JOURNAL OF CATALYSIS **177,** 284–295 (1998)
ARTICLE NO. CA982147

Kinetics and Mechanism for the H/D Exchange between Ethylene and Deuterium over Pt(111)

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Received August 13, 1997; revised October 24, 1997; accepted October 29, 1997

The H/D exchange between ethylene and hydrogen (or deuterium) on Pt(111) surfaces was monitored by laser-induced thermal desorption in combination with Fourier-transform mass spectrometry (LITD/FTMS) and by reflection–absorption infrared spectroscopy (RAIRS). In the case of coadsorbed $C_2D_4 + H_2$ the LITD experiments show that the H/D exchange reaction takes place at temperatures as low as 215 K, well below those needed for the decomposition of ethylene to ethylidyne. It was also found that exchange on adsorbed C_2D_4 is significantly easier with H_2 than with C_2H_4, indicating that this H/D substitution requires surface hydrogen but not the dissociation of ethylene, and suggesting that ethyl moieties are the most probable intermediates for the reaction. It was also determined that the dosing order of the reactants influences the kinetics of the reaction, which means that specific surface ensembles are required in the exchange; both the rate and the degree of H/D substitution in ethylene are increased by dosing hydrogen (deuterium) beforehand. In addition to the LITD experiments, the rate of formation of ethylidyne that takes place above 250 K was also monitored with RAIRS. It was shown that, when coadsorbed with deuterium, the extent of deuterium substitution in the resulting ethylidyne is largely determined by H/D exchange between the original ethylene molecules and surface hydrogen, and that direct H/D exchange between ethylidyne and surface hydrogen is measurable only at low ethylidyne coverages and higher temperatures. Finally, it was established that the rate of ethylidyne formation does not depend on the coverage of hydrogen on the surface, a result that points to an ethylidene intermediate in that reaction. The data are discussed on the basis of a mechanism in which the H/D exchange and ethylidyne formation are parallel processes which involve different surface species. © 1998 Academic Press

1. INTRODUCTION

The reactivity of alkenes adsorbed on metal surfaces is a determining factor in the overall conversion of hydrocarbons on transition metal catalysts, and this in turn is key for the design of many processes in the chemical industry (1–3). It is therefore desirable to understand the chemistry of those adsorbed alkenes at a molecular level. One approach to address this problem is to employ surface-sensitive spectroscopies to study model systems such as alkenes adsorbed on well-defined single-crystal metal surfaces and under vacuum. In this context, ethylene adsorbed on Pt(111) surfaces has been considered to be representative for a whole range of alkene–metal interactions, and has consequently been given a great deal of attention in recent years (4–33).

The chemistry of ethylene on Pt(111) may at first seem straightforward, but the results obtained so far have shown that it is in fact quite complex. One reason for this complexity is that there are at least two forms of adsorbed ethylene, namely, a π bonded species observed either at low temperatures or in coadsorbed systems, and a di-σ bonded species that appears at higher temperatures (9, 19, 24, 29, 31–33). Furthermore, diffuse low-energy electron diffraction (LEED) studies have led to the proposal that the di-σ ethylene occupies both hcp and fcc sites on the surface, and that its molecular axis is tilted (6). A second difficulty originates from the fact that the heating of adsorbed ethylene on Pt(111) leads to the simultaneous activation of several processes, namely, molecular desorption, decomposition to ethylidyne, hydrogenation to ethane, and, when labeled adsorbates are used, H/D exchange (4, 8, 11, 13, 14, 21, 22, 25, 30).

The selectivity in the conversion of adsorbed ethylene toward these different reactions appears to depend at least in part on the nature of the initial adsorption. This is nicely illustrated by recent isothermal kinetic measurements with collimated beams of mixed hydrogen and ethylene which show that the production of ethane is closely correlated with the presence of weakly adsorbed ethylene, possibly a π-bonded state (7). *In-situ* characterization of the surface species involved in ethylene hydrogenation under high pressure conditions using both infrared spectroscopy (9) and sum frequency generation (10) also point to the crucial role of the π-bonded species in this process.

