Mechanistic Changes in the Conversion of Ethylene to Ethylidyne on Transition Metals Induced by Changes in Surface Coverages

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Abstract: The thermal chemistry of trideuterioethylene on Pt(111) surfaces was characterized by reflection−absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD). The vibrational data indicate that thermal activation of a saturated layer of adsorbed ethylene by heating the surface to 350 K produces surface ethylidyne species with an isotopic composition of about 45% perdeuterioethylidyne and 55% dideuterioethylidyne. The hydrogen TPD data confirm that result, and also highlight the fact that the proportion of hydrogen-to-deuterium elimination from the original ethylene molecules changes with initial coverage. To explain these observations a previously proposed three-step mechanism is used where ethylene first isomerizes to ethylidene and ethylidene then either isomerizes back to ethylene or dehydrogenates to ethylidyne. The changes in hydrogen isotope removal probability with coverage are explained by changes in the relative rates between the latter two steps because of the fact that the outgoing hydrogen in the dehydrogenation step requires an empty surface site that may be blocked by ethylene molecules at high coverages.

1. Introduction

Alkylidyne groups are well-known both in discrete organometallic compounds and on solid surfaces.[1] There have been reports of alkylidyne complexes with one[2,3] and two[4,5] metal centers, but the most common type by far is one where the moiety is located at the center of a three-atom metal triangle.[6−8] On transition metal surfaces alkylidynes usually adopt a C_3 symmetry similar to that in the trimetallic clusters where the bottom carbon atom is nested in 3-fold hollow sites and the C−C bond is parallel to the surface normal.[9−11] The electronic structure of these alkylidynes is still a matter of some controversy, but perhaps the most accepted proposal is that the carbon atom attached to the metal is sp-hybridized and bonds to the three metal atoms via delocalized molecular orbitals.[12,13]

Alkylidyne species have proven quite stable, and form easily via thermal activation of other compounds. Discrete alkylidyne clusters can be prepared by using the corresponding 1,1,1-trihaloalkanes, via the decomposition of acetylenic or alkylidene complexes, or by substitution of the R group in existing alkylidyne compounds.[8] Similar conversions have been reported

in some instances on metal surfaces, but the most common way to prepare alkylidyne moieties on solids is via the thermal activation of chemisorbed olefins. In particular, ethylidyne has been reported to form upon heating ethylene to around room temperature on Pt(111),[14] Pt(100),[15] Rh(111),[16] Rh(100),[17] Pd-(111),[18] Ru(0001),[19] and Ir(111)[20] single crystals as well as on supported platinum,[21] palladium,[22] and nickel[23] catalysts, and the analogous formation of larger alkylidynes (*n*-propylidyne to *n*-pentylidyne) has been observed as well.[24−28] Extensive work has been performed on the characterization of these surface systems, but a complete understanding of the mechanism of the alkene-to-alkylidyne conversion is still lacking. Since alkylidynes have been shown to intervene in catalytic hydrogenation−dehydrogenation and hydrocarbon reforming reactions,[29−33] such knowledge is particularly important in explaining the details of many industrial processes.

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As a representative of alkene conversion reactions, the conversion of ethylene to ethylidyne on Pt(111) surfaces in particular has been studied extensively with a number of surface-sensitive techniques. Unfortunately, the data available for this system so far have not yet resulted in the proposal of a clear mechanism. Given that in order to produce ethylidyne ($Pt_3\equiv$ $C-CH_3$) from adsorbed ethylene ($Pt-CH_2-CH_2-Pt$) one hydrogen atom has to be abstracted from the molecule and another has to migrate from one carbon atom to the other, it is reasonable to assume that the mechanism for such a conversion consists of at least two steps and, as a consequence, involves the formation of one or more intermediates. Ethyl, vinyl, and ethylidene moieties have all been proposed as intermediates for this reaction, but none have yet been identified unequivocally.

An ethyl ($Pt-CH_2-CH_3$) intermediate was initially proposed by Somorjai et al. for the ethylene-to-ethylidyne conversion on the basis of calculated activation energies for several possible mechanisms,[34] but later experimental results provided arguments against this pathway. In particular, temperature-programmed desorption and infrared spectroscopy data from ethyl iodide on Pt(111) indicated that ethyl groups convert to ethylene via β-H elimination at temperatures much lower than those required for the formation of ethylidyne.[35−37] The formation of a vinyl ($Pt-$ $CH=CH_2$) intermediate during the conversion of ethylene to ethylidyne was first suggested on the basis of an enhancement in the desorption of H_2 from trideuterioethylene ($CD_2=CDH$) from that expected on pure stoichiometric grounds.[38] Secondary ion mass spectrometry data from vinyl iodide on Pt(111) later supported the idea of a direct conversion of vinyl to ethylidyne on Pt(111) around 120 K,[39] but that low-temperature step was not confirmed by infrared spectroscopy experiments, which revealed a more complex reaction in which vinyl goes through the formation of ethylene before producing ethylidyne.[40] Finally, ethylidene ($Pt=CH-CH_3$) was initially proposed as an intermediate during the formation of ethylidyne on potassium-covered Pt(111).[41,42] More recently, Cremer et al. reported the appearance of a C−H vibration mode at 2957 cm^{-1} in sum frequency generation (SFG) experiments during the conversion of ethylene to ethylidyne on clean Pt(111), which they assigned to ethylidene (or perhaps ethyl) intermediates.[43] Ethylidene moieties prepared via the decomposition of 1,1-diiodoethane can in fact convert into ethylidyne surface species via a direct step at temperatures as low as 150 K.[44]

