

HYDROGENATION AND H, D EXCHANGE STUDIES OF ETHYLIDYNE (CCH₃) ON Rh(111) CRYSTAL SURFACES AT 1 ATM PRESSURE USING HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY

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We have combined high resolution electron energy loss spectroscopy (HREELS) with a high-pressure/low-pressure (HPLP) system to study the behavior of the monolayer structure of stable hydrocarbon species that form on single-crystal metal surfaces during catalytic reactions at atmospheric pressure. We find that a monolayer of adsorbed ethylidyne (CCH₃) on Rh(111) at 310 K does not hydrogenate to ethylene or ethane in one atmosphere of static D₂. The methyl group hydrogens exchange with deuterium is a slow process. The amount of exchange depends strongly on the amount of uncovered, bare-metal surface, but little on the hydrogen pressure. A mechanism for H, D exchange involving ethylidene (CHCH₃) as an intermediate is proposed.

1. Introduction

Understanding how heterogeneous catalysts work requires knowing the structure and reactivity of the adsorbed overlayer at the catalyst surface. Evidence for overlayer structure and catalytic reaction intermediates (not necessarily the same) has been obtained indirectly, mostly from kinetic studies, trapping intermediates at low temperatures, and from chemisorption and thermal desorption measurements in ultra-high vacuum (UHV). In order to utilize surface science techniques that require UHV for the determination of monolayer structures that form during high pressure catalytic reactions, we have incorporated high resolution electron energy loss spectroscopy (HREELS) in a high-pressure/low-pressure (HPLP) system.

The HPLP system makes surface analysis of a catalyst (by HREELS as well as low energy electron diffraction (LEED) and Auger electron spectroscopy (AES)) possible in UHV prior to and immediately following (within minutes) a

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high pressure gas exposure or catalytic reaction. By detecting surface vibrations, HREELS is a sensitive probe of surface species [1,2]. Surface periodicity is not required, but single crystal surfaces are used as well-defined model catalysts. The vibrational spectrum is a fingerprint of monolayer structure; the vibrational frequencies are a function of atomic configurations and bond strengths. We have begun using HREELS in combination with a high pressure (HP) cell to detect stable surface species after atmospheric pressure reactions and to follow hydrogen (deuterium) transfer and reactivity in hydrocarbon monolayers under catalytically interesting conditions. HREELS is ideal for hydrocarbon monolayer structure determination because of its sensitivity to carbon-hydrogen vibrations.

We have used the HREELS/HPLP method to study the reactivity of an ethylidyne (CCH_3) monolayer on the Rh(111) crystal surface with 1 atm of H_2 and D_2 . This monolayer is the stable room temperature structure for chemisorbed ethylene on Rh(111) [3,4] as well as Pt(111) [5,6] and Pd(111) [7]. Our results show that the stability of this monolayer extends to atmospheric pressures. One atmosphere of hydrogen does not rehydrogenate this ethylidyne to ethylene or ethane on Rh(111), but the methyl group hydrogens do undergo H, D exchange. The rate of H, D exchange depends little on D_2 pressure but strongly on the amount of available bare metal surface.

2. Experimental

The design considerations and specifications of this [8] and other [8,9] HPLP systems have been described. A schematic diagram of the two-tier HPLP system with HREELS used here is shown in fig. 1. The HREEL spectrometer design and operation are described elsewhere [10]. We describe here the procedure for the use and performance of the HREEL spectrometer with the high pressure cell.

Both the upper and lower portions of the HP cell translate with welded bellows seals. The crystal translates on-axis with the upper portion of the HP cell to the HREEL spectrometer by an extended-travel manipulator. To seal the HP cell, the upper bellows are contracted so that the upper half of the HP cell locks against the top of the chamber. A hydraulic piston behind the lower half-cell drives and pressurizes a knife-edge seal between the two halves to 2100 psi. The volume of the HP cell together with the external circulation loop is about 0.5 liter.

The Rh(111) single crystal was a 0.5 cm^2 disk, .030 inch thick, polished on both sides by standard methods [3]. The crystal was mounted with 0.020 inch Pt wire spotwelded between the crystal edges and 1/8 inch Ta rods. Crystal temperatures between 300 and 1500 K were obtained by resistive heating, monitored by a chromel-alumel thermocouple spot-welded to one face of the

crystal. Crystal cleanliness was checked by HREELS and AES. The cleaning procedure has been described elsewhere [10]; after heating in O_2 , it was found necessary to Ar^+ sputter in order to remove trace amounts of boron oxides detectable by HREELS (740 cm^{-1}). Annealing to 1400 K in vacuum dissolved trace amounts of carbon into the bulk.

Gases used as supplied were: Matheson H_2 , 99.9%; D_2 , ~ 99.5 at%; C_2H_4 , 99.5%; Merck, Sharp and Dohme C_2D_4 , 99 at%. Gas dosing was performed with a microcapillary array doser in UHV or by pressurizing the HP cell. Exposures in UHV are given uncorrected for ion gauge sensitivity, but corrected for a five times enhancement of the doser. Gas exposures (pressures) in the HP cell were measured with a Heise gauge (absolute) and were generally 1 atm of static gas.

