ref. 32.

^d N. Avery and N. Sheppard, ref. 29.

Table II

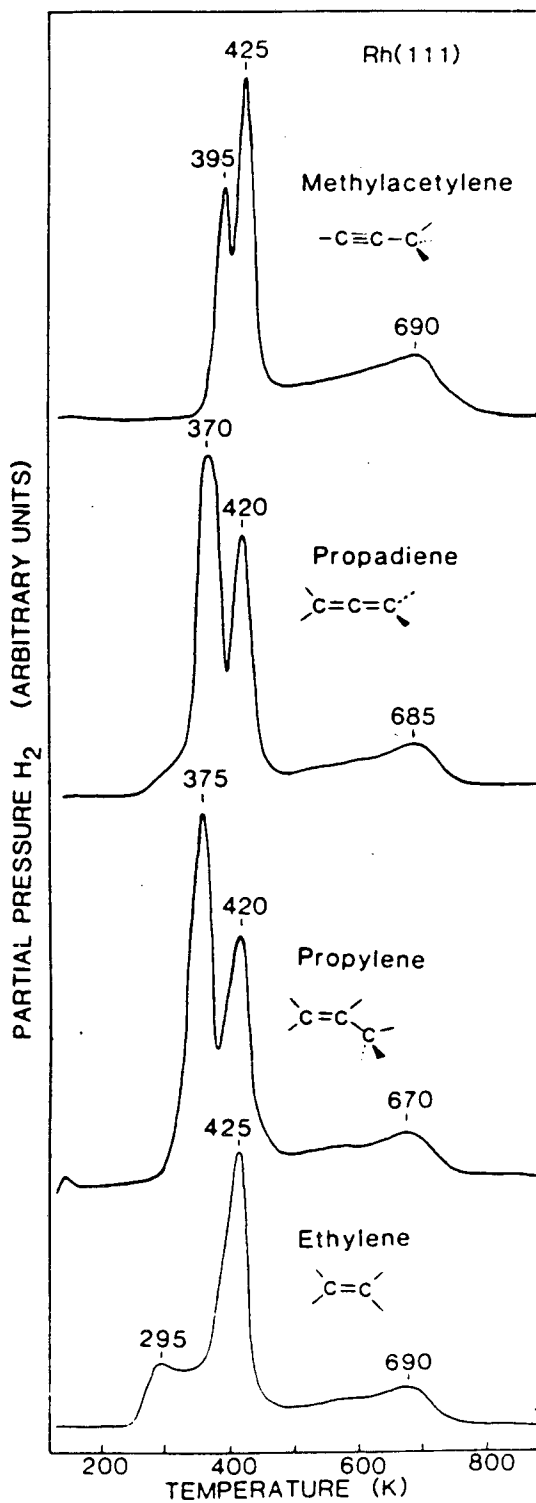
H₂, HD, and D₂ Desorption Peak Areas for C₃H₃D₃ and C₃H₃D Thermal Decomposition on Rh(111)

Dose	Area(s) [#] Integrated	Absolute Amounts (arb. units) ⁺			Percentages			H:D Ratio
		H ₂	HD	D ₂	H ₂	HD	D ₂	
6.0 L C ₃ H ₃ D ₃ propylene-3,3,3-d ₃	all peaks	5.6	8.4	7.5	26	39	35	H:D≅1:1
	peak 1	3.8	3.3	1.2	45	40	15	H:D≅2:1
	peak 2	1.3	3.0	3.2	18	40	42	H:D≅1:2
	peak 3	0.4	2.1	3.1	8	37	55	H:D≅1:3
6.0 L C ₃ H ₃ D methylacetylene-1-d ₁	all peaks	14.1	8.6	1.8	58	35	7	H:D≅3:1
	peak 1	4.0	1.4	0.1	73	24	3	H:D≅6:1
	peak 2	5.5	3.1	0.5	61	34	5	H:D≅3:1
	peak 3	4.5	4.1	1.2	46	42	12	H:D≅2:1

[#] Integrated areas of overlapping peaks were calculated by dropping a perpendicular from the minima between the overlapping peaks to the baseline. Peak 1 = ~270-390K; Peak 2 = ~390-440 K; Peak 3 = ~440-800K.

⁺ Amounts of HD and D₂ have been converted to the same units as H₂ using the sensitivity factors $S_{H_2}/S_{D_2}=2.0$ and $S_{H_2}/S_{HD}=1.5$ (see text). Arbitrary units are different for C₃H₃D₃ and C₃H₃D.