On the basis of the results summarized above, ethylidene appears at this point to be the most promising candidate for the intermediate in the conversion of ethylene to ethylidyne.[45] The main argument against this proposal comes from the enhanced H_2 desorption in the TPD experiments with $CD_2=CDH$ cited before.[38] However, even though such a result is inconsistent with an irreversible two-step mechanism via an ethylidene intermediate, it could be explained by the inclusion of an ethylene−ethylidene preequilibrium preceding the formation of ethylidyne. In that respect, it is also interesting to note that since α-hydride elimination from ethylidene to ethylidyne requires empty surface sites to accommodate the hydrogen released, it is suppressed at high surface coverages, where ethylene is formed instead. Indeed, the data from our study of the chemistry of 1,1-diiodoethane on Pt(111) surfaces highlighted the fact that the availability of empty surface sites plays a key role in the kinetics of ethylidyne formation.[44] It was proposed there that while the isomerization of ethylene to ethylidene is likely to be rate limiting at low coverages, α-H elimination from ethylidene to ethylidyne must be the slower step at high coverages. This hypothesis implies that the ratio of hydrogen-to-deuterium released during the conversion of trideuterioethylene should change as the initial ethylene coverage is increased. In this report we prove that this is indeed the case. The main conclusion from our present studies is that ethylidyne formation does appear to involve the formation of an ethylidene intermediate, but that the rate of the subsequent α-H elimination from that species to ethylidyne slows down relative to its isomerization back to ethylene as the surface becomes more crowded, and that this changes the dynamics of the overall conversion.

2. Experimental Section

The experiments reported here were performed in an ultrahigh vacuum (UHV) chamber evacuated to a base pressure of about 4×10^{-11} Torr and equipped with an ion gun for sputtering, a mass spectrometer for temperature-programmed desorption (TPD), and an FTIR spectrometer for reflection−absorption infrared spectroscopy (RAIRS), as described elsewhere.[37,46]

RAIRS was performed by taking the IR beam from a Mattson Sirius 100 FTIR spectrometer and focusing it at grazing incidence through a sodium chloride window onto the sample in the UHV chamber. The reflected beam was then passed through a second sodium chloride window and a polarizer and refocused on a mercury−cadmium−telluride (MCT) detector. Averages of 1000 scans (about 300 s acquisition time) with 4 cm^{-1} resolution were taken and ratioed against spectra for the clean surface recorded immediately before dosing. All the IR spectra were taken at sample temperatures below 130 K. The ionizer of the UTI-100C mass quadrupole employed for the TPD experiments was covered with a retractable cone with a small front opening which could be positioned within 1 mm of the sample for signal enhancement as well as for discrimination from background gases. The mass spectrometer was connected to a personal computer and run with home-written software designed for data collection of up to 15 masses during a single experiment. The temperature of the sample in the TPD experiments was ramped at a linear rate of 8 K/s by using homemade electronics. The data for the desorption of the isotopomers of ethylene in Figures 2 and 3 were deconvolved by using the cracking patterns of the pure compounds obtained with our instrument.[47,48]

The Pt(111) single crystal was mounted on a sample holder with capabilities for both cooling to 100 K and resistive heating to above 1000 K. The temperature was measured with a chromel−alumel thermocouple spot-welded to the back of the crystal. The platinum surface was routinely cleaned by cycles of sputtering with Ar$^+$ ions at room temperature, oxidation in 2×10^{-7} Torr oxygen at 700 K, and annealing in vacuum at 1000 K. The isotopically labeled ethylene gases were obtained from Cambridge Isotope Laboratories (C_2D_4, 99% D purity, and C_2D_3H, 98% D purity) and used as supplied. Their purity was routinely checked by mass spectrometry. Exposures are reported in langmuirs (1 L = 1×10^{-6} Torr·s) after correcting for differences in ion gauge sensitivities.

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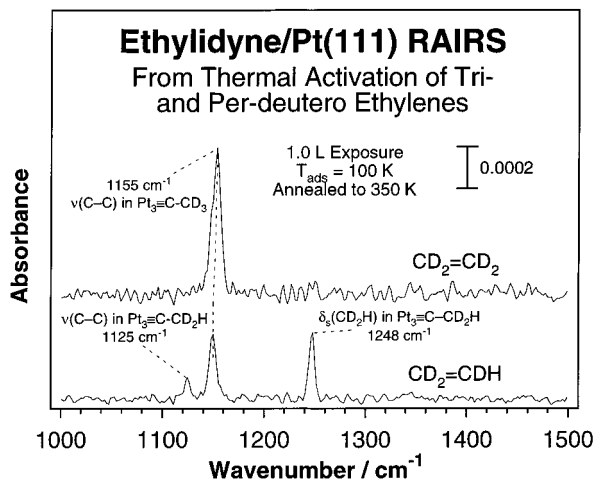(40) Zaera, F.; Bernstein, N. *J. Am. Chem. Soc.* **1994**, *116*, 4881.