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0021-9517/98 $25.00

Scanning tunneling microscopy (STM) experiments have shown that the decomposition of adsorbed ethylene to ethylidyne requires a specific surface molecular ensemble on the surface. Indeed, those images show that the decomposition of ethylene does not take place uniformly over the whole substrate, but rather at the edges of ethylene islands (18). A further complication arises from the fact that ethylidyne formation requires both hydrogen migration and dehydrogenation steps, which implies that at least one intermediate is formed during that conversion. Much research has focused on the identification of that intermediate, for which ethyl (27), vinyl (25, 34), and ethylidene (13, 35) species have been proposed. Alkyl iodides have proven quite useful for this endeavor, because they can be used as precursors for the preparation of hydrocarbon adsorbed intermediates without perturbing the surface of the metal in a significant way (36–38). Experiments with ethyl iodide (39–41) and vinyl iodide (15) in particular have shown that both ethyl and vinyl groups convert to ethylene between 200 and 240 K, before transforming to ethylidyne, making those moieties improbable intermediates for the conversion of ethylene to ethylidyne. In contrast, ethylidene moieties decompose to ethylidyne in a single reaction step around 150 K, as revealed by experiments with 1,1-diiodoethane on Pt(111) (35), and are therefore the best candidate for the intermediate in that reaction.

In addition to the hydrogenation and ethylidyne formation reactions, H/D exchange is also known to occur in mixed layers of C_2D_4 with either C_2H_4 or H_2 (14, 21, 28). This reaction produces partially deuterated ethylene, which at sufficiently high temperatures converts to partially deuterated ethylidyne (14). In this paper we focus on the kinetics of the H/D exchange reaction between adsorbed ethylene and surface hydrogen and on the characterization of the subsequent formation of the partially deuterated ethylidyne. The relevance of H/D exchange reactions in catalysis derives from the fact that they provide a clear measure of the extent of C−H bond activation (and formation) on a given catalyst. Laser-induced thermal desorption/Fourier-transform mass spectrometry (LITD/FTMS), a technique that allows for the characterization of the coverages and deuterium content in the chemisorbed ethylene molecules, was applied first to measure the rates of the H/D exchange reaction in mixed layers of C_2D_4 with either H_2 or C_2H_4. Reflection absorption infrared spectroscopy (RAIRS) was then used to monitor both the rate of ethylidyne formation and the deuterium content in the ethylidyne formed from such mixed layers as a function of the reaction temperature. The results from these experiments are compared here with previous data for ethylene hydrogenation and ethylidyne formation, and are discussed on the basis of a reaction scheme in which ethylidyne formation and H/D exchange occur as parallel processes.

2. EXPERIMENTAL

The laser-induced thermal desorption (LITD) and reflection–absorption infrared spectroscopy (RAIRS) experiments were carried out in two separate ultrahigh vacuum (UHV) chambers. The LITD chamber has a base pressure in the 10^{-11} Torr range, and is equipped with an Ar^+ sputtering gun for sample cleaning, an Auger electron spectrometer (AES), optics for low-energy electron diffraction (LEED) (16, 20, 42), and a special analyzer cell for the Fourier-transform mass spectrometer (FTMS) used in conjunction with the LITD experiments. The RAIRS chamber has a base pressure below 1×10^{-10} Torr, and is equipped with an Ar^+ sputtering gun, a UTI-100C quadrupole mass spectrometer, and a setup for RAIRS experiments (14, 35, 41). In both the LITD and RAIRS experiments the Pt(111) single crystals were mounted on manipulators that allowed for their translation and rotation inside the vacuum chambers. The crystals could be heated resistively to above 1100 K and cooled rapidly with liquid nitrogen to temperatures below 100 K, and their temperature could be monitored by using a chromel–alumel thermocouple spot-welded to the sample. The Pt(111) surfaces were cleaned by cycles of Ar^+ sputtering, heating in oxygen (approximately 3×10^{-7} Torr at about 770 K), and flashing into a vacuum to approximately 1100 K. The C_2H_4 (99.5%) and H_2 (99.999%) were obtained from Matheson, the C_2D_4 (99%) and D_2 (99.5%) were purchased from Cambridge Isotope Laboratories, and all gases were used without further treatment. The C_2H_4/C_2D_4 mixtures were prepared by condensing the appropriate amounts of C_2H_4 and C_2D_4 into glass bulbs, and their composition was determined *in-situ* by monitoring the 30/27 amu intensity ratio in the mass spectrum of the gas phase (which had to be divided by 0.93 in order to correct for the different sensitivity for C_2D_4 and C_2H_4 (43)).