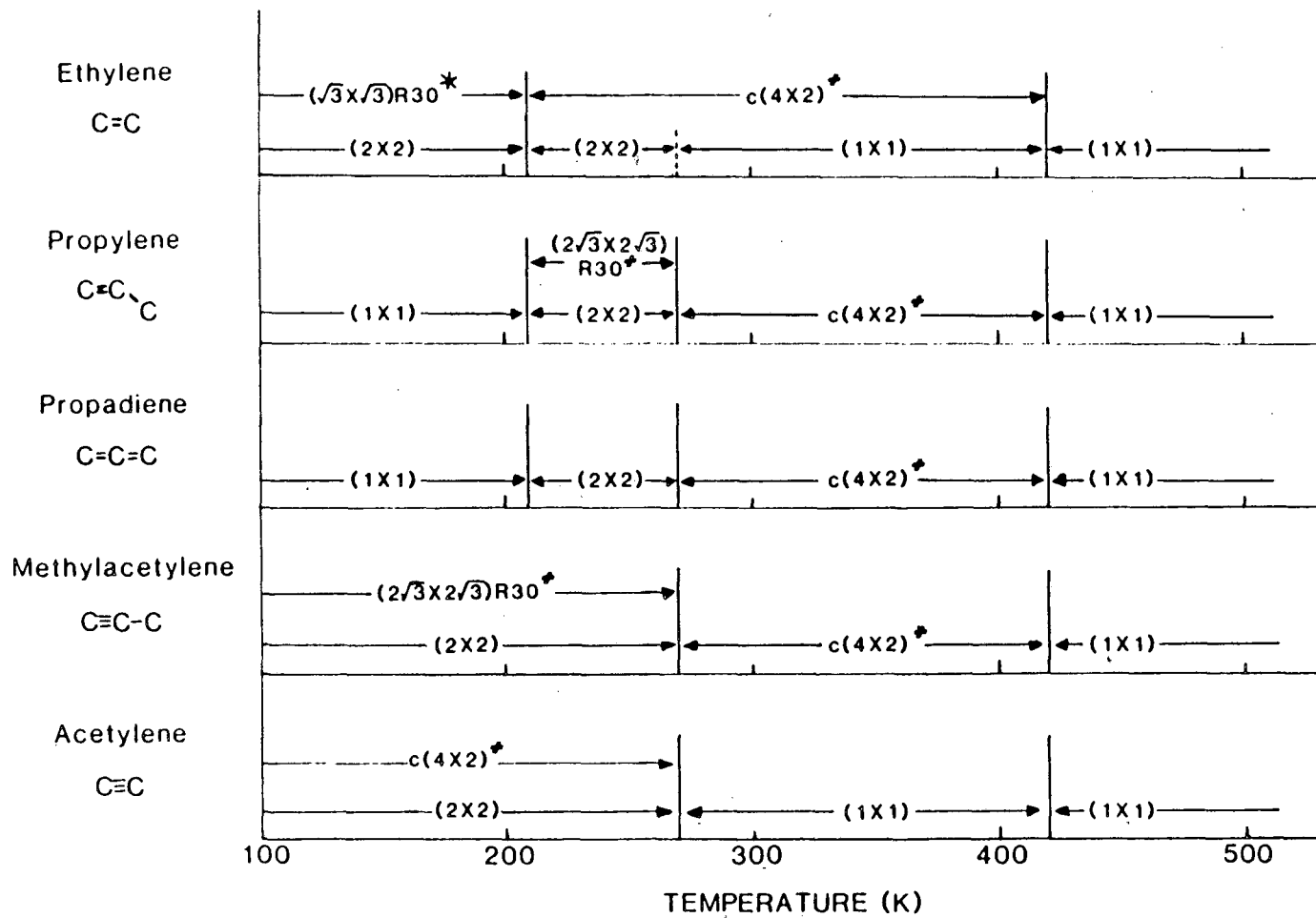
^{*} The ratio of H to D atoms on the surface that would produce the indicated percentages of H₂, HD, and D₂.