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Figure 1. Reflection−absorption infrared spectra (RAIRS) from ethylidyne on Pt(111), prepared by first dosing the surface with 1.0 L of either perdeuterio- (top trace) or trideuterio- (bottom trace) ethylene at 100 K and then annealing it to 350 K. The three peaks at 1125, 1155, and 1248 cm^{-1} are assigned to the C−C stretch in dideuterio- and trideuterioethylidyne and the methyl symmetric deformation mode in dideuterioethylidyne, respectively. These data indicate that about 45% of the ethylidyne produced by thermal activation of trideuterio-ethylene is fully deuterated (the rest being dideuterioethylidyne), corroborating previous reports on the enhancement in normal hydrogen over deuterium removal at saturation coverages.
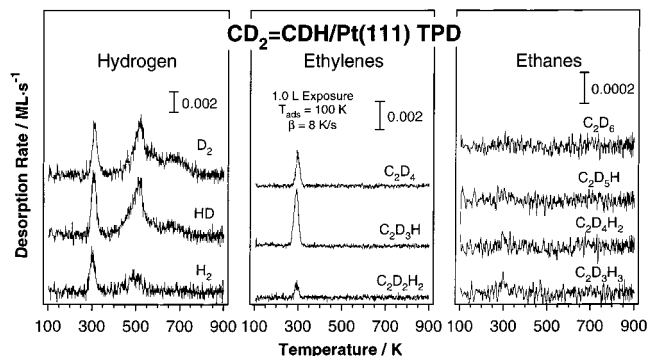
Figure 2. Temperature-programmed desorption (TPD) traces from 1.0 L of trideuterioethylene adsorbed on Pt(111) at 100 K. The left panel shows the traces for hydrogen (H_2, HD, and D_2) desorption, the middle panel those for ethylene ($C_2D_2H_2$, C_2D_3H, and C_2D_4), and the right panel the ones for ethane ($C_2D_3H_3$, $C_2D_4H_2$, C_2D_5H, and C_2D_6). Hydrogen desorbs in two main regimes, around 300 K (during ethylidyne formation) and above 400 K (during ethylidyne decomposition). Ethylene desorbs molecularly at temperatures slightly below 300 K, but significant H−D scrambling occurs beforehand. Almost undetectable amounts of $C_2D_3H_3$ and $C_2D_4H_2$ are produced as well.

3. Results

RAIRS experiments were performed first to check on the identity of the ethylidyne formed by thermal activation of trideuterioethylene chemisorbed on Pt(111). Figure 1 displays the data obtained after exposing the surface to 1.0 L of either CD_2=CDH or CD_2=CD_2 at 100 K and then annealing it to 350 K. The top trace, which corresponds to the experiment with the perdeuterio isotopomer, displays one single peak at about 1155 cm^{-1} due to the C−C stretching mode of perdeuterioet-hylidyne (Pt$_3$≡C−CD$_3$).[9] The lower spectrum, the one from the trideuterio compound, displays that feature as well but, in addition, presents two additional bands at 1125 and 1248 cm^{-1} which can be easily assigned to the C−C stretching and CD$_2$H symmetric deformation (umbrella) modes in dideuterioethyli-dyne (Pt$_3$≡C−CD$_2$H), respectively.[49] By comparing the relative
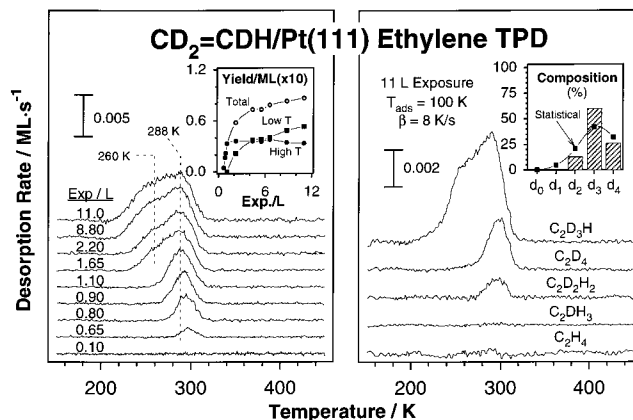
Figure 3. Left panel: Trideuterioethylene molecular TPD traces from Pt(111) as a function of initial exposure at 100 K. Two states are easily identified in these data, one high-temperature ($\sim$290 K) peak that starts to develop about 0.60 L and saturates by 1.10 L, and a second weakly bound state ($\sim$260 K) that grows afterward. Left inset: Yields for the low- and high-temperature molecular desorption states (in monolayers) as a function of initial exposure. Right panel (bottom to top): C_2H_4, C_2DH_3, $C_2D_2H_2$, C_2D_4, and C_2D_3H TPD traces from 11.0 L of CD_2=CDH adsorbed on Pt(111) at 100 K. Significant H−D exchange occurs at low temperatures, but only on the strongly chemisorbed ethylene (the 290 K state). Right inset: Relative TPD yields for the different ethylene isotopomers that desorb in the experiment displayed in the right panel.

intensities of the ν(C−C) peak for perdeuterioethylidyne in both spectra it was determined that about 45% of the trideuterioet-hylene converts to perdeuterioethylidyne, the rest resulting in the formation of the dideuterioethylidyne moiety. This is consistent with previous TPD experiments, and can be explained by a normal kinetic isotope effect in the C−H bond-breaking step.[38]

Figure 2 displays TPD traces from 1.0 L of CD_2=CDH adsorbed on Pt(111) at 100 K. The left panel shows the traces for H_2, HD, and D_2 (2, 3, and 4 amu, respectively), the middle those for the three main ethylene isotopomers ($C_2D_2H_2$, C_2D_3H, and C_2D_4), and the right the ones for the ethanes ($C_2D_3H_3$, $C_2D_4H_2$, C_2D_5H, and C_2D_6). Hydrogen desorption occurs in two main stages, the first around 305 K due to the conversion of ethylene to ethylidyne, and the second above 400 K corre-sponding to the dehydrogenation of ethylidyne to surface carbon. Trideuterioethylene (31 amu) molecular desorption is seen at about 290 K, and significant amounts of H−D exchanged ethylenes (C_2D_4, 32 amu, and $C_2D_2H_2$, 30 amu−after subtracting the contributions from the perdeuterio and trideuterio isoto-pomers) are seen at that temperature as well. Finally, small amounts of ethanes, $C_2D_3H_3$ (33 amu) and $C_2D_4H_2$ (34 amu) in particular, are observed around 300 K, even though the combined yield of those never amount to more than 1% of a monolayer. All these results corroborate previous reports on the thermal chemistry of CD_2=CDH.[38,50]

