# Determination of the Mechanism for Ethylidyne Formation from Chemisorbed Ethylene on Transition-Metal Surfaces

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**Abstract:** The effect of deuterium substitution has been studied in relation with the conversion of chemisorbed ethylene to ethylidyne on Pt(111). Thermal desorption (TDS) experiments with a 3:1 $C_2D_4$:$C_2H_4$ mixture yielded traces for $H_2$, HD, and $D_2$ that resemble those obtained with pure $C_2H_4$ or $C_2D_4$, indicating that the reaction is intramolecular. Additional TDS using $CHD{=}CD_2$ resulted in an enhanced $H_2$ desorption at the expense of $D_2$ for the first desorption peak, which is associated with the ethylidyne formation. Our recent kinetic data indicate that the reaction rate for ethylidyne formation displays first-order dependence on ethylene coverage and a normal isotope effect upon deuterium substitution. The TDS results with $CHD{=}CD_2$ then prove that the hydrogen atom involved in the slow step for ethylene conversion is the same that desorbs from the surface first, so a mechanism that invokes ethylidene ($S{=}CH{-}CH_3$, S = surface) as an intermediate can be discounted. We propose the formation of vinyl ($S{-}CH{=}CH_2$) fragments instead.

The chemisorption and thermal decomposition of ethylene over platinum(111) surfaces has been extensively studied by several groups using a range of modern surface science techniques.[1-3] Chemisorption at low temperatures is molecular, with the carbon-carbon bond axis parallel to the surface and a carbon-carbon bond length of 1.49 Å.[4,5] Thermal desorption experiments indicate that dehydrogenation occurs in a stepwise fashion starting around room temperature.[2] After the loss of one hydrogen, ethylene rearranges to form a new moiety, ethylidyne ($S{\equiv}C{-}CH_3$, S stands for surface), in which the carbon-carbon bond is perpendicular to the surface, the molecule is located in a 3-fold hollow site with the $\alpha$ carbon bonded to three platinum atoms, and there are three hydrogens bonded to the $\beta$ carbon.[6,7] Additional dehydrogenation above 450 K results in the formation of hydrocarbon fragments with $C_xH$ stoichiometry, where $x$ has a value between 1 and 2.

Although the structures of chemisorbed ethylene and ethylidyne have been carefully established, the mechanism by which ethylene transforms into ethylidyne remains a mystery. Understanding the reactivity of these adsorbed hydrocarbons is particularly important in view of their role during the catalytic hydrogenation of ethylene. We have shown[8,9] that the steady-state catalytic hydrogenation of ethylene over Pt(111) at room temperature and atmospheric pressures occurs not on the bare metal surface but in the presence of either an ethylidyne layer or a related hydrocarbon fragment. To explain these results, we have proposed a mechanism by which hydrogen atoms may be transferred from the platinum surface to ethylene molecules weakly chemisorbed on a second layer on top of the strongly bonded carbonaceous moieties. We suspect that the intermediate(s) involved in the conversion of ethylene into ethylidyne are closely related to those intervening in the mechanism for ethylene hydrogenation. We have recently studied the kinetics of ethylidyne formation on Pt(111) by using near-edge X-ray absorption spectroscopy (NEXAFS)[10] and determined the kinetic parameters for both $C_2H_4$ and $C_2D_4$ conversion to ethylidyne. We found a noticeable isotope effect in the reaction rates.

In this paper we report thermal desorption experiments after dosing either with a mixture of normal and fully deuterated ethylene or with trideuterioethylene. Because of the changes in reaction rates for ethylene conversion with deuterium substitution, the relative yields of $H_2$ and $D_2$ desorption in these experiments contain information about the mechanism for that reaction. The data presentyed here argue against the formation of ethylidene ($S{\equiv}CH{-}CH_3$) and are consistent with vinyl moieties ($S{-}CH{=}CH_2$) being reaction intermediates.