The details of the LITD/FTMS experiments have been described elsewhere (20, 42, 44). In short, a small spot (~0.01 cm diameter) of the surface is heated rapidly (10^{11} K/s) by means of an Excimer laser pulse (248 nm, 20 ns pulse width) to cause the thermal desorption of the adsorbed molecules in that area. The power of the laser beam was carefully adjusted to avoid damage of the metal surface and to remove essentially all (>95%) ethylene molecules from within the irradiated area. A small fraction (0.001%) of the desorbed neutrals is then ionized by an electron beam (70 eV, $\sim 2\,\mu A$) and trapped in the analyzer cell by the appropriate combination of electric and magnetic fields. Finally, the image currents induced in the detector plates by the cyclotron motion of those ions are digitized and Fourier-transformed to obtain the mass spectra of the surface species.

To follow the kinetics of the H/D exchange in ethylene adsorbed on Pt(111) with LITD/FTMS, the ethylene and hydrogen were first adsorbed at 170 K on the clean sample. In this system hydrogen was dosed by backfilling the chamber, but ethylene was supplied via a doser, which means that its exposures could not be measured directly. The ethylene coverage was nevertheless determined independently by using the C(LVV) Auger signal intensities and calibrating them against the spectrum for saturation coverage (0.25 ML); by assuming a constant sticking coefficient for ethylene on Pt(111) for coverages up to 0.2 ML (7, 45), the dosing rate was estimated to be about 0.004 ML/s. The sample was moved to the LITD/FTMS cell after dosing, and heated to the desired reaction temperature by using a feedback temperature controller. Mass spectra for up to 48 different spots were then obtained as the reaction proceeded by moving the laser beam across the sample; typically the data points were taken at a rate of 1–2 laser desorption spots per minute in the experiments reported in this paper. The LITD intensities given in the figures correspond to integrated signal intensities in the mass spectra obtained after Fourier transformation.

The RAIRS experiments were performed by taking the IR beam from a Mattson Sirius 100 FTIR spectrometer, focusing it through a sodium chloride window on the Pt surface at grazing incidence, passing it after reflection through a second sodium chloride window and a polarizer, and refocusing it into a mercury-cadmium-telluride (MCT) detector (14, 35, 41). The final IR spectra were obtained by taking the average of 1000 scans from the adsorbate-covered Pt surface at 4 cm^{-1} resolution (about 300 s acquisition time) and dividing them by similar spectra from the clean surface taken immediately before dosing. The RAIRS data were taken at sample temperatures of 180 K or lower except for the kinetics experiments, in which case they were obtained at the reaction temperature (238 K). All the gases were dosed with the sample in place in the RAIRS position by backfilling the vacuum chamber.

3. RESULTS

3.1. *H/D Exchange in Chemisorbed Ethylene: LITD Experiments*

In this section laser-induced thermal desorption (LITD) data are presented for the isothermal kinetics of the H/D exchange reaction between chemisorbed C_2D_4 and either surface hydrogen or C_2H_4 on Pt(111) at temperatures between 215 and 235 K. Figure 1 shows typical LITD mass spectra in the 25–40 amu range for a mixed layer of C_2D_4 and H_2 taken right after adsorption and after 570 and 1170 s from the time the sample temperature was raised to 225 K. The H/D exchange is best followed both by the decay of the 32 amu signal intensity, which is proportional to the C_2D_4 coverage, and by the increase of the 31 amu signal intensity, which measures the C_2D_3H coverage. Note that the intensities of those two peaks are not obscured by cracking of other products, and therefore provide accurate direct information on the kinetics of the H/D exchange reaction; the signal intensities could therefore be converted to coverages by appropriate calibration (see below). Additional information on the extent of the H/D exchange could be obtained by using the signal intensities in the 26–30 amu range. Unfortunately, the mass spectra of each species in that region is quite complex and interferes with the detection of the others. The overall spectra could in principle be deconvolved by using the cracking patterns of each individual compound, but such a procedure proved to not be very reliable in this study, so only qualitative information was extracted from the data in the low amu range. Specifically, the signal for 29 amu was used to estimate the amount of C_2DH_3 formed, and this in turn was interpreted as representative of multiple exchange steps.