The details of the desorption of the different possible ethylenes from thermal activation of CD_2=CDH on Pt(111) were explored in more detail by performing TPD experiments as a function of initial exposure. The left frame of Figure 3 displays the traces for the desorption of the molecular (31 amu) species after a number of different doses. No desorption is seen for exposures below 0.60 L, but at that point a peak starts to grow around 300 K. The molecular desorption feature grows and shifts to lower temperatures with increasing ethylene doses until peaking at 288 K for 1.10 L, after which a low-temperature

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shoulder begins to develop at about 260 K. The yield for C_2D_3H in the high-temperature peak saturates at about 0.035 ML after doses above 1.00 L, while the low-temperature state keeps growing asymptotically to a value of approximately 0.060 ML (Figure 3, left inset; for a description of the coverage calibration, see below). The adsorbed ethylene undergoes significant H−D exchange as well, as manifested by the peaks for C_2D_4 and $C_2D_2H_2$ in the TPD presented in the right panel of Figure 3 (see also the middle panel of Figure 2). The desorption of those molecules appears as soon as the coverage on the surface is enough to lead to molecular desorption, and the composition of the desorbing ethylene isotopomer mixture remains approximately constant at all coverages;[51] the relative yields for the different isotopomers at saturation amount to ratios of approximately 0.26:0.60:0.13:0.01:∼0 for C_2D_4:C_2D_3H:$C_2D_2H_2$:C_2DH_3:C_2H_4 (Figure 3, right inset). H−D exchange is only seen in the high-temperature TPD feature, the same as in the case of perdeuterioethylene.[50]

To determine the yields for the different desorbing species as a function of coverage (from the areas under the TPD traces), the raw mass spectrometer signals needed to first be calibrated in terms of desorbing rates and then integrated over time. The calibration was achieved by following a series of steps, namely: (1) the hydrogen signals were corrected by their respective sensitivity factors, as determined experimentally via calibration experiments using H_2 and D_2;[38] (2) this correction was checked by comparing the measured versus expected values for two specific quantities extracted from the hydrogen TPD data, namely, the ratio of total D to total H that desorbs from the surface (measured = 2.91 ± 0.17, 95% confidence, vs expected = 3), and the fraction of the total hydrogen (H_2 + HD + D_2) that desorbs in the first (300 K) peak (measured = 0.255 ± 0.015, 95% confidence, vs expected = 0.25); (3) the relative sensitivity for ethylene was determined by fitting the combined yields of all desorbing products to a linear dependence on the ethylene exposures, a procedure that assumes a constant sticking coefficient for ethylene;[52,53] and (4) the saturation coverage for ethylene was assumed to be 0.25 ML, not including the weakly bound low-temperature molecular TPD state.[52] The error in the values of the desorption rates introduced by this analysis was estimated to amount to less than 20%, and the yields obtained by integration of the TPD traces to be accurate within 10%. Also, these errors are systematic, and therefore do not affect the data presented in Figure 6.

The results from the calculations described above are summarized in Figure 4, which displays the total yields for hydrogen (H_2 + HD + D_2) and ethylene (sum of all isotopomers) from TPD experiments with CD_2=CDH on Pt(111) as a function of initial exposure. The production of hydrogen increases approximately linearly up to about 0.8 L, at which point saturation is reached. Ethylene production only starts around 0.65 L, as mentioned above, but keeps increasing past the 1.0 L mark because of the build-up of the weakly adsorbed ethylene layer. The amount of chemisorbed ethylene that desorbs molecularly at saturation amounts to roughly 20% of the total, while the rest dehydrogenates to ethylidyne and later to surface carbon. Finally, the uptake of ethylene as a function of exposure, as calculated by adding all desorbing products, follows closely that measured by using a molecular beam technique (the results of which are presented as a solid line in Figure 4 for comparison).[53]

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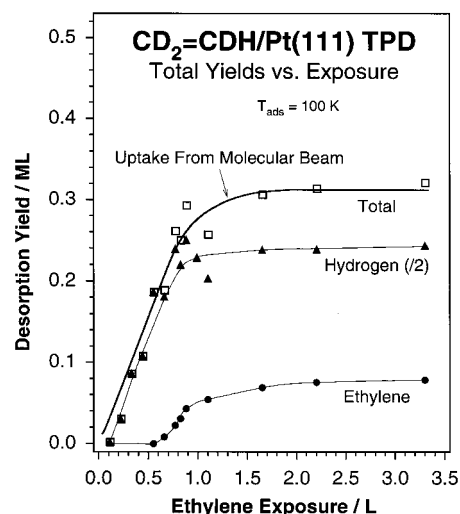
Figure 4. Desorption yields for the total amount of hydrogen (H_2 + HD + D_2) and chemisorbed ethylene ($C_2D_2H_2$ + C_2D_3H + C_2D_4) that desorbs in TPD experiments with trideuterioethylene on Pt(111) as a function of initial exposures. The calibration procedures are explained in detail in the text. The uptake of normal ethylene, measured by using a variation of the King and Wells method for measuring sticking coefficients,[53] is displayed as a solid line for comparison. The agreement between the two techniques is quite good.
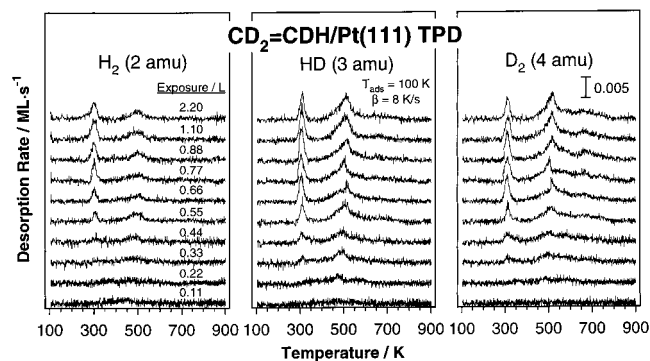
Figure 5. H_2, HD, and D_2 TPD traces from trideuterioethylene adsorbed on Pt(111) at 100 K as a function of initial exposure. Two distinct temperature regimes are identified in all cases after exposures above about 0.40 L, but the relative intensities of the signals in each state and for each isotopomer change as a function of ethylene coverage. Notice in particular how the intensity of the H_2 low-temperature peak grows relative to the high-temperature feature and in comparison with those for HD and D_2 as the coverage approaches saturation.