Gases are pumped from the HP cell through a rapid-pump valve at the manipulator top with a liquid nitrogen-trapped, 2 inch diffusion pump. Pump-down is typically ten minutes or until the ion gauge pressure above the liquid nitrogen trap is 1×10^{-6} Torr. Upon opening the HP cell, outgassing of the cell causes the chamber pressure to rise to about 4×10^{-8} Torr, water being

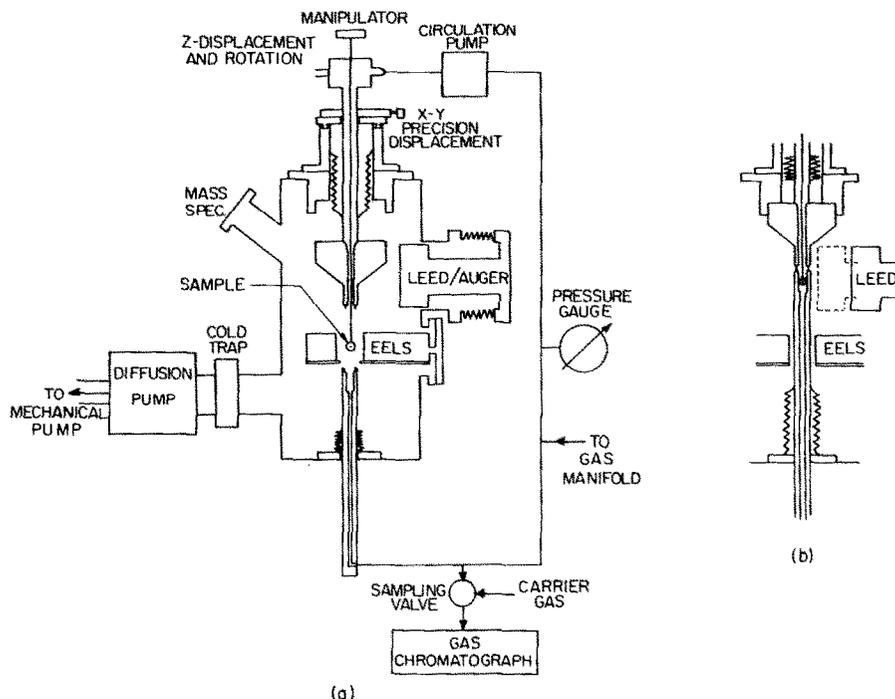


Fig. 1. (A) Schematic diagram of a two-tier HPLP system containing a spectrometer for HREELS, with the high-pressure cell open. (B) Detail with high-pressure cell closed.

the major contaminant. A pressure of about 5×10^{-9} Torr is reached after 15 min, but usually it is several hours before the chamber returns to the base pressure (2×10^{-10}).

After retraction of the HP cell, the crystal is lowered into the HREEL spectrometer and precisely positioned using travel gauges to previous settings. In the H, D exchange reactions where surface structure is largely unchanged, a minimum of spectrometer retuning was required and a spectrum begun within the minutes of lowering the cell. Changing the crystal bias to compensate for work function changes was the only tuning usually required. Elastic scattering count rates in this work varied from 0.3 to 1.5×10^5 counts s^{-1} depending largely on the degree of surface order. Resolution (full width at half maximum of the elastically scattered beam) was 45–65 cm^{-1} . No major changes in the work function of the graphite-coated lenses after repeated HP work were found. Over 40 high pressure exposures of H_2 , CO, and C_2H_4 have been made without spectrometer bake-out.

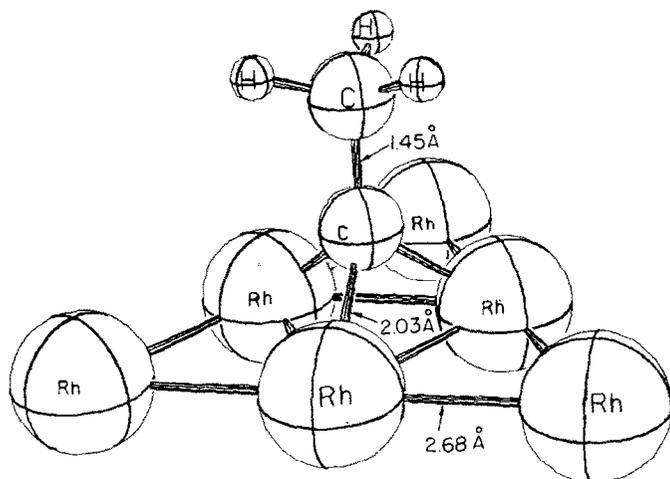
3. Results and discussion

3.1. Ethylidyne

The adsorption of ethylene on Rh(111) at room temperature to produce surface ethylidyne (CCH_3) species (fig. 2) has been well-studied previously [3,4]. Fig. 3 shows the HREEL spectra for saturation coverages (saturation coverage = 1 $CCH_3/4$ Rh atoms or 1 C/2 Rh atoms) of CCH_3 and CCD_3 on Rh(111) produced by a 15 L exposure at 310 K to C_2H_4 or C_2D_4 . These spectra are consistent with those found in previous HREEL studies [4], but offer improved resolution. The assignment of the loss peaks to vibrational modes of surface ethylidyne are given in table 1, in complete agreement with frequencies, intensities, and H/D shifts observed in infrared spectra (and normal mode analysis) of $(CH_3C)Co(CO)_9$ [11]. Except for the degenerate methyl group rock (ρCH_3), the antisymmetric methyl hydrogen bending ($\delta_{as}CH_3$), and the antisymmetric methyl stretching ($\nu_{as}CH_3$) modes, the vibrational modes are dipole active (A_1 type), establishing C_{3v} symmetry for the surface complex. Angular-dependent HREELS studies reported elsewhere [12] establish the dipole contribution to the loss peaks and the surface symmetry.