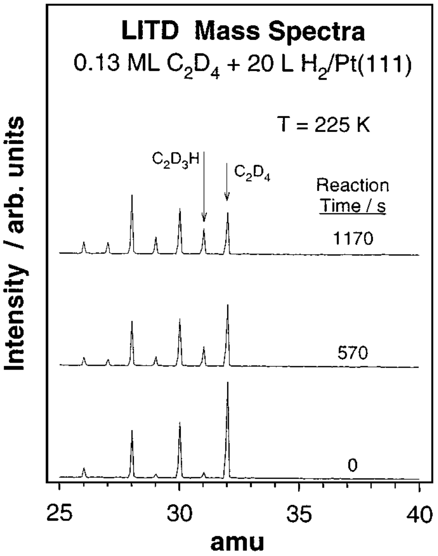

FIG. 1. Typical mass spectra from LITD/FTMS experiments designed to characterize the kinetics of H/D exchange reactions between C_2D_4 and surface H on Pt(111). In this case the adsorption of 0.13 ML of C_2D_4 was followed by a dosing of 20 L of H_2, and the reaction was carried out at 225 K. The exchange is manifested here both by a decrease of the 32 amu signal (C_2D_4) and by a simultaneous growth of the 31 (C_2D_3H), 29, and 27 (multiply-exchanged C_2X_4) amu signals during the course of the reaction.

Figure 2 shows the time evolution of the 31 amu (C_2D_3H) signal at 215 K after dosing a Pt(111) surface either with 30 s of C_2D_4 (0.12 ML) and 20 L of hydrogen (in that sequence) or with 30 s (0.12 ML) of a 1 : 1.5 C_2H_4/C_2D_4 mixture. The results in Fig. 2 clearly show that while in the case of coadsorbed hydrogen the H/D exchange reaction starts immediately at 215 K, in the presence of C_2H_4 a measurable amount of C_2D_3H is detected only after about 1000 s. In fact, the C_2D_3H in the latter case is most likely the result of a reaction with background hydrogen, because blank experiments with C_2D_4 alone yielded similar results. These observations lead to two main conclusions, namely,

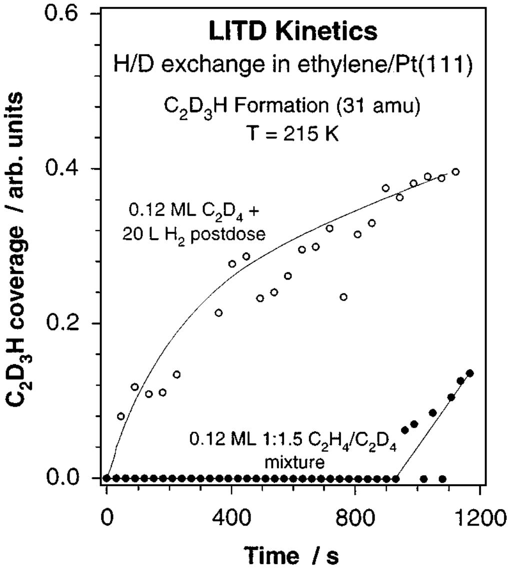

FIG. 2. Time evolution of the C_2D_3H (31 amu LITD/FTMS signal) production at 215 K from 0.12 ML of C_2D_4 adsorbed on Pt(111) and subsequently exposed to 20 L of H_2 dose (open circles), and from 0.12 ML of a 1 : 1.5 C_2H_4/C_2D_4 mixture (closed circles), all adsorbed at 170 K. The immediate formation of C_2D_3H in the case of the $C_2D_4 + H$ layer but not for the $C_2H_4 + C_2D_4$ mixture indicates that H/D exchange in ethylene involves surface hydrogen and that the ethylene molecules do not dissociate at 215 K.