Figure 5 presents the H_2, HD, and D_2 TPD traces from our coverage-dependence study of the thermal chemistry of CD_2=CDH on Pt(111). It can be seen there that the low-temperature (300 K) hydrogen desorption peaks do not appear as clear distinct features until exposures above about 0.35 L, which means that the formation of ethylidyne must not be clean at low coverages (that is, its dehydrogenation must take place soon after it is formed). This was corroborated by RAIRS, since no ethylidyne could be identified on the surface for doses below 0.4 L, although that could also be explained by the low cross section of the vibrational features. Above 0.4 L, on the other hand, the hydrogen TPD traces develop an appearance that remains qualitatively the same up to saturation. There are nevertheless subtle but important differences among the TPD spectra for H_2, HD, and D_2. Specifically, it is clear that the low-temperature peak is more intense relative to the one at 500 K for the case of H_2 when compared to those for HD or D_2 at saturation, indicating that there is an enhancement in hydrogen
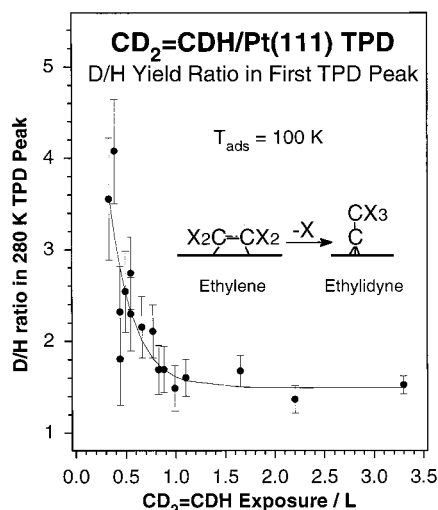
Figure 6. Deuterium-to-normal hydrogen yield ratio in the first (300 K) peak of the hydrogen TPD shown in Figure 5 as a function of initial trideuterioethylene exposure. This TPD peak, which corresponds to the release of a hydrogen (or deuterium) atom during the conversion of ethylene to ethylidyne, displays isotopic compositions which not only deviate from those expected from stoichiometric considerations (which would predict a D/H ratio of 3:1) but also change with surface coverage. The variation from deuterium-removal dominance at low coverages to hydrogen-elimination preference at saturation is explained in this report by a change in relative rates between the isomerization of ethylidene to ethylene and its dehydrogenation to ethylidyne due to the blocking of the empty sites needed for the hydrogen released in the latter step (see text).

removal from ethylene under those conditions from what would be expected based on stoichiometric considerations. This is the effect discussed in the Introduction, and also reported in a previous publication.[38] On the other hand, the opposite trend is seen in the experiments with lower doses: notice in particular the small nature of the first peak in the H₂ TPD for the 0.44 and 0.55 L CD₂=CDH doses. The relative yields for the different isotopomers of hydrogen clearly change with exposures.

This latter effect is better illustrated in Figure 6, which shows the ratios obtained for total deuterium ($2D_2$ + HD) over total hydrogen ($2H_2$ + HD) desorption below 400 K as a function of initial trideuterioethylene dose. Because of small fluctuations in the MS signal among different TPD traces, each point was normalized to an overall deuterium-to-hydrogen ratio for the CD₂=CDH molecule of 3.0, as expected based on stoichiometric grounds (the experimental average was 2.91 ± 0.17, as mentioned above, but each trace yielded a slightly different number). Figure 6 clearly shows the trend mentioned in the previous paragraph, namely, the change in the ratio of the D/H released during the formation of ethylidyne from trideuterioethylene as a function of surface coverage. At low coverages that ratio appears to be about 4, higher than that expected from the stoichiometry of the original molecule (the stoichiometric D/H ratio in CD₂=CDH is 3), implying that there is a preference for the removal of deuterium atoms from the chemisorbed reactant, and consequently for the formation of dideuterioethylidyne. As the trideuterioethylene coverage is increased, however, the D/H ratio from the first TPD peak decreases until reaching a value of approximately 1.5 at saturation. This means that at saturation the behavior mentioned above reverses so that the hydrogen atom is the one removed preferentially: the TPD data indicate that about 40% of the ethylidyne produced under these latter circumstances is fully deuterated, a number close to that estimated by the RAIRS data (45%).