3.2. Ethylidyne + 1 atm H_2

These experiments show the remarkable stability of an ethylidyne monolayer. The HREEL spectra of a saturation coverage of ethylidyne on Rh(111) before and after exposure to 1 atm H_2 for 5 min at 310 K are shown in fig. 4. The spectra are nearly identical. Vibrational frequencies are the same to within



Rh(III) + ethynidyne

Fig. 2. Ethynidyne on Rh(111): the stable, room temperature, chemisorbed structure of ethylene.

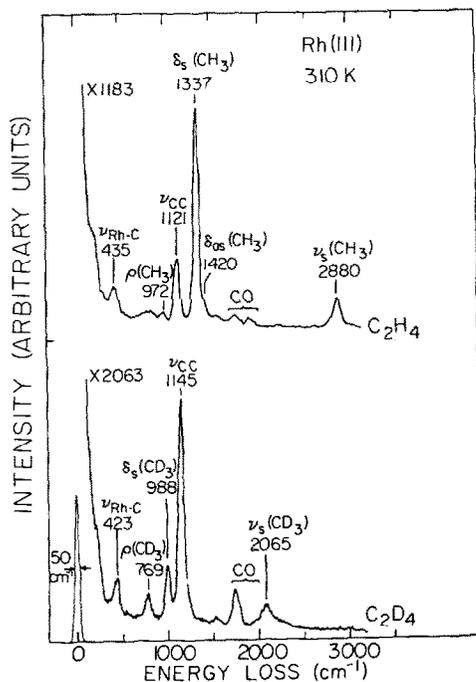


Fig. 3. Specular HREEL spectra obtained following saturation exposure of ethylene to Rh(111) at 310 K to form surface ethynidyne.

Table 1

Comparison of the vibrational frequencies (cm^{-1}) of the ethylidyne surface species formed on Rh(111) with those of the ethylidyne cluster compound [11]

Assignment	$\text{CH}_3\text{CCo}_3(\text{CO})_9$	$\text{CH}_3\text{C-Rh(111)}$
$\nu_{\text{as}}(\text{CH}_3)/\nu_{\text{as}}(\text{CD}_3)$	2930(m)/2192(w) e	2920(vw)/2178(vw) e
$\nu_{\text{s}}(\text{CH}_3)/\nu_{\text{s}}(\text{CD}_3)$	2888(m)/ - a_1	2880(w)/2065(vw) a_1
$\delta_{\text{as}}(\text{CH}_3)/\delta_{\text{as}}(\text{CD}_3)$	1420(m)/1031(w) e	1420(vw)/ - e
$\delta_{\text{s}}(\text{CH}_3)/\delta_{\text{s}}(\text{CD}_3)$	1356(m)/1002(vw) a_1	1337(s)/988(w) a_1
$\nu(\text{CC})$	1163(m)/1182(ms) a_1	1121(m)/1145(m) a_1
$\rho(\text{CH}_3)/\rho(\text{CD}_3)$	1004(s)/828(s) e	972(vw)/769(vw) e
$\nu_{\text{s}}(\text{MC})$	401(m)/393(m) a_1	435(w)/419(w) a_1

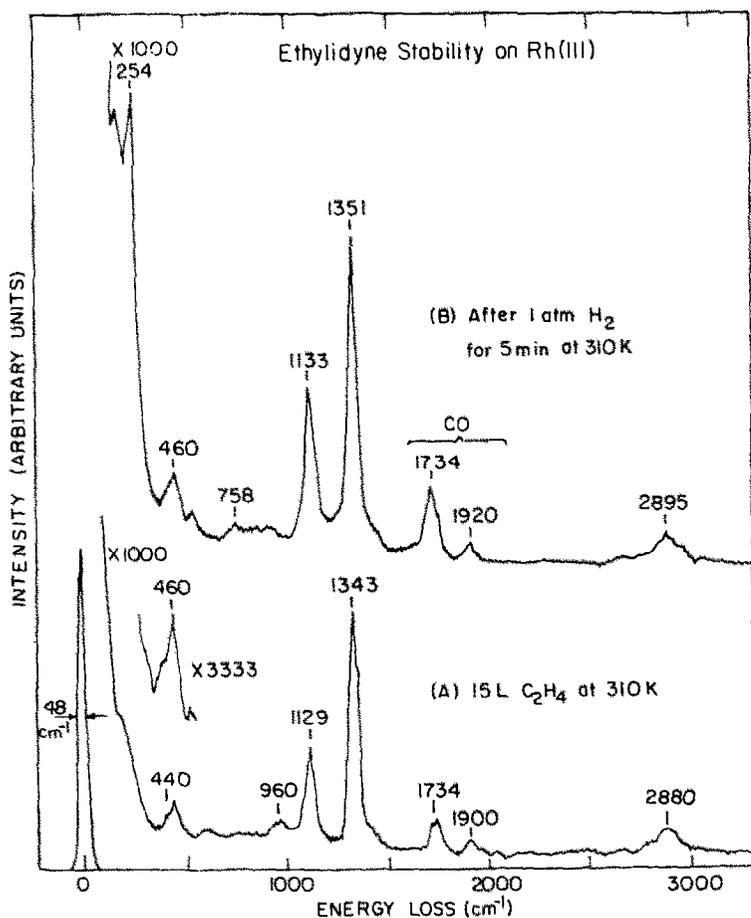


Fig. 4. Surface ethylidyne at saturation coverage on Rh(111) is extremely stable at 310 K to rehydrogenation. HREEL spectra of a Rh(111) surface: (A) saturated with ethylidyne under UHV conditions, and (B) following exposure of this monolayer to 1 atm H_2 for 5 min at 310 K.

experimental uncertainty. There is no evidence for decreased ethylidyne coverage by rehydrogenation to ethylene or ethane. Ethylidyne is even more stable towards rehydrogenation of Rh(111) than on Pt(111) where ^{14}C radiotracer studies [13] have shown some hydrogenation and removal of surface ethylidyne (turnover rate $< 10^{-4}$ / Pt atom \cdot s) under these conditions. Preliminary HREELS studies on Pt(111) support this conclusion.