(1) that the H/D exchange in ethylene requires surface hydrogen (or deuterium), and (2) that this surface hydrogen cannot be supplied by the decomposition of ethylene at 215 K, otherwise H/D exchange would have been observed in the experiments with the C_2H_4/C_2D_4 mixture as well. The low reaction temperature for the H/D exchange between chemisorbed C_2D_4 and surface hydrogen also strongly suggests that the activation barrier of this reaction is lower than those for either the formation of ethylidyne or the desorption of ethylene.

The dependence of the rate of H/D exchange on C_2D_4 coverage is illustrated in Fig. 3, which shows the time evolution of the 29 and 31 amu LITD signals at 215 K in experiments where various doses of C_2D_4 were followed by a 20 L hydrogen exposure. The somewhat counterintuitive trend observed here is that the H/D exchange is more extensive even in absolute terms at the lower C_2D_4 coverages: while the LITD signal intensities for both the 31 and 29 amu peaks remain quite low even after 1000 s of reaction in the case of a 50-s C_2D_4 dose (a coverage of about 0.20 ML), after a C_2D_4 exposure of 10 s (about 0.04 ML) not only a significant conversion is observed early on, but the intensity of the 29 amu signal exceeds that of the 31 amu peak as well, indicating that extensive exchange (more than one deuterium atom per ethylene molecule) has taken place. These results can be understood in terms of the relative coverages of H and C_2D_4 on the surface in each case, because since the hydrogen was dosed after the ethylene, it could only occupy the few remaining empty sites (7), and that made the H/C_2D_4 ratio higher in the low C_2D_4 dose experiments. Note that the hydrogen exposures used here are high enough to fill all the unoccupied sites left after the ethylene adsorption.

The temperature dependence of the H/D exchange reaction in the $C_2D_4 + H_2$/Pt(111) system is indicated by the data in Fig. 4, which displays the time evolution of the 29 (left), 31 (center), and 32 (right) amu LITD signals obtained at various reaction temperatures between 215 and 235 K after sequentially dosing 30 s of C_2D_4 (0.12 ML ethylene)

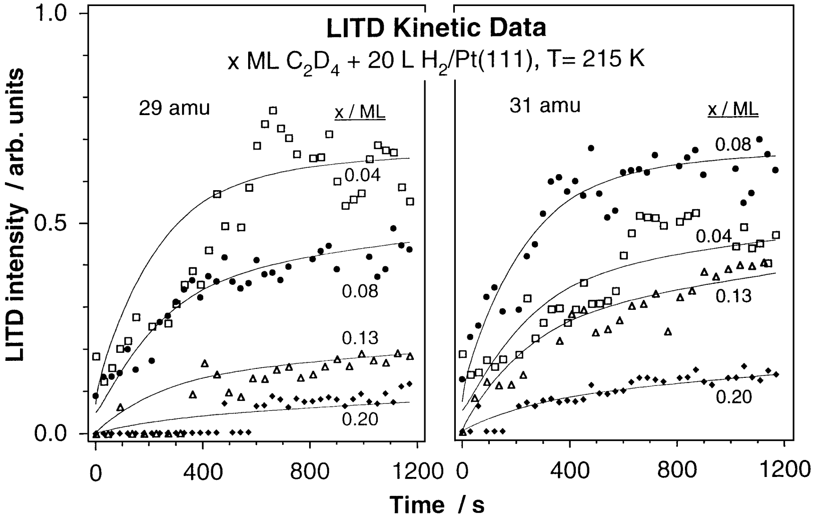

FIG. 3. Time evolution of the 29 (left) and 31 (right) amu signals in LITD/FTMS kinetic experiments at 215 K with 0.04, 0.08, 0.13, and 0.20 ML of C_2D_4 on Pt(111), each postexposed at 170 K to 20 L of H_2. The solid lines are drawn only to provide an easy guide to the eye. The data in this figure show that the degree of H/D exchange decreases with increasing C_2D_4 coverage.