## Experimental Section

The apparatus used for these experiments consists of an ultrahigh vacuum (UHV) stainless steel bell jar pumped with a turbomolecular pump to a base pressure of about $1 \times 10^{-10}$ Torr. This chamber is equipped with a quadrupole mass spectrometer capable of detecting masses in the 1-800 amu range. The ionizer of the quadrupole is located inside an enclosed compartment with a couple of apertures about 7 mm in diameter in the front and back for gas sampling and exit to the quadrupole rods, respectively. The sample was positioned within 1 mm of the front aperture, resulting in an enhanced sensitivity of about a factor of 5 for desorption from the front face of the crystal and additional discrimination against desorption from the edges and back of the crystal and from the supporting wires. The mass spectrometer is interfaced to a computer, allowing the detection of signal from up to 10 separate atomic mass units (amu) in a single thermal desorption experiment.

The system was also equipped with a concentric hemisphere electron energy analyzer for Auger (AES) and X-ray photoelectron (XPS) spectroscopies and with an ion sputtering gun for sample cleaning. The sample manipulator allowed for resistively heating the crystal up to 1300 K and cooling to 90 K within 5 min. The thermal desorption experiments reported here were done using a heating rate of about 10 K/s.

The platinum (111) single crystal was cut and polished by using standard procedures. It was cleaned under vacuum by a combination of oxygen treatments and sputtering-annealing cycles until no impurities were detected by using either AES or XPS. Normal ethylene was obtained from Matheson (99.5%, C.P. purity) and used without further treatment. Deuterated ethylene was acquired from Matheson as well (99 at. % D) and also used as received. An approximately 3:1 $C_2D_4$:$C_2H_4$ mixture was prepared by sequentially filling a glass bulb with a given pressure of each gas (partial pressures in the 10-100-Torr range, as measured with a Bourdon gauge) and condensing at liquid nitrogen temperatures. The final composition was determined by measuring the 30/27 amu signal ratio of the mass spectrum, which was 2.36. That number should correspond to the $C_2D_4$:$C_2H_4$ ratio if we assume equal fragmentation probabilities for both gases in the mass spectrometer ionizer.

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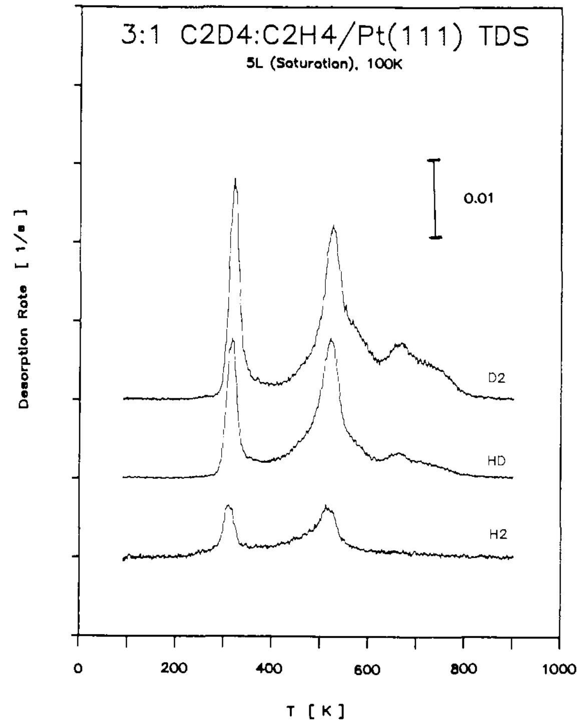

**Figure 1.** 2 ($H_2$), 3 (HD), and 4 ($D_2$) amu thermal desorption spectra for ethylene adsorbed on Pt(111). The platinum surface was exposed to 5 langmuirs of a 3:1 $C_2D_4$:$C_2H_4$ mixture below 200 K; heating rate = 10 K/s.

Trideuterioethylene was prepared by a gas-phase exchange reaction between $CD_2$=CDCl (CIL, 98 at. % D) and tributyltin hydride. We achieved over 70% conversion after leaving the mixture in a 1-L bulb for a couple of months at room temperature. The resulting mixture was vacuum distilled at 178 K, and we estimate the purity of the final product to be higher than 95% by using gas chromatography–mass spectrometry. We also calculated the isotopic purity to be over 90% by using a test described below.