Fig. 4 also shows no evidence for contamination by other molecules that may coadsorb during high pressure gas exposure. Contamination from hydrocarbons and CO in the ambient was expected. On clean Rh(111) during 1 atm H_2 exposures, hydrocarbon contaminants from the HP cell loop adsorb dissociatively on the surface, giving fingerprint HREELS peaks at about 800 and 1400 cm^{-1} . Similar features were found in a recent study of surface structure following the Fisher–Tropsch synthesis on Fe(110) and assigned to CH and C_xH fragments [14]. But fig. 4 shows no evidence for formation of such surface species in this case. Fig. 4 also shows no change in the relative intensity of the contaminant CO ($< 5\%$ of a monolayer) peaks at 1938 and 1745 cm^{-1} , further evidence that the ethylidyne coverage does not change.

The stability of an ordered $c(4 \times 2)$ ethylidyne monolayer towards hydrogenation on Rh(111) was unexpected for such an open overlayer. Even exposure of a saturation coverage of CCD_3 to 10 Torr of C_2H_4 failed to produce any detectable CCH_3 by coadsorption or replacement. We conclude that C_2H_4 cannot reach the surface and dissociate. The methyl group packing is shown in fig. 5. There does indeed appear to be room for H_2 but not C_2H_4 to reach the surface and dissociate. TPD studies show that about $1/4$ monolayer of H atoms can be coadsorbed in a similar CCH_3 saturated monolayer on Pt(111) by exposure to 1 atm of H_2 [15]. Apparently the strong metal–carbon bonds prevent complete hydrogenation of the carbyne carbon. Partial hydrogenation of the carbyne carbon is, however, likely based on the LEED studies reported next and the H, D exchange reported in section 3.3.

Previous LEED studies [3] showed that careful annealing of the adsorbed monolayer produced by exposure of Rh(111) to ethylene at 240 K could produce a well-ordered $c(4 \times 2)$ CCH_3 structure. Exposure of Rh(111) to 15 L C_2H_4 at 310 K does not produce this structure, but instead the one shown in fig. 6A. The diffuse intensity of the $(1/3, 1/3)$ positions is sometimes resolved to a triangle of spots, but the unit cell for this partially-ordered phase remains unexplained. Exposure of this surface to 1 atm of H_2 causes a two-dimensional phase transition from the structure characterized by the LEED pattern in fig. 6A to a structure with a sharp $c(4 \times 2)$ LEED pattern as shown in fig. 6B. This transition occurs without significant change in the coverage of ethylidyne or contamination by other species, since the HREEL spectra are identical for the two phases.

One plausible explanation for the influence of 1 atm H_2 on the ordering of the ethylidyne monolayer is the partial hydrogenation of the carbyne carbon

followed by deprotonation to give the exchanged species.

Unfortunately, we have not been able to detect adsorbed hydrogen on Rh(111) by HREELS. HREEL spectra of a CCH_3 monolayer after treatment

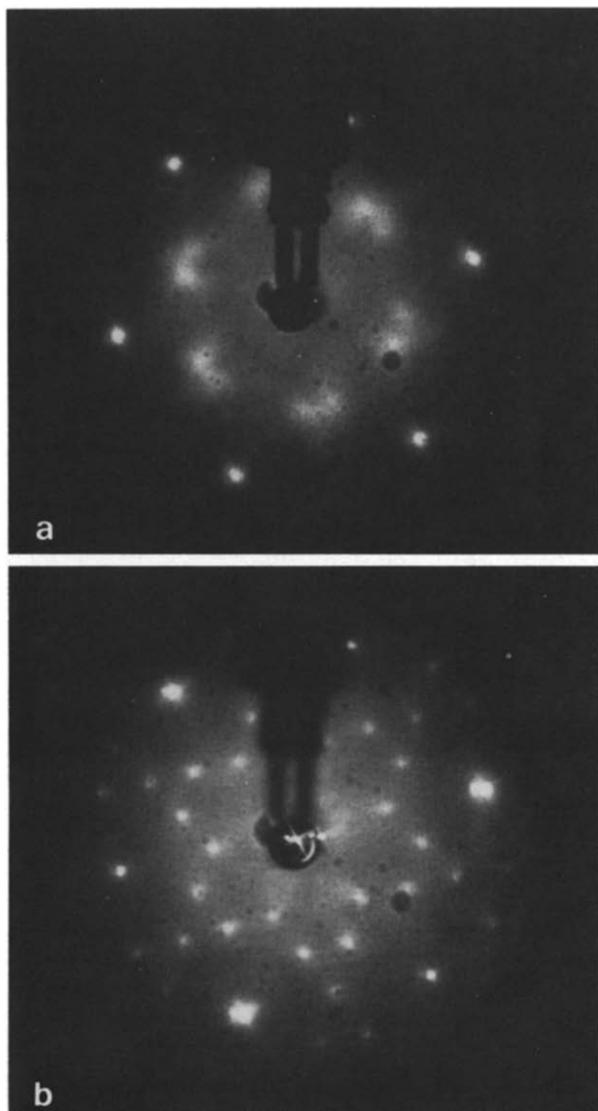


Fig. 6. LEED photographs corresponding to the same conditions as in fig. 4: (A) 15 L C_2H_4 at 310 K, and (B) following exposure of this monolayer to atm H_2 for 5 min at 310 K. A phase transition and improved ordering of the ethynidyne monolayer is observed, even though no new species stable in UHV are formed.

with 1 atm H₂ or of clean Rh(111) in UHV with 10⁻⁷ Torr background H₂ or D₂ show no peaks obviously assignable to M–H or M–D vibrations. Previous temperature programmed desorption (TPD), however, suggests that H atoms are present on the surface in both cases [17,15]. The absence of a detectable Rh–H stretch by HREELS is partially due to the covalent nature of the Rh–H bond. Previous study of H₂ adsorption on Pt(111) has shown the difficulty of detecting the Pt–H vibration [18].