XBL 8512-4936

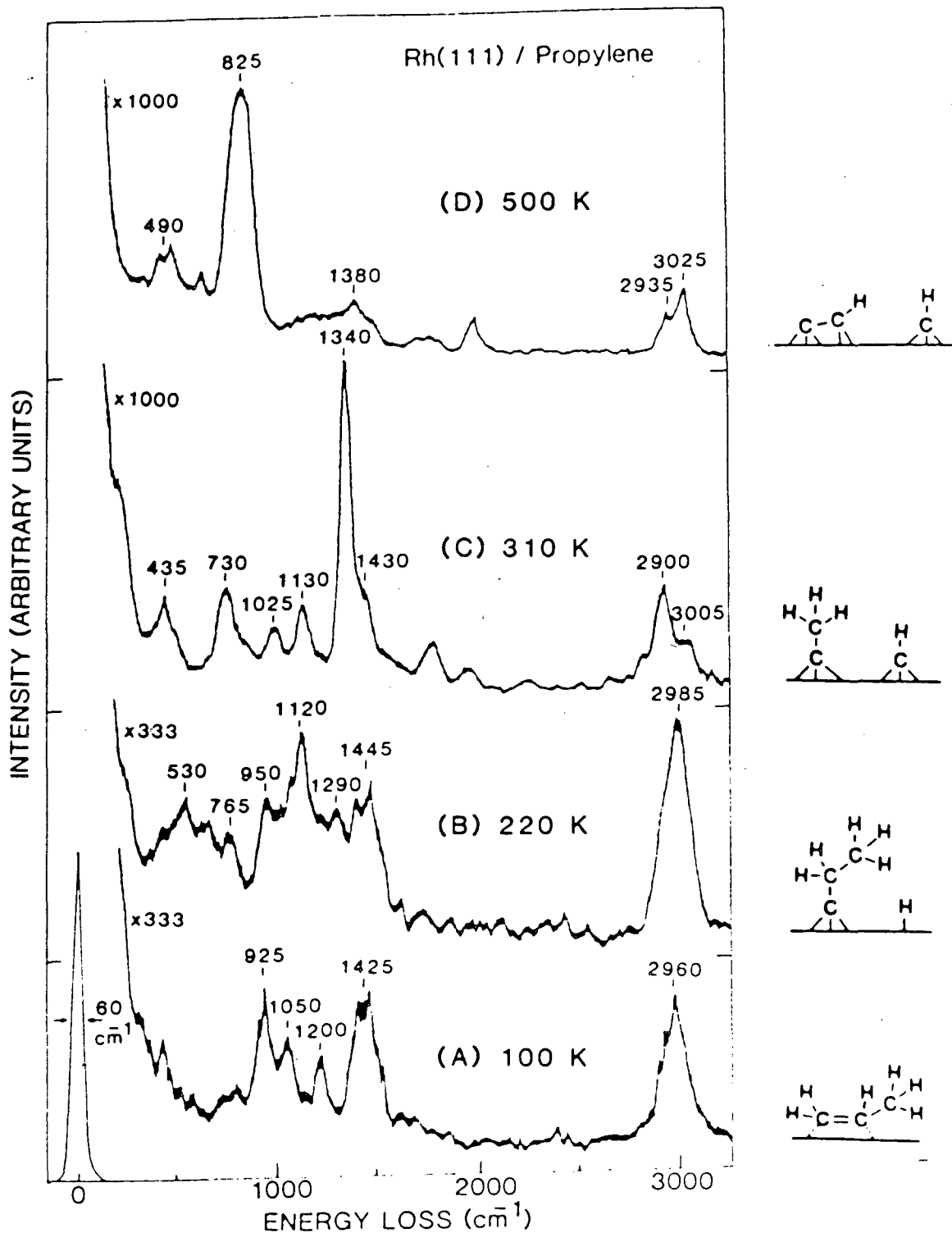
Fig. 1

LEED Patterns for C₂ and C₃ Hydrocarbons on Rh(111) †



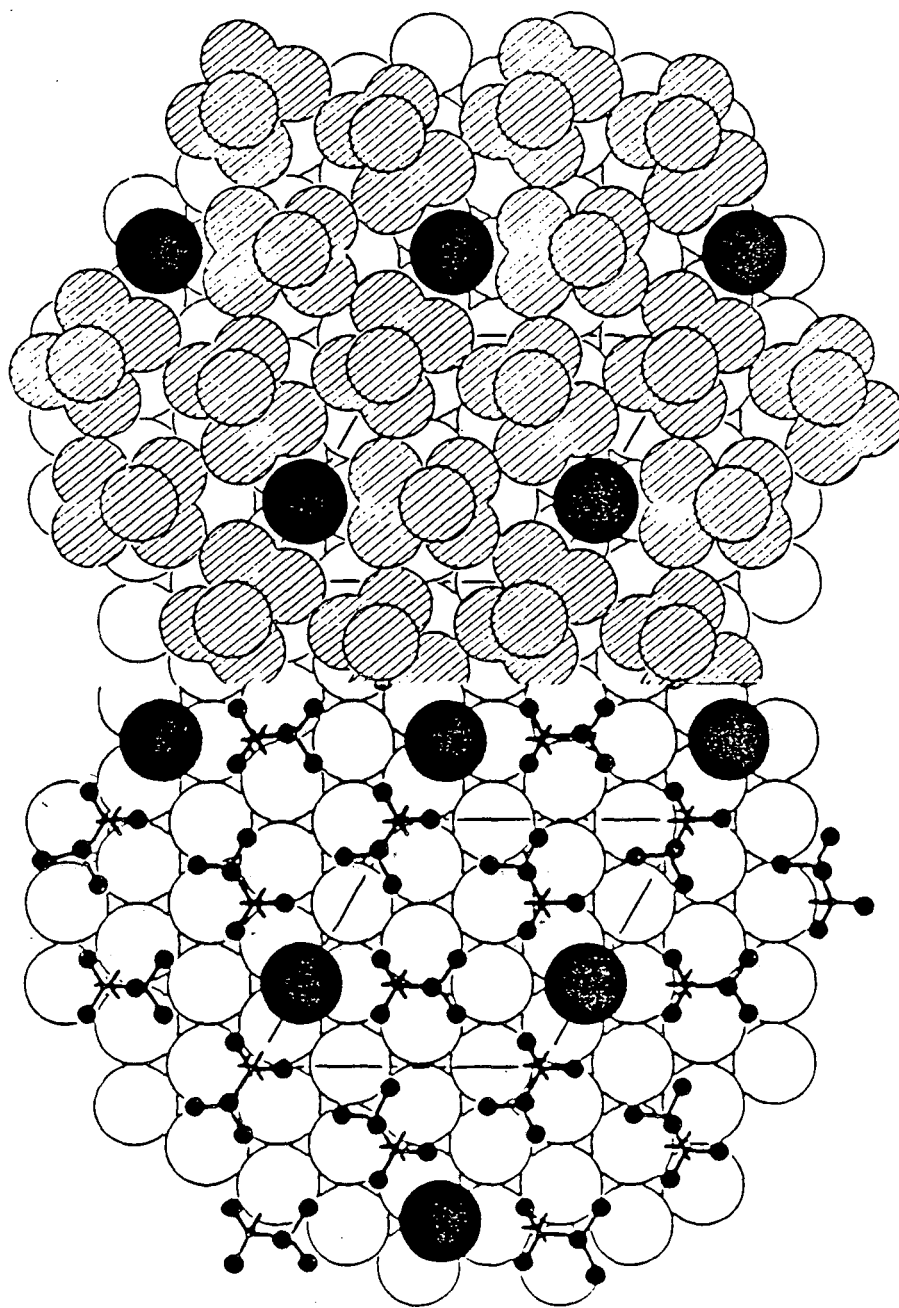