Scheme 1
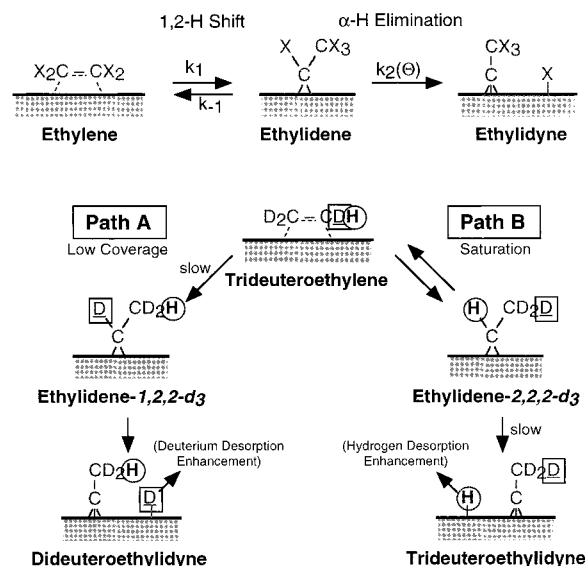
4. Discussion

In this report we present RAIRS and TPD data for the thermal conversion of trideuterioethylene chemisorbed on Pt(111) to complement previous studies on the mechanism of the formation of ethylidyne moieties.[30,38,40,45,49] As already summarized in the Introduction, early work in this area has led to the proposal of ethylidene as the most likely intermediate for that reaction.[44,45] There is ample precedent in the organometallic literature for the two main steps required by this mechanism, namely, the 1,2-H shift needed to isomerize ethylene into ethylidene,[54,55] and the subsequent α-H elimination from ethylidene to produce ethylidyne.[56-59] The difficulty with this idea in the case of the surface conversion is that a simple mechanism involving those two consecutive, irreversible steps is inconsistent with our reported TPD results from saturation coverages of CD₂=CDH.[38] In our latest discussions we suggested that such a discrepancy could be resolved if a third step, the reverse isomerization of ethylidene back to ethylene, is added to the mechanism, and if the relative rates of the ethylidene conversion steps change significantly with coverage (Scheme 1).[44] The TPD data provided here offer corroborating evidence for the validity of such an hypothesis.

The TPD kinetic arguments used both in our previous report[38] and here, although indirect, are quite straightforward. They are based on the idea that the first peak in the hydrogen TPD during the thermal decomposition of ethylene on Pt(111), that around 300 K, is due to the decomposition of ethylene to ethylidyne.[30,60] This step involves the removal of one out of the four hydrogen atoms in the reactant molecule, which means that, in the absence of any kinetic isotope effects, the conversion of trideuterioethylene (CD₂=CDH) would be expected to yield one H atom per three D atoms. It is, however, known that the formation of

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ethylidyne displays a normal kinetic isotope effect, the rate with C_2H_4 being about 2 to 3 times faster than that with C_2D_4.[38,61,62] The relative yields for perdeuterioethylidyne and dideuterioethylidyne from trideuterioethylene are therefore expected to deviate from the expected 1:3 ratio, but the direction of that deviation depends on the mechanistic details of the reaction.

Perhaps the simplest way to view the changes in relative yields for the different ethylidyne isotopomers induced by the kinetic isotope effect is as follows. On one hand, the kinetic isotope effect that makes the reaction go faster with H than with D atoms must be associated with the C−H (or C−D) bond-breaking (or bond-forming) step that limits the rate of the overall reaction. On the other, the hydrogen detected in the first peak of the TPD traces corresponds to that being removed from the ethylene molecules during their conversion to ethylidyne. This means that if there is an enhancement in normal hydrogen production in the first TPD peak from adsorbed CD_2=CDH compared to the stoichiometric ratio, that hydrogen is likely to be the same as that involved in the rate-limiting step. More importantly, if the enhancement is in deuterium production, then the slow reaction must involve a different hydrogen atom.

With the previous explanation in mind, we can now analyze the data from Figure 6 in terms of the mechanism illustrated in Scheme 1. At low coverages the TPD results show an enhancement in deuterium removal from trideuterioethylene which, according to our analysis above, corresponds to a rate-limiting step involving a different hydrogen (deuterium) than that detected in the first peak of the TPD. This is consistent with the simplest mechanism where the initial irreversible conversion of ethylene to ethylidene is followed by a rapid dehydrogenation of ethylidene to ethylidyne (steps k_1 and k_2 in Scheme 1). In this scenario the magnitude of k_{-1} is negligible compared to that of k_2, and the overall rate is controlled by k_1. When starting with trideuterioethylene, the normal kinetic isotope effect favors the 1,2-H shift with the normal hydrogen atom, therefore enhancing the yield for the production of ethylidene with Pt_2=CD−CD_2H stoichiometry (Scheme 1, Path A). α-D elimination from that moiety releases a deuterium atom and produces dideuterioethylidyne (Pt_3≡C−CD_2H), as seen experimentally.

At high coverages, near saturation, the opposite occurs. The TPD data indicate that it is the desorption of normal hydrogen which becomes the most favorable, that is, the same hydrogen involved in the rate-limiting step is the one removed from the ethylene molecule during the production of ethylidyne. In our original work we argued that this suggested the involvement of a vinyl species in the conversion of ethylene,[38] but later work proved that such intermediates do not convert easily to ethylidyne.[40] We now advance the notion that the TPD results are still consistent with the idea of ethylidene formation as long as at saturation k_{-1} contributes to the conversion and k_2 becomes the rate-limiting step. Notice that it is not sufficient to just switch the slow step in a two-step irreversible mechanism to account for the changes seen in the TPD data with increasing coverage, because that would imply that when k_2 becomes the bottleneck (at high coverages) ethylene would convert rapidly to ethylidene, and that ethylidene would then be stable up to the temperatures needed for its α-H elimination to ethylidyne. There is no direct spectroscopic evidence to date for any intermediate during the conversion of ethylene into ethylidyne on transition metal surfaces (there is a report indicating a discrepancy between the rates of ethylene consumption and ethylidyne formation *at low coverages*, but no intermediate could be identified in that study either[63]). Hence our need to include a third step, the reversible isomerization of ethylidene back to ethylene (k_{-1}). We propose that at high coverages there is a rapid equilibrium between ethylene and ethylidene, and that ethylidene then slowly converts to ethylidyne (Scheme 1, Path B). Making k_{-1} much larger than k_1 ensures that the population of ethylidene does not ever build up on the surface, and assuming that the second step (k_2) is slower than the first (k_1) accounts for the hydrogen desorption enhancement seen in the TPD at saturation.