3.3. Ethylidyne + 1 atm D₂

3.3.1. HREELS peak assignment

In addition to the stability of ethylidyne towards rehydrogenation or contamination by replacement or coadsorption, we have studied ethylidyne H, D exchange. HREELS is a sensitive probe for identifying the partially deuterated ethylidyne species at the surface. The symmetry of ethylidyne is lowered from C_{3v} to C_s on partial deuteration. This lower symmetry means more vibrational modes are dipole active and expected to have large scattering amplitudes in the specular direction in HREELS. Besides this symmetry reduction, partial deuteration requires a new approximate normal mode description because of the large percentage mass change. The methyl group modes are now best described as a combination of CH₂ + CD or CD₂ + CH vibrations.

Exposure of a saturation CCH₃ monolayer to 30 L D₂ at 310 K gave the HREEL spectrum shown in fig. 7A. Indeed two new peaks characteristic of methyl group H, D exchange are seen at 1246 and 1407 cm⁻¹. (The 806 cm⁻¹ peak is due to contamination in the original CCH₃ monolayer.) Neither peak is present in the spectrum of CCD₃ and therefore must be the result of partial exchange. However, less than 20% completely exchanged methyl groups would be hard to detect in this experiment, because of the weak carbon–deuterium dynamic dipole (see fig. 3B). Treatment of a similar ethylidyne monolayer with 1 atm D₂ for 5 min at 320 K gave the HREEL spectrum shown in fig. 7(B), which differs little from the spectrum in fig. 7A. The amount of H, D exchange of a saturation coverage of ethylidyne in 1 atm D₂ is surprisingly insensitive to D₂ pressure.

We also followed H incorporation in deuterated ethylidyne. Treatment of CCD₃ with 1 atm H₂ for 2 min at 310 K, as shown in fig. 7C, results in new peaks at 1246, 1300–1450, 2920, and a small increase in the peak at 780 cm⁻¹. The absence of a peak at 1340 cm⁻¹ for the intense symmetric methyl deformation (δ_s CH₃) mode means there are few completely exchanged methyl groups.

Peak assignments are made by comparison with variously deuterated methyl chlorides [19,20] whose peak frequencies and approximate mode descriptions are shown in fig. 8. The ν_{C-Cl} modes have been replaced with expected C–C

stretching frequencies of ethylidyne for comparison with HREEL spectra.

Definitive peak assignments in the partially deuterated ethylidyne spectra are hampered by the presence of mixtures of variously deuterated species on the surface; at a resolution of 50 cm^{-1} , peaks due to the various CCH_xD_y species overlap (as can be seen from the shaded modes in fig. 8). However, by comparing many HREEL spectra of variously deuterated ethylidyne mixtures with those of the partially deuterated methyl halides [19,20], we are able to make in table 2 tentative peak assignments of partially-deuterated ethylidyne.

In the case of CD_2H , comparison is also made with a normal coordinate calculation by Skinner et al. [11] on $(\text{CCD}_2\text{H})\text{Co}(\text{CO})_9$. Similar calculations

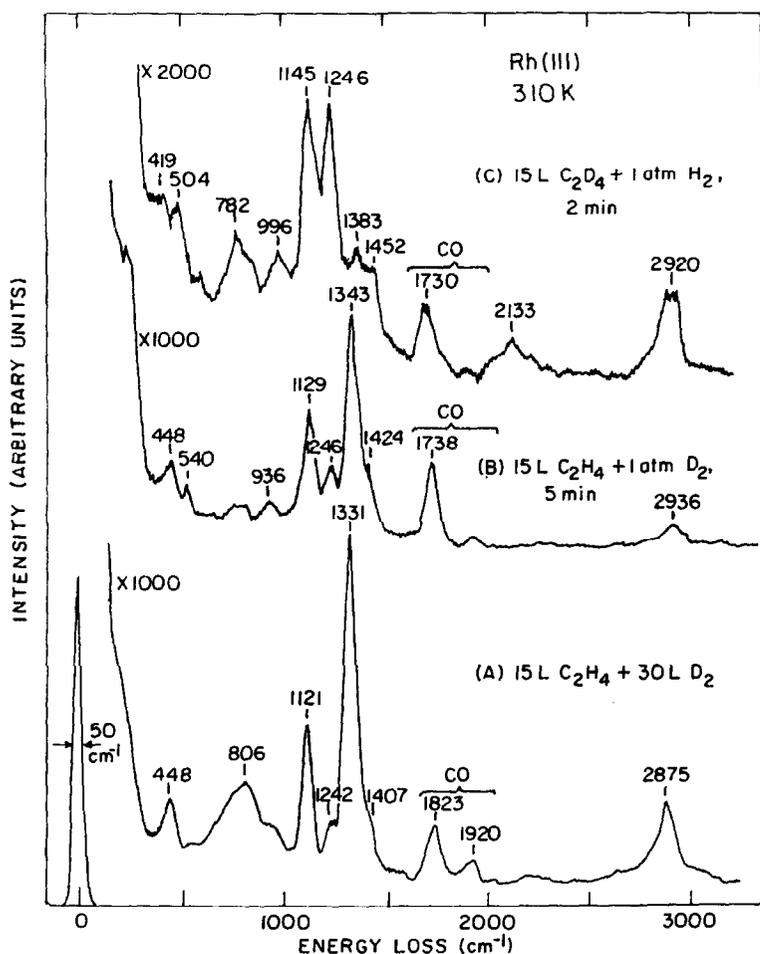


Fig. 7. H, D exchange in the saturated ethylidyne monolayer on Rh(111) at 320 K.