XBL 866-2417

Fig. 2



XBL 862-578

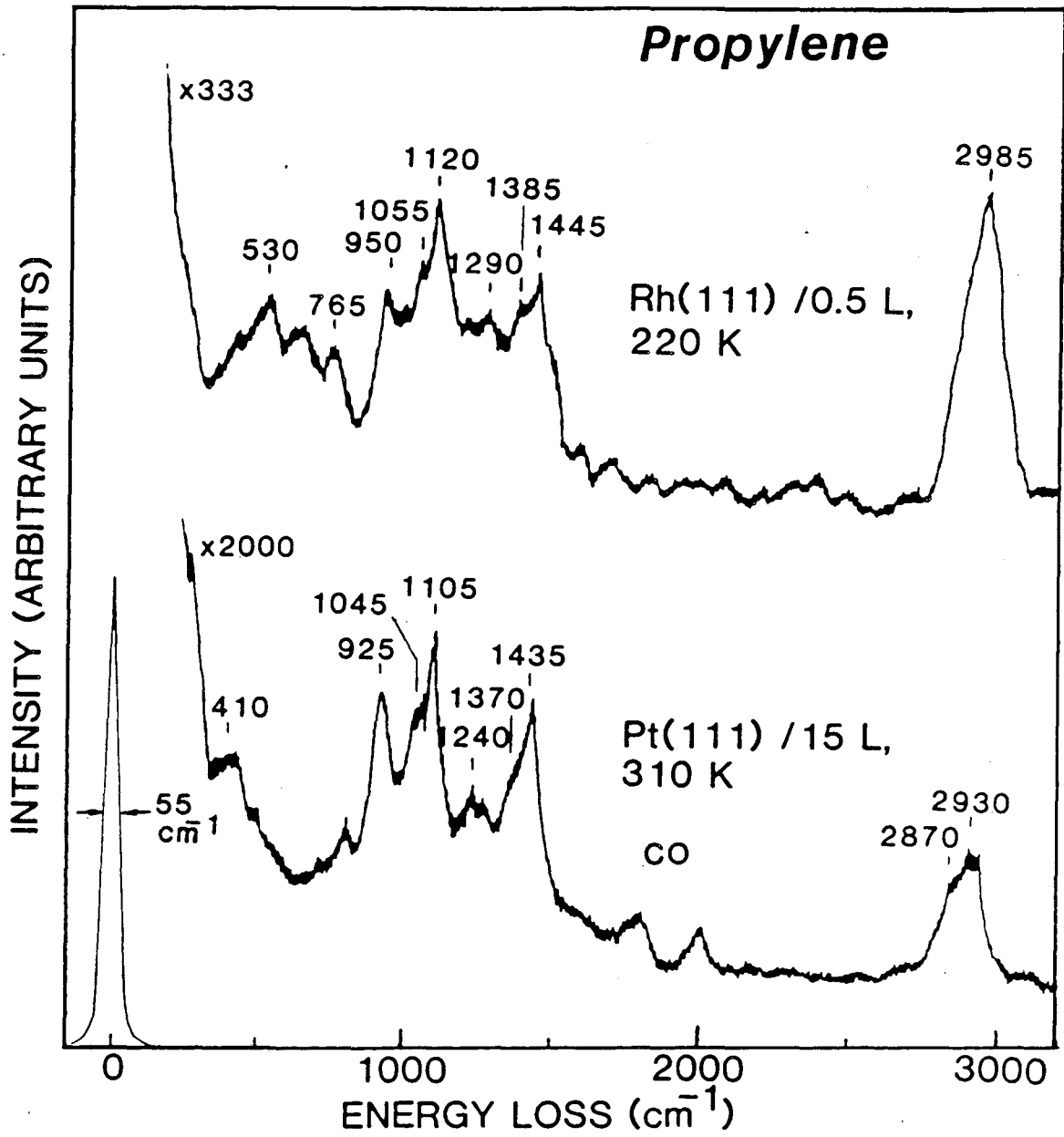
Fig. 3



$RH(111) + (2\sqrt{3} \times 2\sqrt{3})R30^\circ C_3H_5$ (propylidyne) + (1)