The previous explanation for the changes in selectivity in the isotopic composition of the ethylidyne produced by thermal activation of trideuterioethylene on Pt(111) as a function of coverage can be quantified by using general kinetic ideas. First, the rate of the overall conversion can be equated to that of the rate-limiting step. Next, the steps depicted in Scheme 1 can be treated as elementary, and to a first approximation can be described in terms of simple molecularity-based rate laws. With this in mind, the rate of ethylidyne formation, $R_{ethylidyne}$, for the low coverage case can be described by the rate of the first step:

$$R_{ethylidyne}^{low\theta} = s \cdot k_1 \cdot \theta_{ethylene} \tag{1}$$

where $\theta_{ethylene}$ is the coverage of ethylene on the surface and s is a statistical factor to account for the number of H (or D) atoms available for the reaction (i.e., 4 for normal hydrogen removal from C_2H_4). The ratio of dideuterio- to trideuterioethylidyne produced from CD_2=CDH is then given by:

$$\frac{R_{CCD_2H}}{R_{CCD_3}} = \frac{(k_{1,H} + 2k_{1,D}) \cdot \theta_{C_2D_3H}}{k_{1,D} \cdot \theta_{C_2D_3H}} = \frac{k_{1,H} + 2k_{1,D}}{k_{1,D}} \tag{2}$$

Here the subindices H and D in the reaction rate constants refer to the isotopic nature of the hydrogen (H or D) atom involved in the reaction (in the 1,2-hydrogen shift for k_1). Notice that there are three possible ways to make dideuterioethylidyne from trideuterioethylene but only one to produce trideuterioethylidyne (Scheme 1). Now, defining the kinetic isotope effect as kie ≡ k_H/k_D, eq 2 can be rewritten as:

$$\frac{R_{CCD_2H}}{R_{CCD_3}} = \frac{(kie) \cdot k_{1,D} + 2k_{1,D}}{k_{1,D}} = k_{ie} + 2 \tag{3}$$

For a value of kie = 2,[61] the fraction of dideuterioethylidyne formation at low coverages becomes 80%, about the same as that estimated from the data in Figure 6.

The same analysis can be worked out for trideuterioethylene saturation coverages. In that case there is an ethylene−ethylidene preequilibrium (Scheme 1), and the rate-limiting step is the subsequent α-hydride elimination from ethylidene:

$$R_{ethylidyne}^{saturation} = s \cdot k_2 \cdot \theta_{ethylidene} \tag{4}$$

Since the kinetic isotope effects in k_1 and k_{-1} are expected to be similar (that is, the energy difference between ethylene and ethylidene is not expected to change much with deuterium substitution), it can be assumed that the isotopic distribution of H and D atoms in the resulting ethylidene is random. This means that the relative coverages of ethylidene-*1,2,2-d_3* vs ethylidene-*2,2,2-d_3* follow a 3:1 ratio. Therefore, at saturation:

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$$\frac{R_{CCD_2H}}{R_{CCD_3}} = \frac{3k_{2,D}}{k_{2,D}} = \frac{3k_{2,D}}{(kie) \cdot k_{2,D}} = \frac{3}{kie} \qquad (5)$$

Using kie = 2 again the amount of dideuterioethylidyne produced at saturation is estimated at 40% of the total; the experimental value is somewhere between 55 and 60%. In summary, a simple kinetic analysis of the mechanism proposed for the conversion of ethylene to ethylidyne can account for the experimental results at all coverages.

A few additional considerations need to be discussed further in order to make our mechanism consistent with the rest of the experimental data available to date on this system. For one, it is necessary to justify the proposed change in relative rates with coverage. Specifically, k_2 needs to be faster than k_1 at low coverages but slower at saturation. A possible reason for this could be that while isomerization reactions can take place on one adsorption site, the dehydrogenation of ethylidene to ethylidyne requires an additional empty site for the outgoing hydrogen. As a consequence k_2 is expected to be a function of the coverage of empty sites, and that decreases as the initial coverage of adsorbed ethylene is increased. In fact, the slowing down of ethylidene decomposition with coverage due to this effect was seen directly in experiments with 1,1-diiodoethane.[44] Three other pieces of experimental data support this idea. First, RAIRS kinetic work indicated that the rate of ethylene disappearance on the surface diverges from that of ethylidyne formation at low coverages, suggesting that another unidentified (ethylidene?) species accumulates on the surface.[63] Second, scanning tunneling microscopy (STM) studies of the ethylene-to-ethylidyne conversion proved that at saturation the reaction occurs at the interface between ethylene and ethylidyne islands, presumably because there is more space there to accommodate the expelled hydrogen atoms.[64] Note, however, that our proposed mechanism is somewhat different than that suggested by the Hemminger group,[63,64] but this does not represent a major problem, because their and our ideas address different aspects of the reaction: while their model attempts to incorporate the spatial inhomogeneities they observed on the surface into the reaction kinetics, we try to explain the changes in isotopic reactivity with coverage by using a molecular-level set of reactions (within individual sites). Last, the absence of dipole coupling in the methyl deformation vibrational modes in mixtures of $Pt_3 \equiv {}^{12}C - {}^{13}CH_3$ and $Pt_3 \equiv {}^{13}C - {}^{12}CH_3$ at low coverages indicated that under those conditions the ethylidynes end up well dispersed over the surface and therefore surrounded by enough empty sites to allow for their formation via fast dehydrogenation steps.[65]