Table 2

Dipole-allowed vibrational frequencies (cm^{-1}) for partially deuterated methyl groups: assignment for ethylidyne on Rh(111) and comparison with similar species; Rh(111) assignments were made using the average peak frequencies from many partially deuterated ethylidyne spectra

	δCD_2 wag	δCD_2 scissor	$\delta_s\text{H}$	$\nu_s\text{CD}_2$	νCH	Source
	880	1019	1256	2117	2919	Calculation [11]
	784	1000	1239	2166	2952	Ethylidyne Rh(111)
	813	1034	1209	2195	3023	Methyl halides [20]
	$\delta_s\text{CD}$	δCH_2 scissor	δCH_2 wag	νCD	$\nu_s\text{CH}_2$	Source
	810	1430	1248	2169	2918	Ethylidyne Rh(111)
	769	1425	1222	2236	2998	Methyl halides [20]

Methyl Group Modes in Various Deuterated Methyl Chlorides

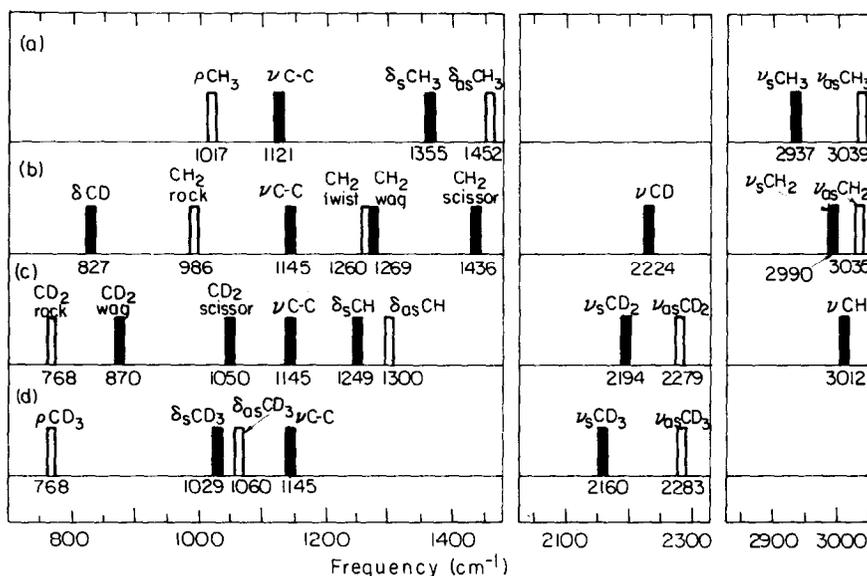


Fig. 8. Methyl group vibrational frequencies and approximate mode descriptions in variously deuterated methyl chlorides. Shaded peaks are modes of A_1 or A' symmetry and are dipole allowed, while unshaded peaks are modes of E or A'' symmetry and are not dipole allowed. C-Cl modes are replaced by approximate C-C stretching frequencies for direct comparison with ethylidyne. (A) CH_3Cl , (B) CDH_2Cl , (C) CDHCl , (D) CD_3Cl .

with the same force constants and geometry on $(\text{CCH}_3)\text{Co}(\text{CO})_9$ and $(\text{CCD}_3)\text{Co}(\text{CO})_9$ gave good agreement with adsorbed ethylidyne frequencies. The agreement here is best with the $\delta_s\text{CH}$, the least overlapping peak. The most distinctive feature of both partially-exchanged species is a band at about 1250 cm^{-1} . The frequency corresponds to a CH_2 wag for the monodeuterated species and a CH in-plane bend for the dideuterated species.

3.3.2. H, D exchange rate

We have also studied the H, D exchange rate of ethylidyne. Some results from these studies are shown in fig. 9. Fig. 9A (like fig. 7B) shows deuterium exchange in CCH_3 at room temperature for 5 min at a saturation coverage of ethylidyne. Fig. 9B shows the vibrational spectrum after the same monolayer is additionally treated with 1 atm D_2 for 2 min at 350 K. Raising the temperature 40 K still does not cause any significant change in the total ethylidyne coverage (as also monitored indirectly by CO adsorption), but increases the amount of exchange, indicated by the growth of the 1246 and 1432 cm^{-1} peaks. Exposing this D and CCH_3 covered surface at 300 K to UHV for 36 h results in additional exchange between the remaining adsorbed deuterium and partially exchanged ethylidyne, as shown in fig. 9C.