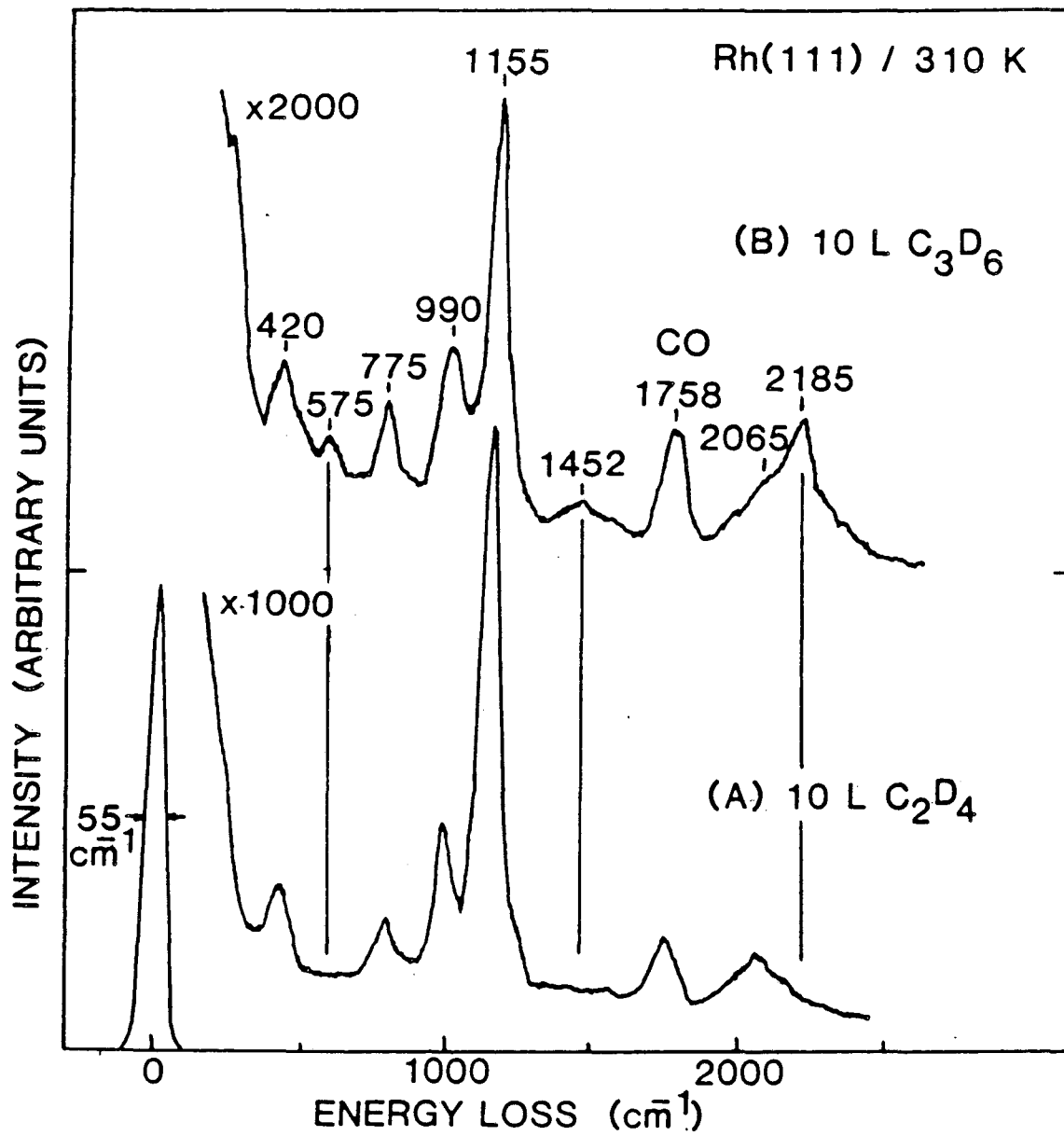
XBL 813-5410

Fig. 4



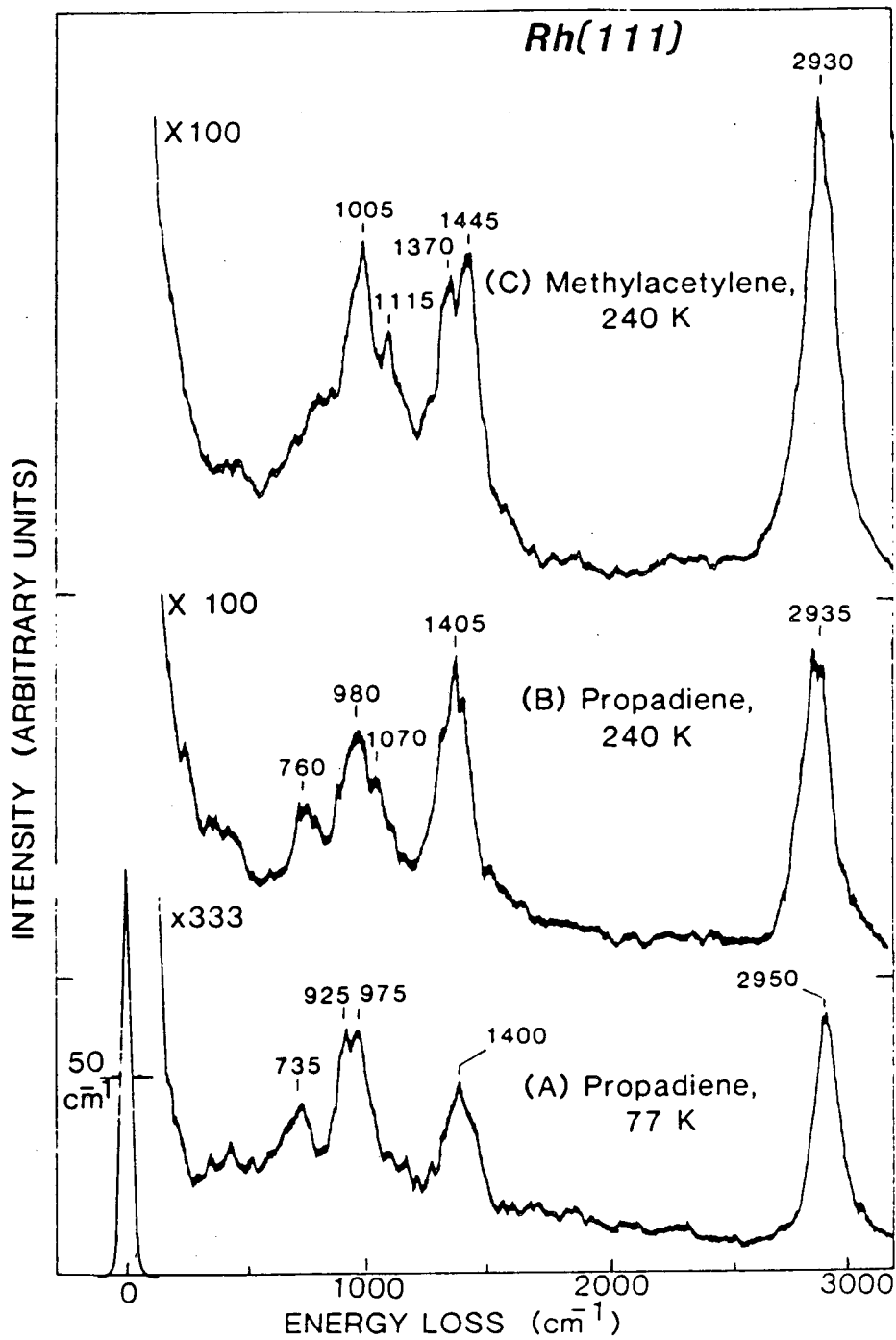
XBL 866-2416

Fig. 5