The thermal desorption experiments were performed after sample cleaning and cooling to below 100 K. To minimize background adsorption, the crystal was quickly flashed to 600 K and cooled to below 200 K prior to gas dosing (5 langmuirs, 1 langmuir = 1 × $10^{-6}$ Torr·s). The time between flashing and dosing was of the order of 100 s. Since the background pressure was about 1 × $10^{-10}$ Torr and the residual gas was mostly hydrogen, this corresponds to a $H_2$ exposure of about 0.01–0.02 langmuir. Blank TDS experiments determine that preadsorbed hydrogen amounted to about 0.02–0.03 monolayer of atomic hydrogen. This amount of hydrogen was subtracted from the area of the $H_2$ trace before calculating the area ratios shown in Table II.

## Results

The main experimental results of this report are summarized in the thermal desorption spectra (TDS) shown in Figures 1 and 2. The TDS data are presented in terms of desorption rates as a function of crystal temperature. To convert the mass spectrometer signal to desorption rates, few calibration experiments needed to be done. Under the high pumping speeds of our experiments, the desorption rate $R(t)$ is related to the mass spectrometer signal $D_{MS}$ by the following equation:

$$R(t) = \left[\frac{C_{MS}Sn^*}{A\rho_{Pt}}\right]D_{MS} = KD_{MS}$$

where $R(t)$ is expressed in monolayers per second, $C_{MS}$ is the conversion factor for the mass spectrometer (from volts to Torr), $S$ is the pumping speed of the system in L/s, $n^*$ is the number density at 300 K and 1 Torr (3.219 × $10^{19}$ $L^{-1}$, used to convert Torr·L to molecules), $A$ is the crystal area (about 1 $cm^{-2}$), and $\rho_{Pt}$ is the density of platinum atoms on the crystal surface (1.5 × $10^{15}$ atoms/$cm^2$ for Pt(111)).

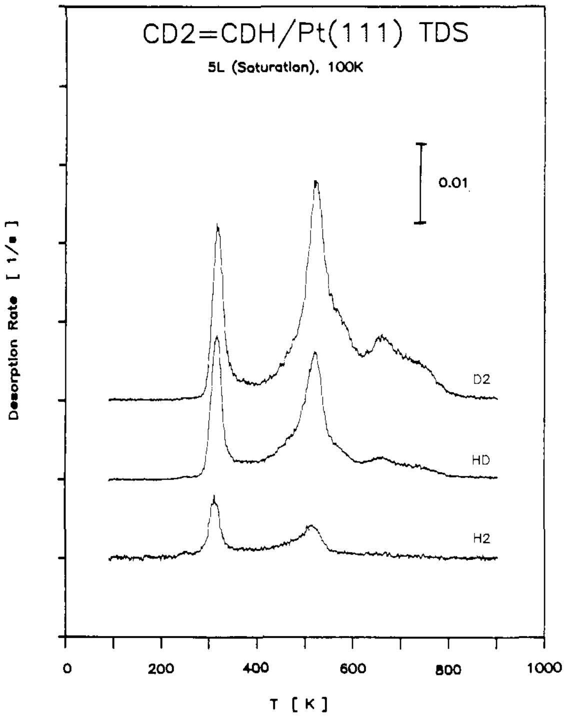

**Figure 2.** 2 ($H_2$), 3 (HD), and 4 ($D_2$) amu thermal desorption spectra after exposing a Pt(111) surface to 5 langmuirs of CHD=$CD_2$ below 200 K; heating rate = 10 K/s.