It is difficult to quantitatively determine the amount of H, D exchange from the HREEL spectra even with the peaks assigned. The major problem is quantifying the dynamic dipoles perpendicular to the surface (that should be proportional to dipole scattering peak intensity) for the different molecules in the isotopic mixture CCH_xD_y . Because of different dynamic dipole strengths, and overlapping peaks, the peak heights do not change linearly with the concentration of the various molecules in a particular CCH_xD_y mixture. However, using the CH_2 wag dynamic dipole equal to the C–C stretch dynamic dipole [21] and comparing the intensity of the 1120 and 1246 cm^{-1} peaks (assumed to be all CH_2 wag for small amounts of exchange), we estimate using fig. 9A that 5 min of 1 atm D_2 over CCH_3 gives 20% exchange (number of D atoms per three times number of methyl groups) [22]. This value corresponds to methyl group H replacement at a turnover rate of $< 10^{-3}/\text{Rh atom} \cdot \text{s}$. This rate is faster than ethylidyne rehydrogenation. We are currently using temperature programmed desorption to help confirm this estimation.

Subsaturation coverages of CCH_3 exchange much more rapidly. Reaction of $< 50\%$ saturation coverage (1.5 L C_2H_4 exposure) CCH_3 with 30 L D_2 is shown in fig. 10. The presence of the $\delta_s\text{CD}_3$ peak at 984 cm^{-1} and the nearly complete loss of the $\delta_s\text{CH}_3$ at 1340 cm^{-1} indicate complete exchange in some methyl groups. Some partially exchanged ethylidyne is still observed as evidenced by the 1218 cm^{-1} peak.

3.3.3. H, D exchange mechanism

The spectra in figs. 7 and 9 with peaks assigned as in table 2 can be used to

show that deuterium atoms are incorporated in the CCH_3 methyl group one at a time. Compare the intensities of the 1246 and 1430 cm^{-1} peaks. The 1430 cm^{-1} peak is characteristic of the CH_2 scissor in CH_2D . It is the same intensity as the 1246 cm^{-1} CH_2 wag when deuterium exchange first begins, as

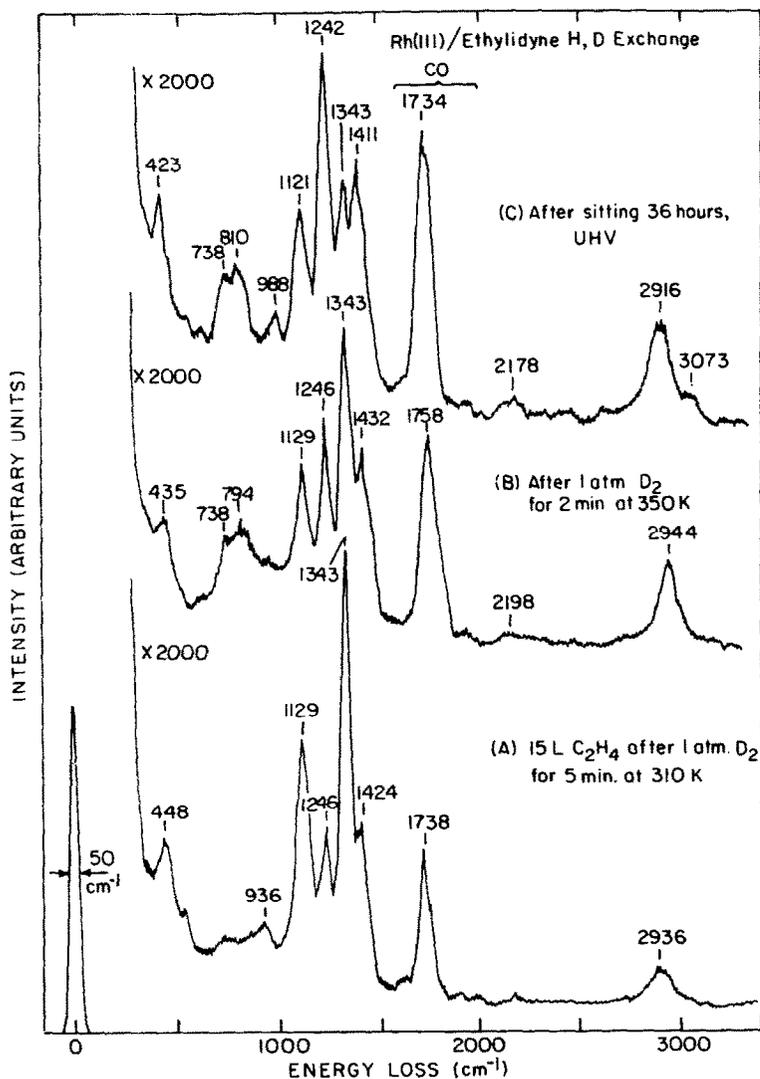


Fig. 9. Increasing temperature and time influence the extent of H, D exchange in ethylidyne. Under these conditions, almost no ethylidyne species have undergone complete exchange, and some species remain that have undergone no exchange.

seen in figs. 8A, 8B, 9A and 9B. With continued exchange, the 1246 cm^{-1} peak grows in relative intensity (fig. 9C). Since neither the 1246 nor 1430 cm^{-1} peak is present in CCH_3 or CCD_3 , the change in their relative intensities implies two partially-deuterated species. As CD_2H forms the 1430 cm^{-1} CH_2 scissor has a smaller intensity relative to the 1246 cm^{-1} CH_2 wag that gains a contribution from the $\delta_s\text{CH}$ [22].

The presence of both CCH_2D and CCHD_2 and the gradual conversion of one to the other rules out the exchange mechanism whereby one molecule of D_2 always replaces two H atoms in the methyl group by a concerted exchange. The mechanism for the process that we monitor is single atom H, D exchange. Furthermore, there was no evidence from the HREEL spectrum of complete methyl group deuteration by some rapid exchange process at selected sites after 5–10 min at 310 K and 1 atm D_2 .