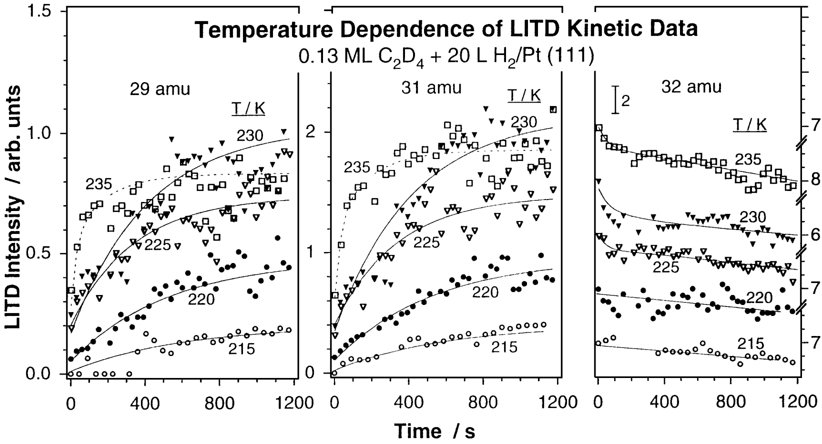

FIG. 4. Time evolution of the 29 (left), 31 (center), and 32 (right) amu signals at 214, 220, 225, 230, and 235 K in LITD/FTMS experiments with 0.13 ML of C_2D_4 on Pt(111) subsequently dosed with 20 L of H_2 at 170 K. The lines are drawn only to provide an easy guide to the eye. The intensity of the 32 amu signal, which corresponds to the C_2D_4 coverage, decreases gradually in all runs, but is preceded by a fast initial decay at 230 and 235 K. The intensities of the 29 and 31 amu signals, which reflect the C_2DH_3 and C_2D_3H coverages, respectively, rise rapidly first but then reach constant levels which depend on the temperature of the reaction.

and 20 L of H_2. In terms of the extent of hydrogen substitution in the original perdeutero ethylene, it was found that below 230 K practically all the C_2D_4 that disappears is converted to C_2D_3H (after taking into account the lower sensitivity of the mass spectrometer for C_2D_3H, since the 31 amu C_2D_3H/32 amu C_2D_4 ratio is about 0.92, and the intensity of the 29 amu signal due to cracking of the C_2D_3H, for which the 29/31 amu ratio is 0.40 (43)). This means that at those temperatures only single exchange is viable on the platinum surface. In addition, for temperatures up to 230 K, the C_2D_3H coverage approaches asymptotically a level defined by the reaction temperature but well below that corresponding to complete conversion.

Figure 4 also shows that above 230 K other processes contribute to the disappearance of the adsorbed C_2D_4. The 32 amu data for 230 and 235 K display a fast decay in the first 300 s of the reaction, when they reach values about 70–75% of the original amount, and then a slower but steady decrease which continues after longer reaction times. The simultaneously measured intensities of the 29 and 31 amu signals also show fast initial growths matching the fast decrease of the 32 amu signal, but become approximately constant after about 1000 s of reaction. This means that the long-term slow decay of the 32 amu signal is not due to the formation of additional exchanged ethylene, and is most likely the result of other processes such as desorption of ethylene or formation of ethylidyne instead.

Despite the complications described above, the initial growth in C_2D_3H coverage can still be described by a first-order rate law, since in the first 200–250 s of reaction the loss of C_2D_3H due to desorption or ethylidyne formation is small (because of the low C_2D_3H coverage), and because the hydrogen coverage does not change significantly either. The reaction rates for the single H/D exchange were therefore estimated from first-order fits to the raw data for the C_2D_3H coverages in the initial phase of the exchange, and the kinetic parameters were determined from the resulting Arrhenius plot (Fig. 5). The values for the activation energy (E_a) and apparent preexponential factor ($\nu \cdot \theta_H$) came out to be 11 ± 2 kcal/mol and $10^{8\pm1}$ s^{-1}, respectively. Notice that this activation barrier is significantly lower than that for ethylidyne formation (15–18 kcal/mol) (4, 16, 25, 46), a