**Table I.** Conversion Factrs for TDS

| mass, amu | $10^9C_{MS}$, Torr/V | $S$, L/s | $K$, $[V·s]^{-1}$ |
|---|---|---|---|
| 2 | 2.77 | 310 | 0.0203 |
| 3 | 3.72 | 340 | 0.0299 |
| 4 | 5.67 | 370 | 0.0498 |

The value for $C_{MS}$ was calculated by measuring the mass spectrometer signal for 2 or 4 amu for a given pressure of $H_2$ or $D_2$, respectively. The measurements were done at several pressures, and the slope of a signal versus pressure plot was calculated by using a minimum square fit. The results are summarized in Table I. Because the pressure was measured by using a Bayard-Alpert nude ion gauge, the readings had to be corrected by the sensitivity factor for hydrogen, which has been reported to be 0.42.[11]

The turbomolecular pump nominal pumping speed for hydrogen ($H_2$) is 310 L/s. The pumping speeds for $H_2$ and $D_2$ were measured experimentally by leaking the gasses until achieving a stable pressure and then suddenly closing the leak valve and following the pressure drop versus time. Our experimental results were close to those reported for the pump for $H_2$, and the pumping speed for $D_2$ was found to be 1.2 times larger than for $H_2$. The values used in this paper are presented in Table I. The values for $C_{MS}$ and $S$ for HD were interpolated between those for $H_2$ and $D_2$. Finally, the values for $K$, as determined here, are also tabulted in Table I. Because the pumping speeds depend strongly on the experimental geometry, the absolute values for the desorption rates can be off by as much as a factor of 2. However, for the purposes of this paper, we are concerned only with the relative values for $H_2$, HD, and $D_2$, and those are accurate within 10%.

Thermal desorption spectra for the 3:1 mixture of $C_2D_4$ and $C_2H_4$ are shown in Figure 1. $H_2$ (2 amu), HD (3 amu), and $D_2$ (4 amu) were all followed simultaneously by using a computer, as mentioned in the Experimental Section. All three traces look quite similar, although the peaks for HD and $D_2$ are slightly shifted to higher temperatures due to the isotope dependence in ethylene decomposition rates.[10] The first peak is centered at 309 K for $H_2$, at 315 K for HD, and at 318 K for $D_2$. Also, there are additional features in the TDS above 600 K for $D_2$ and HD in comparison with the TDS for $H_2$. An analysis of the relative peak areas is given in Table II and will be discussed in detail in the

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**Table II.** Analysis of the TDS Data[a]

| | 2 amu ($H_2$) | | | 3 amu (HD) | | | 4 amu ($D_2$) | | | H/D at. ratio | | $A_{1st\,peak}/A_{total}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| system | $T_{max}$, K | $A_{1st\,peak}$ | $A_{total}$ | $T_{max}$, K | $A_{1st\,peak}$ | $A_{total}$ | $T_{max}$, K | $A_{1st\,peak}$ | $A_{total}$ | 1st peak | total | H atoms | D atoms | H + D atoms |
| 3:1 $C_2D_4$:$C_2H_4$ | 309 | 0.0178 | 0.0674 | 315 | 0.0415 | 0.1812 | 318 | 0.0578 | 0.2515 | 0.43 ± 0.03 | 0.45 ± 0.03 | 0.22 ± 0.02 | 0.23 ± 0.02 | 0.23 ± 0.02 |
| CHD=$CD_2$ | 311 | 0.0183 | 0.0486 | 314 | 0.0436 | 0.1690 | 317 | 0.0473 | 0.2824 | 0.51 ± 0.03 | 0.35 ± 0.03 | 0.27 ± 0.02 | 0.19 ± 0.02 | 0.21 ± 0.02 |

[a] Values are the average over three runs. Areas $A$ were determined within about 10% accuracy.

following section. There is a low-temperature onset in the $H_2$ TDS due to background hydrogen adsorption. This adsorption corresponds to less than 2% of a monolayer and does not modify the main results in this paper (control coadsorption experiments were done to corroborate this fact).

Figure 2 shows similar TDS obtained for CHD=$CD_2$ chemisorbed on Pt(111). Compared with the results from the 3:1 mixture, there is an enhancement in $H_2$ yield in the first peak at the expense of $D_2$ desorption. The opposite is true for the high-temperature region of the TDS. The data analysis is summarized in Table II.