Finally, a word needs to be said about the influence of other competing reactions during the thermal activation of ethylene over Pt(111) on the formation of ethylidyne. This is a topic that has been discussed in some detail in a few of our previous publications.[30,45,49,50,53] It has become quite clear that even though both the hydrogenation of ethylene to ethane and the H−D exchange within chemisorbed ethylene molecules occur concurrently in approximately the same temperature range as the conversion of ethylene to ethylidyne, those reactions follow different parallel mechanisms. Ethylene hydrogenation could indeed take place on the same strongly chemisorbed ethylene that dehydrogenates to ethylidyne, but such a reaction requires additional surface hydrogen, and therefore becomes unfavorable

on clean Pt(111).[30,45,49,50,53] Notice the particularly low yields seen here for the different ethanes (Figure 1), a result that we ascribe at least in part to the low background pressure in our chamber (we estimate the amount of hydrogen adsorbed on the surface from background adsorption during our experiments at less than 1% of a monolayer). More extensive ethane formation can be achieved by hydrogenating the weakly adsorbed (low-temperature molecular TPD peak) ethylene state,[45,53] but that may be more relevant to reactions under catalytic conditions than to those being discussed here.[10,29]

In terms of ethylene H−D exchange, recent work has shown that such a process can take place at temperatures as low as 215 K, almost 100 K below those needed for ethylidyne formation.[51] This isotope exchange takes place via the formation of ethyl intermediates,[49] and therefore does not interfere directly with the dehydrogenation steps that lead to the production of surface ethylidyne. It could, however, affect the quantitative analysis of the data shown in Figure 6, because its occurrence means that although the experiments reported here were performed with pure trideuterioethylene, they may no longer involve pure $CD_2 = CDH$ on the surface by the time the temperatures needed for the dehydrogenation are reached. Assuming that the species on the surface have the same isotopic distribution as those that desorb, the composition of the chemisorbed ethylene at the moment of its dehydrogenation is estimated to approximately follow a 0.26:0.60:0.13:0.01 distribution for C_2D_4:C_2D_3H:$C_2D_2H_2$:C_2DH_3 (close to total isotopic scrambling, which would yield ratios of 0.32:0.42:0.21:0.05). However, as long as the kinetic isotope effect for ethylidyne formation is independent of the number of hydrogen substitutions in the initial ethylene (that is, as long as the rates per C−H and C−D bonds remain constant for all ethylene isotopomers), any isotopic scrambling in the chemisorbed ethylene would lead to a mixture for which the relative yields for H and D desorption would be the same as if working with pure trideuterioethylene. This is so because the enrichment in either H or D due to one type of ethylene isotopomer would be compensated by another. For instance, the 13% of dideuterioethylene in the chemisorbed mixture of our experiments should yield twice the number of hydrogen atoms expected from the same amount of trideuterioethylene, but that is canceled by the lack of production of normal hydrogen from a corresponding 13% of perdeuterioethylene. In the same way, the effects induced on the TPD yields by another 2% of perdeuterioethylene must be compensated by the approximately 1% of monodeuterioethylene produced on the surface. There is a remaining 11% of perdeuterioethylene unaccounted for in terms of H and D mass balance, but that could be due to experimental errors in the deconvolution of the TPD data for the light alkanes, or could perhaps represent the ethylene that converts to ethane. In any case, in the event that the extra H not accounted for in the hydrocarbon species detected by mass spectrometry does not desorb in the first (300 K) hydrogen TPD peak, the mass balance discrepancy mentioned above would introduce only a small systematic error in the data of Figure 6 that would favor the production of more D than expected in the low-temperature TPD state. Such a correction would make the low-T D/H ratios from pure C_2D_3H become about 3.7 after the 0.4 L dose and 1.4 at saturation, so the qualitative trend discussed above would still look the same; the conclusions reached here would not need to be changed.

5. Conclusions

The thermal chemistry of trideuterioethylene on Pt(111) was studied by RAIRS and TPD in order to test the previous

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hypothesis about the mechanism for ethylidyne formation. Room-temperature conversion of the labeled ethylene at saturation leads to the formation of about 45% of trideuterioethylidyne, significantly more than the 25% expected on pure stoichiometric grounds. The amount of normal hydrogen atoms released into the gas phase during that reaction amounts to approximately 40% of the total H + D, the same fraction, within experimental error, predicted by the RAIRS data. Both those results confirm previous reports, and highlight the fact that the hydrogen atom detected by TPD in this process is the same involved in the rate-limiting step of the ethylene-to-ethylidyne surface conversion. A previous proposal that suggested the formation of vinyl species as intermediates in the latter process was revised here in view of newer data, and an alternative model was put forward in which the hydrogen enhancement is explained by a three-step mechanism where ethylene reaches an early equilibrium with surface ethylidene species and where those intermediates then dehydrogenate slowly to ethylidyne.

Coverage-dependent TPD data indicated that the mechanism described above for ethylidyne formation at saturation changes at lower ethylene coverages on the surface. Specifically, it is inferred from the isotopic composition of the first hydrogen TPD peak that after trideuterioethylene exposures around 0.4 L only about 20% of it converts to trideuterioethylidyne and the remaining 80% to dideuterioethylidyne. This reversal of the trend seen at saturation implies that in the low-coverage case the rate-limiting step must not involve the hydrogen (deuterium) atom released during the dehydrogenation step. This is consistent with a straight two-step irreversible conversion of ethylene to ethylidyne via ethylidene, which means that the reverse isomerization of ethylidene to ethylene is negligible under those conditions. The change in relative rates for the conversion of ethylidene to ethylene vs ethylidyne with changing coverages is explained here in terms of the need for empty sites for the extra hydrogen in the latter reaction.