XBL 866-2415

Fig. 6



NBL 866-2426

Fig. 7

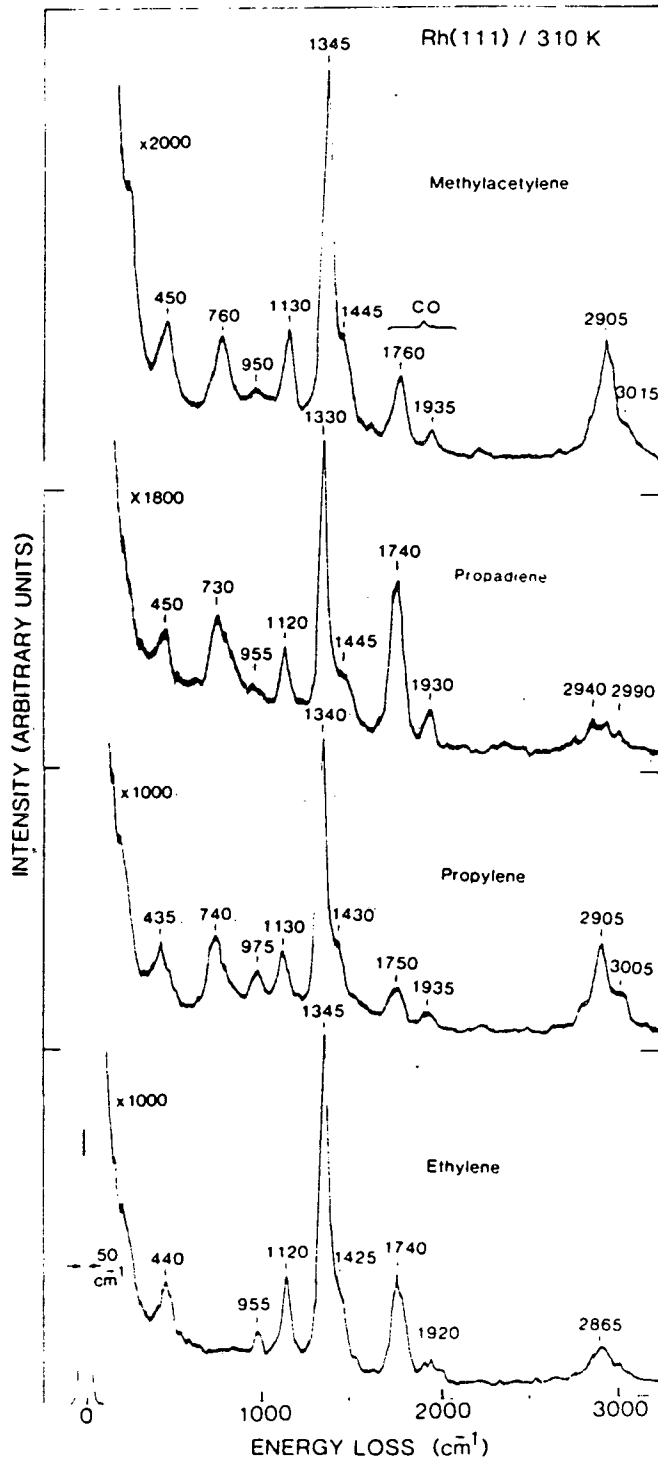
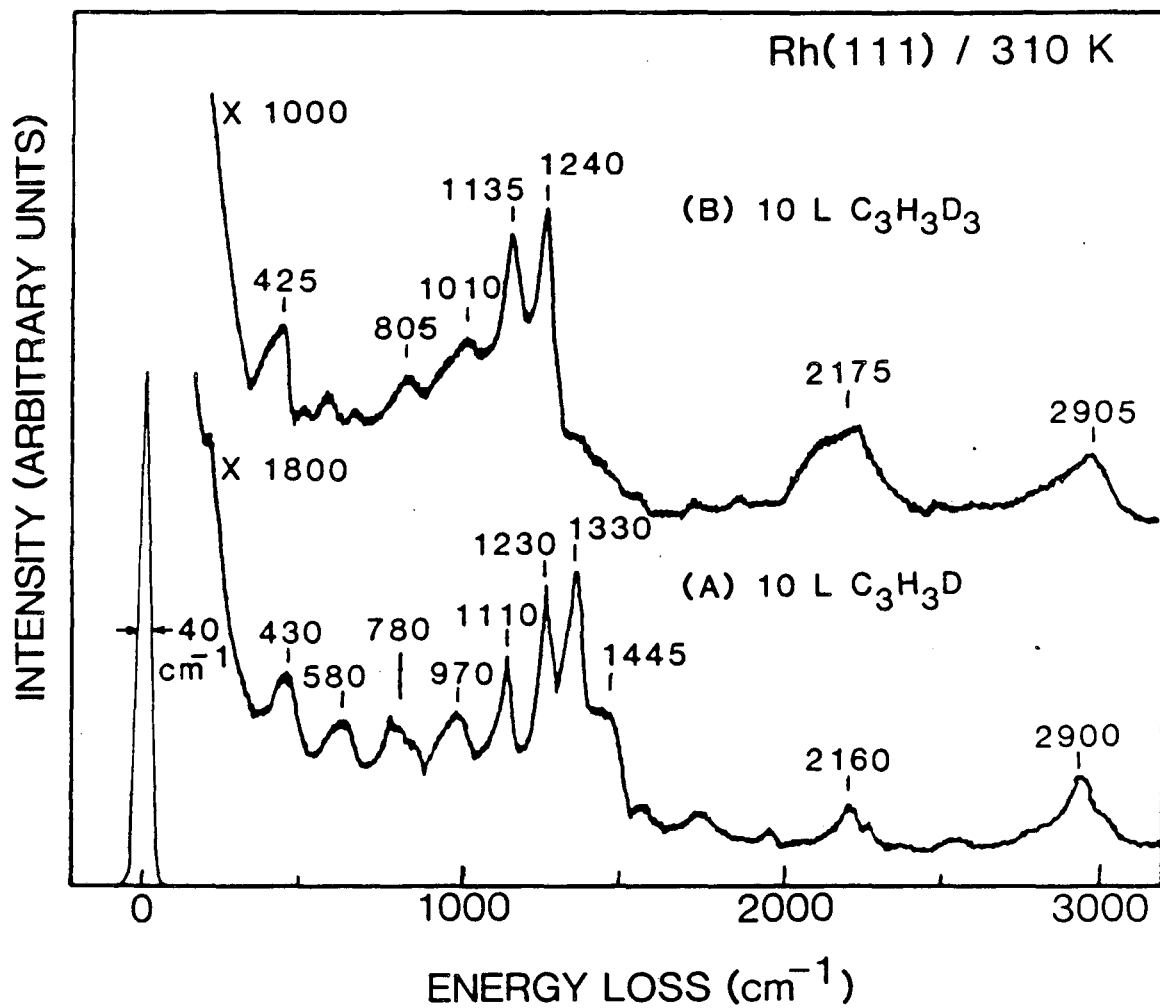