We have done two internal checks to test the reliability of the TDS area data. First, let us consider the overall H/D atomic ratio by using the areas under the entire traces for masses 2, 3, and 4. In the case of CHD=$CD_2$ the H/D ratio should be $^1/_3$, on the basis of the stoichiometry of this compound. We obtained a value of 0.35 ± 0.03 (Table II), in excellent agreement with expectation. For the $C_2D_4$:$C_2H_4$ mixture, the H/D ratio should be equal to the mixture composition (0.43 in this case). Again, the experimental values of 0.45 ± 0.03 agrees with the predicted number. (Ethylene molecular desorption accounts only for less than 10% of the initially adsorbed ethylene[9]).

A second test is based on the stoichiometry of ethylidyne. To go from ethylene to ethylidyne, a hydrogen atom must be lost. These atoms recombine and desorb in a peak around 300 K, clearly separated from other peaks due to subsequent hydrocarbon fragment decomposition. This means that the integrated area (summing contributions from the 2, 3, and 4 amu traces) for the first peak should correspond to 25% of the total area (one out of four H or D atoms in the original ethylene molecule). Our experimental values were 23 ± 2% for the $C_2D_4$:$C_2H_4$ mixture and 21 ± 2% for CHD=$CD_2$ TDS.

## Discussion

The main goal of this project was to determine the mechanism for the conversion of chemisorbed ethylene to ethylidyne on Pt(111) surfaces. Our study relies on the kinetic isotope effect previously reported for this process.[10] The rate of ethylidyne formation has been measured directly on the surface by using SSIMS (static secondary ion mass spectroscopy),[12] NMR,[13] and NEXAFS (near-edge X-ray absorption fine structure).[10] A summary of our NEXAFS data is shown in Figure 3 in the form of an Arrhenius plot. The most important conclusions from the kinetic data are that the reaction rate follows first-order coverage dependence and that there is a clear normal isotope effect, the reaction rate with $C_2H_4$ being 2–3 times faster than with $C_2D_4$. The final kinetic parameters obtained were 15.0 and 16.7 kcal/mol for the activation energies and $3.6 \times 10^{10}$ and $3.5 \times 10^{11}$ $s^{-1}$ for the preexponential factors for $C_2H_4$ and $C_2D_4$, respectively.

The first-order kinetics suggest that ethylidyne formation is unimolecular. The fact that the reaction is intramolecular and not intermolecular can be further checked by using $C_2D_4$–$C_2H_4$ mixtures. If the reaction were intramolecular, there would be an enhancement in $H_2$ desorption during the conversion due to the faster rate for H with respect to D. We determined that the first peak in the $H_2$ TDS from the 3:1 $C_2D_4$:$C_2H_4$ mixture corresponds to 22 ± 2% of the total hydrogen desorption (23 ± 2% for deuterium). The numbers for hydrogen and deuterium are the same within the experimental error, proving the hypothesis of intramolecular reactivity. Additionally, the HD trace looks qualitively the same as those for $H_2$ and $D_2$.

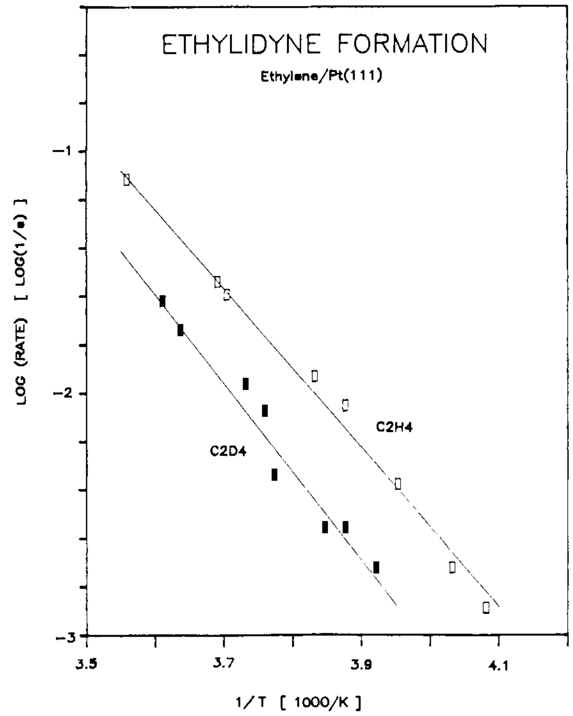

**Figure 3.** Arrhenius plot showing the temperature dependence of the rate constants for ethylidyne formation from $C_2H_4$ (□) and from $C_2D_4$ (■).