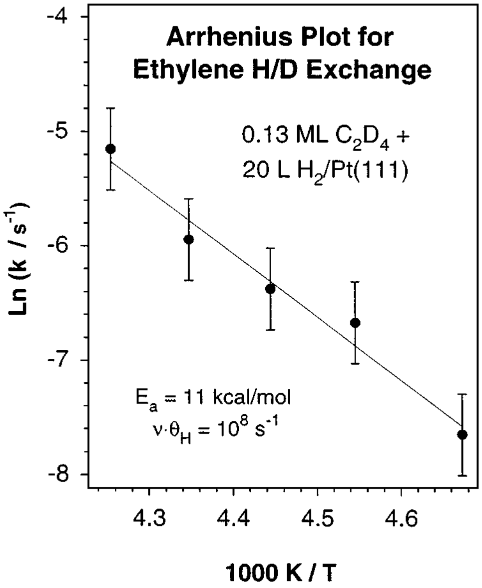

FIG. 5. Arrhenius plot of the pseudo-first-order rate constants for the H/D exchange between C_2D_4 and surface H on Pt(111), as determined from the initial growth of the 31 amu signals in isothermal kinetic runs such as those shown in Fig. 4. The estimated activation energy (E_a) and apparent preexponential factor ($\nu \cdot \theta_H$) from this analysis are 11 ± 2 kcal/mol and $10^{8\pm1}$ s^{-1}, respectively.

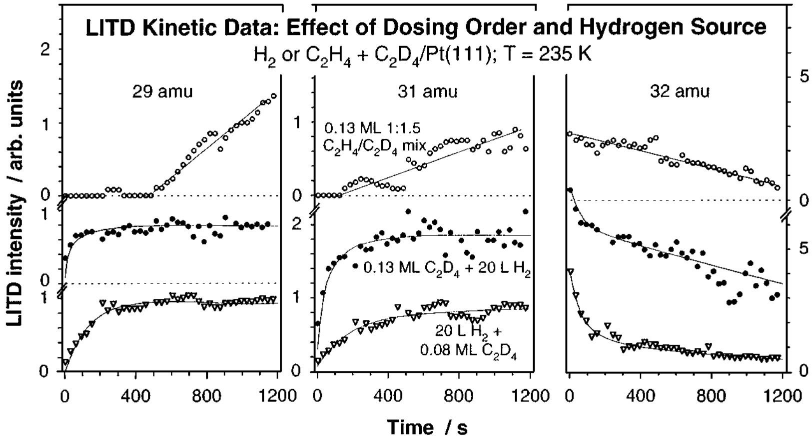

FIG. 6. Time evolution of the 29 (left), 31 (center), and 32 (right) amu signals at 235 K in LITD/FTMS experiments with C_2D_4 and H_2 dosed in both possible sequences and with a 1 : 1.5 C_2H_4/C_2D_4 mixture, all on Pt(111). The solid lines are drawn as guides to the eye, and the dashed lines indicate the zero signal levels. Dosing H_2 before ethylene results both in a faster decay of the C_2D_4 coverage (32 amu signal) and in a higher degree of H/D exchange. Also, the H/D exchange in the case of the C_2H_4/C_2D_4 mixture is slower than in the other two experiments (see also Fig. 2).

fact that explains why the H/D exchange reaction is faster and starts at lower temperatures than any other ethylene-conversion steps under the experimental conditions used here.

Additional LITD experiments indicated that the H/D exchange is sensitive to the order in which the hydrogen and ethylene are dosed as well as to the source of the hydrogen atoms. This is illustrated in Fig. 6, which shows the growth of the 29 and 31 amu signals (left and center panels, respectively) and the decay of the 32 amu signal (right panel) at 235 K in experiments where H_2 was dosed either before or after C_2D_4, and in a third run where a 1 : 1.5 C_2H_4/C_2D_4 mixture was used. The doses in the first two experiments were chosen to produce surfaces with similar hydrogen and ethylene coverages so they could be compared with each other. As pointed out above, the main reaction product is C_2D_3H in the experiments where the ethylene is dosed first, but both a faster decay of the 32 amu signal and a higher degree of H/D exchange are seen when the dosing order is reversed; the intensity of the 29 amu signal becomes slightly larger than that of the 31 amu signal, in contrast to that observed in the H postdosing experiments. A higher local H/C_2D_4 ratio is likely to be obtained when hydrogen is dosed first.