Fig. 8.



XBL 866-2414

Fig. 9

Hydrocarbon Decomposition on Rh(111)

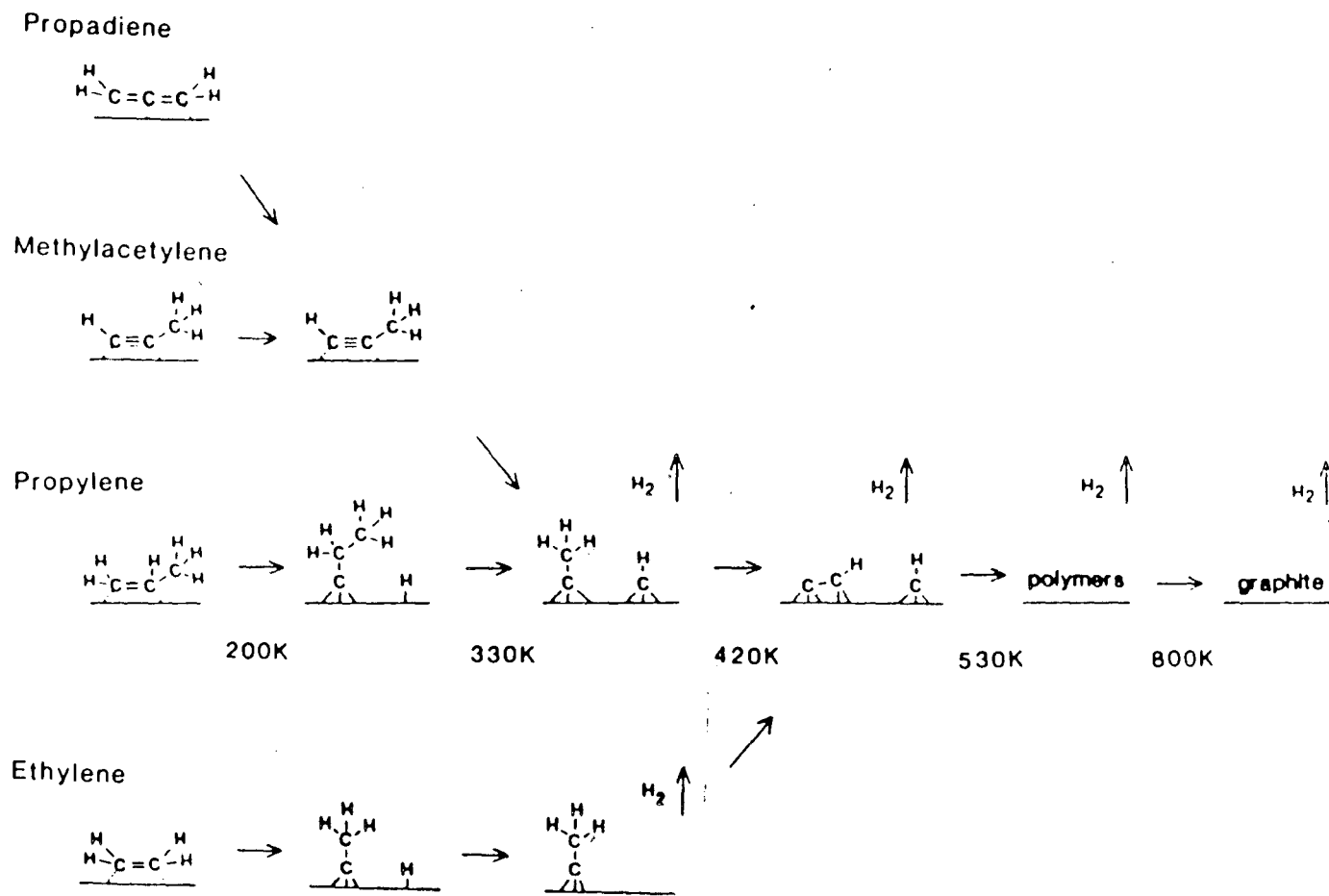
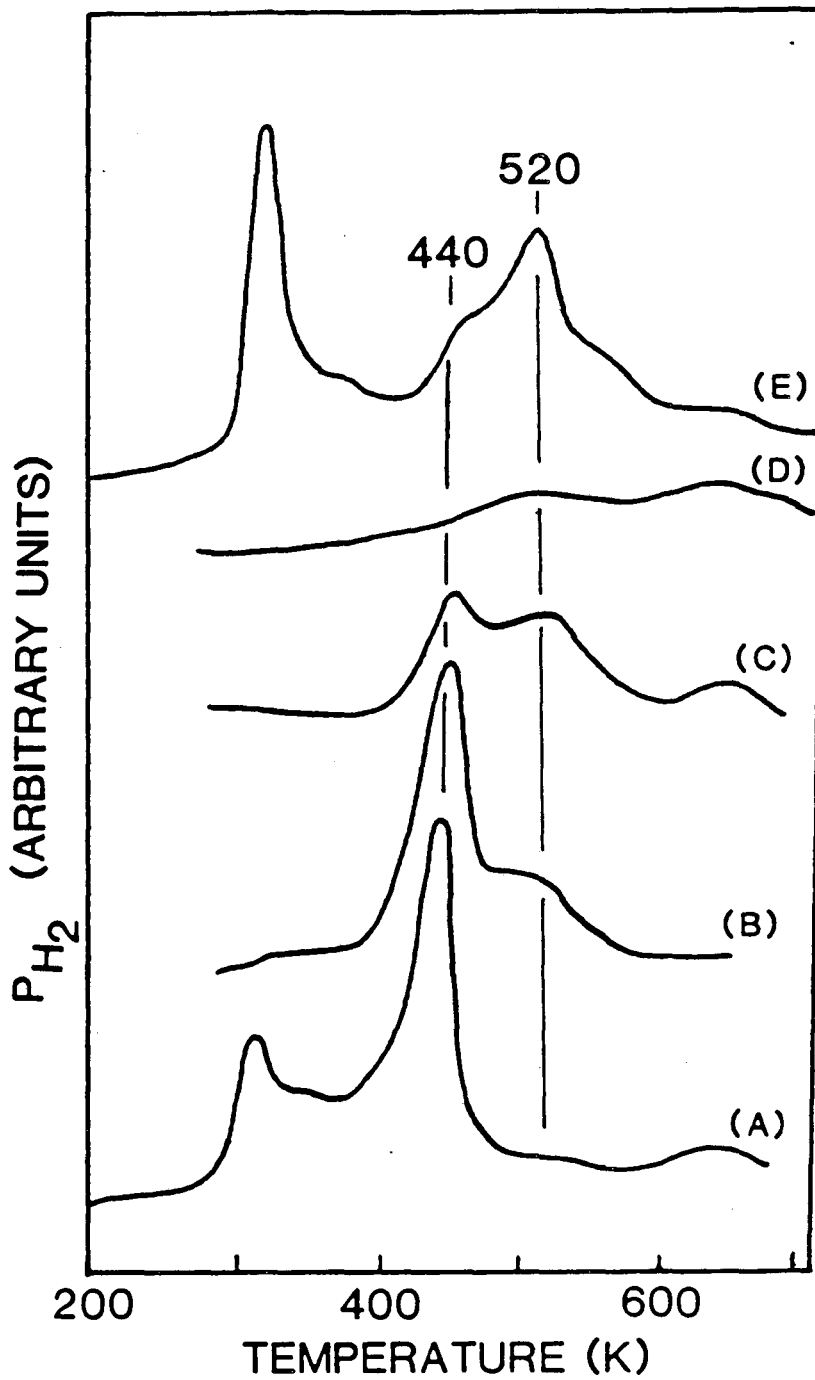