Although the conversion of ethylene to ethylidyne on Pt(111) displays first-order rates suggestive of an unimolecular process, it is unlikely that this reaction occurs in one concerted elementary step. However, no stable intermediate other than chemisorbed ethylene or ethylidyne has been identified on this surface. Therefore, if more than one step is involved in the reaction mechanism, the first step must be rate limiting. We propose here a couple of sequences of two simple elementary steps by which ethylene could transform into ethylidyne. If a hydrogen atom migrates from one carbon atom to the other, a new moiety having a S=CH—$CH_3$ stoichiometry would form (ethylidene). Ethylidene would then immediately lose the α-hydrogen to form ethylidyne (S≡C—$CH_3$). An alternative route can be envisioned in which the C–H bond breaking occurs first and a vinyl would form (S—CH=$CH_2$). The α-hydrogen would then migrate to the β-carbon to form ethylidyne.

Since the reaction is faster with H than with D atoms, the initial step of CHD=$CD_2$ conversion must mainly involve the only hydrogen atom in the molecule. The two mechanisms described before are shown schematically for this compound as reactions 1 and 2. From this scheme we can see that if $D_2$ desorption is

$$\mathrm{CHD{=}CD_2\ (ads) \rightarrow S{=}CD{-}CD_2H \xrightarrow{-1/2D_2} S{\equiv}C{-}CD_2H} \tag{1}$$

$$\mathrm{CHD{=}CD_2\ (ads) \xrightarrow[-1/2H_2]{} S{-}CD{=}CD_2 \rightarrow S{\equiv}C{-}CD_3} \tag{2}$$

dominant in the first TDS peak, it is because the first mechanism is preferred, while detection of $H_2$ as a major product would

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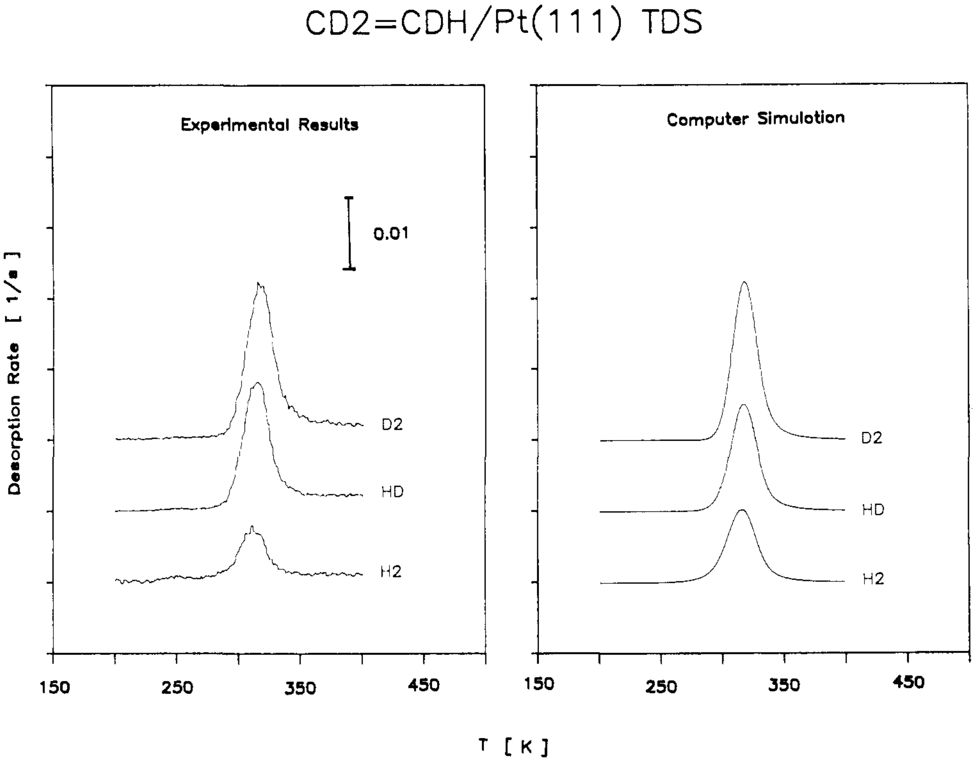