These data are consistent with the exchange mechanism proposed on Pt(111) [23]. In this mechanism, the role of the metal surface is both to atomize H_2 and to help break the methyl group CH bond. The rate-limiting step is

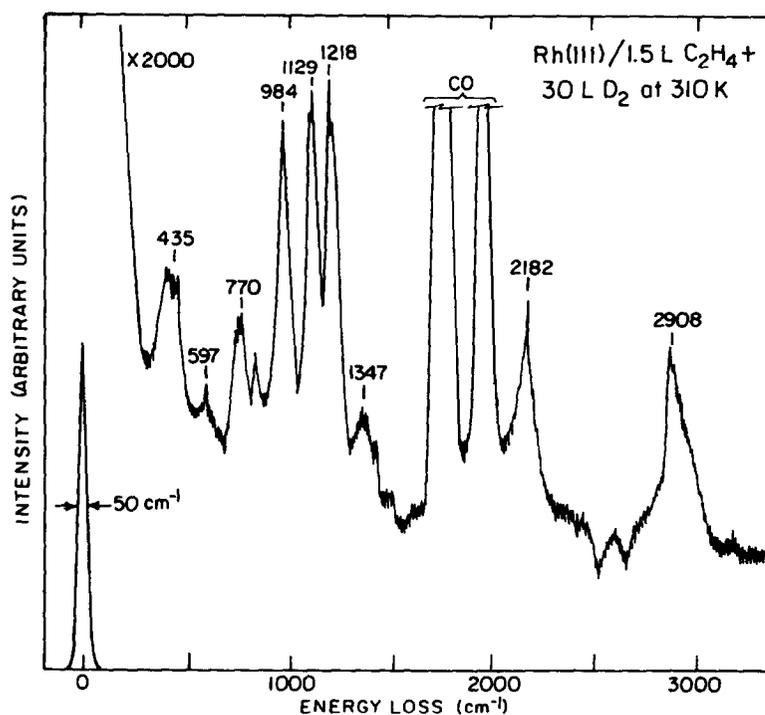
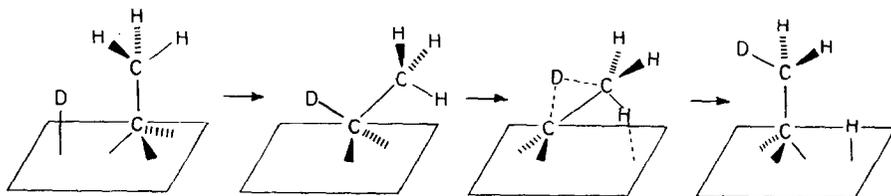


Fig. 10. HREEL spectra taken after a partial monolayer of ethylidyne was exposed to 30 L D_2 under UHV conditions at 310 K. All of the ethylidyne undergoes some deuterium exchange, with a large fraction undergoing complete exchange in the ethylidyne methyl groups.

probably tipping of the CH_3 group for CH bond breaking. The insensitivity of the amount of exchange to the D_2 pressure despite more hydrogen being adsorbed with increased pressure [15,23] and the sensitivity to CCH_3 coverage support this hypothesis.

However, methyl group rocking at its zero point energy [$\frac{1}{2}(988 \text{ cm}^{-1})$] is about 7° from the surface normal [24] – not enough for much surface-aided CH bond scission. We can explain the surface assisted CH bond scission in the methyl group by again postulating ethylidyne as an intermediate. Deuterium incorporation at the carbyne carbon might force the lower carbon into a bridge site with the C–C bond in CDCH_3 tipped about 50° from the surface normal. This moves a methyl group hydrogen nucleus to within 1.8 \AA of a Rh atomic center (Rh–H bond about 1.7 \AA). Carbon–hydrogen bond scission is possibly concurrent with D migration from the carbyne carbon into the methyl group (back-side attack) followed by reorientation of CCDH_2 :

Ethylidyne H, D - Exchange



Since the ethylidyne H,D exchange rate is inversely dependent on CCH_3 coverage and D_2 pressure-independent, the rate limiting step is hydrogenation of the carbyne carbon and tipping of the ethylidyne.

4. Conclusions

We have shown the applicability of HREELS within a HPLP system for studying monolayer structure after HP gas exposure. The HREELS/HP cell combination is a feasible and powerful way of studying surface reactions. We can, with isotopic labelling, study the composition and structure changes in a stable adsorbed monolayer – a relatively unstudied part of catalysis. HREELS, with its sensitivity to carbon–hydrogen bonds, is an ideal tool for unraveling hydrogen transfer in adsorbed hydrocarbon monolayers.

Hydrogen transfer in an ethylidyne monolayer on Rh(111) has been examined in this H, D exchange study. Using the HREELS/HP cell combination, the following conclusions have been reached:

- (1) Saturation coverage of ethylidyne on Rh(111) is stable towards irreversible hydrogenation under 1 atm H_2 at 310 K.
- (2) The relatively open $c(4 \times 2)$ CCH_3 monolayer structure is not con-

taminated by coadsorption or replacement during gas exposures at atmospheric pressure at 300–350 K on Rh(111).

(3) H, D exchange in ethylidyne is a slow process for a saturation coverage CCH_3 overlayer on Rh(111) at 310 K in atm D_2 . Exchange is rapid and extensive at subsaturation ethylidyne coverages of the Rh(111) crystal face.

(4) The H, D exchange rate of saturation coverage of CCH_3 on Rh(111) at room temperature is essentially independent of D_2 pressure. We postulate that this is due to a rate-limiting step of H incorporation at the carbyne carbon to form ethylidene.

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