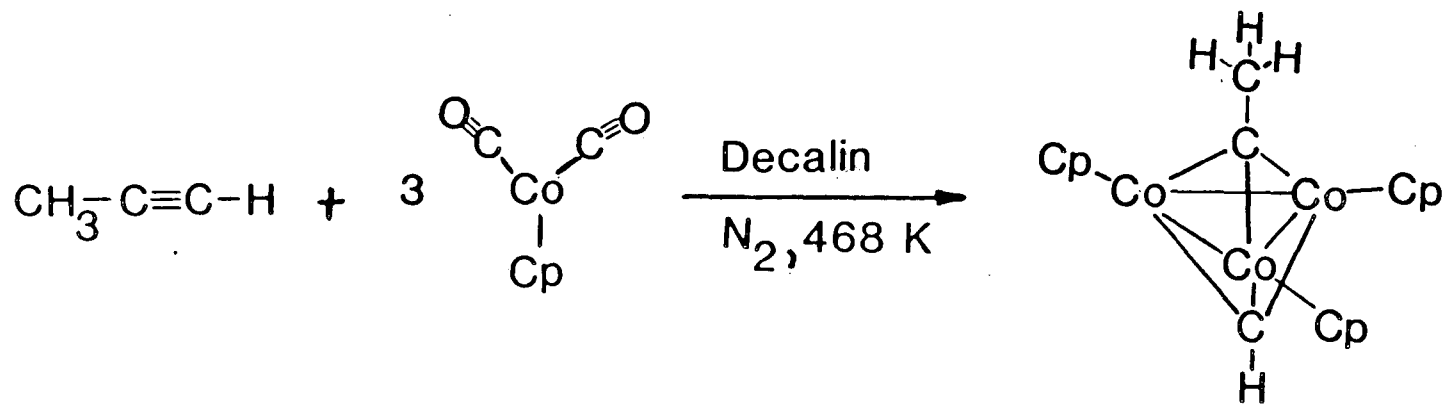
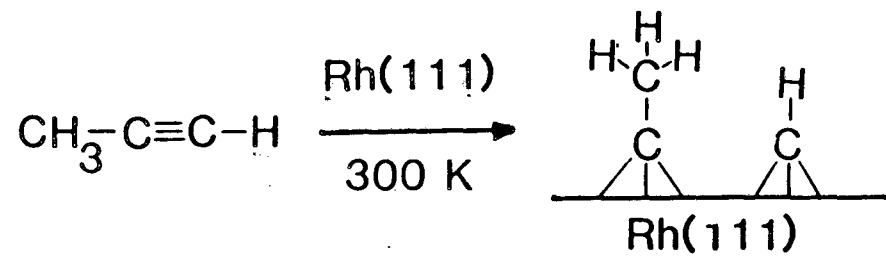
Fig. 10

Pt(111)



XBL 866-2413

Fig. 11



XBL 866-2412

Fig. 12

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