**Figure 4.** Comparison between the experimental results (left) and a computer simulation (right) for chemisorbed CHD=$CD_2$ conversion to ethylidyne on Pt(111). See text for details.

indicate that the second route is operative. Our results show that $H_2$ desorption in the first peak (corresponding to ethylidyne formation) is enhanced and $D_2$ desorption is depleted with respect to the $C_2D_4$:$C_2H_4$ mixture, favoring the interpretation that invokes the formation of vinyl moieties as intermediates.

Although the CHD=$CD_2$ TDS data show an increase in $H_2$ desorption at 300 K compared to the 3:1 $C_2D_4$:$C_2H_4$ mixture, a considerable amount of $D_2$ desorption is also observed. To obtain a more quantitative idea of the importance of vinyl formation in the overall reaction, we have done a computer simulation of the surface reaction for chemisorbed CHD=$CD_2$. We used the values obtained with NEXAFS for the activation energies and preexponential factors for the rate-limiting step. We also know that hydrogen recombination is fast at the reaction temperatures, so the actual values of its kinetic parameters are not critical in the simulation.[10] We decided to use 10 kcal/mol and $5 \times 10^{-8}$ $s^{-1}$ for the activation energy and preexponential factor, respectively, since those values reproduce $H_2$ TDS from chemisorbed $H_2$ reasonably well, although activation energies as high as 19 kcal/mol have been reported.[14] Simulations done using such high values yielded results that were similar to those shown here. A comparison between experimental and calculated TDS is shown in Figure 4. The calculations were done assuming initial coverages of 0.25 and 0.02 monolayer for CHD=$CD_2$ and H respectively (1 monolayer = 1 chemisorbed atom or molecule/Pt atom). The two results agree quite well, although the calculations show a little lower yield for HD desorption and peak maxima that are slightly shifted with respect to the experimental data. It must be pointed out that we used no adjustable parameters in these simulations. The ratio H/D from the calculations came out to be 0.55, just a little bit higher than the experimental value (H/D(exptl) = 0.51 ± 0.03).

Additional support for the mechanism involving vinyl formation can be obtained from the peak maxima of the TDS traces. If ethylidene were formed, $D_2$ desorption would result from D atom recombination product of fast reaction steps, and it would desorb at the same temperature as $H_2$ and HD. However, our data indicate that the $D_2$ TDS peaks at 317 K, 6 K higher than $H_2$. This temperature shift is again consistent with vinyl formation, as can be seen from our calculations (Figure 4, right panel, $H_2$ peaks at 315 K and $D_2$ at 318 K).

Finally, the data presented here cannot rule out many other more complex mechanisms. What is clear from our results is that the hydrogen atom involved in the limiting step is the same observed in the first thermal desorption peak. That observation allow us to discard a family of mechanisms, including those that start with ethylidene formation. We have previously suggested that ethylene hydrogenation under high pressures may take place through the formation of ethylidene,[8] but such specie has not yet been detected on clean metal surfaces (Koel et al. have reported the formation of ethylidene on a Pt(111) surface modified by potassium[27]). Here we have shown that, at least under hydrogen-deficient conditions (such as those in ultrahigh vacuum), ethylidene is not formed. Vinyl moieties, on the other hand, have been fully characterized on Ni(100) surfaces.[15,16]

The conclusions presented here comes from studies done on Pt(111) single-crystal surfaces, but we would expect similar reactions to take place in many other systems. Ethylidyne formation has now been characterized on many transition-metal surfaces, including single crystals of Pt(111),[6,7] Pt(100),[17,18] Rh(111),[19] Rh(100),[20] Pd(111),[21] Ru(100),[22] and Ir(111)[23] and supported Pt,[24] Pd,[25] and Ni[26] catalysts over $Al_2O_3$ or $SiO_2$. Most of these

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cases have shown equal reactivity toward ethylene conversion, and therefore we would expect similar results from experiments such as those described here.

## Conclusions

Thermal desorption of deuterated or partially deuterated chemisorbed ethylene on Pt(111), together with kinetic measurements using NEXAFS, have given us new insights on the mechanism of ethylidyne formation. The kinetic studies show that the limiting step of the reaction is unimolecular and that there is a normal isotope effect in the reaction rates between hydrogen and deuterium. It is also clear that if the process does not occur in one elementary step, the first is the rate limiting. TDS results using a $C_2D_4$:$C_2H_4$ mixture proved that the reaction is indeed intramolecular, as we would have expected from an unimolecular process. Finally, the experiments using $CHD{=}CD_2$ indicate that the hydrogen atom involved in the slow step is the same that desorbs first in the thermal desorption. This rules out ethylidene as an intermediate, and we propose the formation of vinyl as a transient moiety on the surface.

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**Registry No.** $C_2H_4$, 74-85-1; $C_2H_3$, 67624-57-1; Pt, 7440-06-4.

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# Calculation of Excited-State Geometries via the Time-Dependent Theory of Resonance Raman Spectroscopy: Application to Complexes of the Type $Rh_2(O_2CCH_3)_4(MPh_3)_2$, M = P, As, or Sb, at Resonance in Each Case with the Lowest $^1A_{2u}$ Excited State

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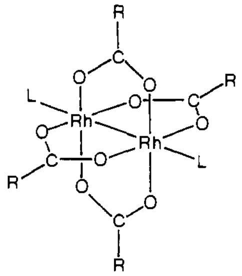
**Abstract:** The calculation of both the excitation profiles of all the resonance-enhanced Raman bands and the intensities of all the observed overtone and combination bands of the rich resonance Raman spectra of the axially disubstituted dirhodium tetraacetate complexes $Rh_2(O_2CCH_3)_4(MPh_3)_2$, M = P, As, or Sb, is reported. The calculation uses the time-dependent theory of Lee and Heller. The geometric changes attendant upon excitation of each molecule from the ground to the first excited state, i.e. at resonance with the lowest $^1A_{2u} \leftarrow {}^1A_{1g}$ transition, are calculated. All the excitation profiles and the resonance Raman spectra are fitted by use of a single set of parameters, $\Delta$ (the displacement in dimensionless normal coordinates), $E_{00}$ (the zero-zero electronic transition wavenumber), and $\Gamma$ (the damping factor). The largest bond length changes in all of the molecules are in the Rh-Rh and Rh-O bonds.

The calculation of the geometries of molecules and ions in excited electronic states from resonance Raman spectra has traditionally been carried out via a Franck-Condon analysis of the intensities of Raman bands in spectra for which $\omega_I$ (the excitation line wavenumber) coincides with $\omega_0$ (the wavenumber of the electronic transition in question).[2] Examples of such analyses include cases in which the resonant band is structured (e.g. $MnO_4^-$)[3] as well as unstructured (e.g. $S_2^-$).[4] An alternative treatment of resonance Raman data with certain advantages over the Franck-Condon treatment is that based on the transformation of the Kramers-Heisenberg-Dirac formula to the time domain, viz. the Lee-Heller treatment.[5] The distortions of a variety of metal-containing compounds have been calculated by use of preresonance Raman intensities and the applicable short-time approximation of the theory.[6-12]

The present paper is concerned with the results of the time-dependent analysis of excitation profiles and resonance Raman spectra applied to a set of complexes that are known to display particularly rich resonance Raman spectra. These are dirhodium tetraacetate complexes which are diaxially substituted with group V ligands, viz. $Rh_2(O_2CCH_3)_4(MPh_3)_2$, M = P, As, or Sb. Such complexes have the skeletal $D_{4h}$ structure illustrated below (L = $MPh_3$, R = $CH_3$).



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