The H/D exchange reaction in the case of the 1 : 1.5 C_2H_4/C_2D_4 mixture was slower than in the H pre- or post-dosing experiments, as indicated by the lack of the fast initial phase observed in the evolution of the 32 amu signal in the other cases (Fig. 6, top traces). This follows from the fact that the hydrogen atoms needed for the exchange have to be produced by the decomposition of some of the normal ethylene. The kinetics in this case appears to be quite complex, because only C_2D_3H (31 amu) can be detected in the first 500 s of the reaction but then the intensity of the 29 amu signal increases rapidly to a level higher than that of the 31 amu signal. As this cannot be due solely to cracking in the mass spectrometer, some C_2DH_3 must form at that point, most likely via the incorporation of deuterium atoms from C_2D_4 into the C_2H_4. The fact that only C_2D_3H is detected initially indicates that hydrogen atoms become available earlier than deuterium atoms (despite the fact that the C_2H_4/C_2D_4 mixture contains more deuterium atoms), perhaps because there is a kinetic isotope effect in the ethylene decomposition step. In addition, the formation of C_2DH_3 at 235 K implies that decomposition of ethylene indeed occurs at a measurable rate after 1000 s, and supports the conclusion that the slow decay of the 32 amu signal in the hydrogen postdosing experiments is at least partially due to the decomposition of ethylene.

Finally, it should be noted that ethylene hydrogenation was not detected under the conditions used in these LITD experiments, since no significant amount of ethane was found in any of the experiments presented above.

3.2. *Ethylidyne Formation and H/D Exchange: RAIRS Experiments*

The H/D exchange between surface hydrogen/deuterium and isotopically labeled ethylene that takes place on Pt(111) at 215 K leads to the formation of partially deuterated ethylidynes at higher temperatures (above ~250 K) (4, 14, 16, 18, 20, 25, 46). In this section we focus on RAIRS experiments dealing with the formation of these partially deuterated ethylidynes. Figure 7 shows the 950–1450 cm^{-1} range of RAIRS data obtained after dosing 5.0 L of C_2D_4 on a Pt(111) surface under an atmosphere of 5×10^{-8} Torr H_2 at various temperatures between 275 and 403 K. A hydrogen background pressure was necessary to maintain a reasonable steady-state hydrogen coverage on the Pt(111) surface, because

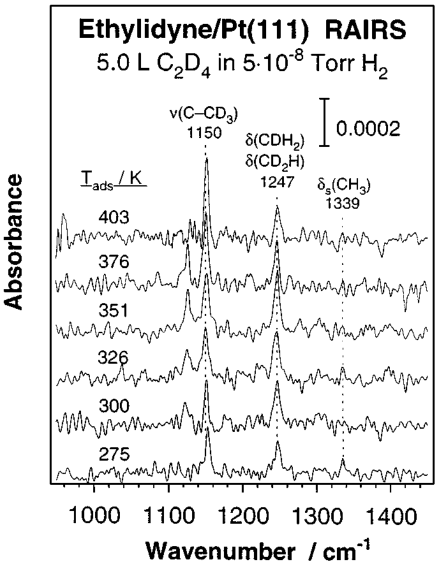

FIG. 7. RAIRS data from the ethylidyne formed by adsorption of 5.0 L of C_2D_4 at 275, 300, 326, 351, 376, and 403 K on Pt(111) under an atmosphere of 5×10^{-8} Torr H_2. The signals at 1339, 1247, and 1150 cm^{-1} are indicative of the formation of nondeuterated, partially deuterated, and per-deuterated ethylidyne, respectively, and the additional signal around 1120 cm^{-1} (not marked) is due to the ν(C–C) mode of both nondeuterated and partially deuterated ethylidynes. Note that the relative amounts of nondeuterated and partially deuterated ethylidyne in this system decrease with increasing reaction temperature.

hydrogen desorption starts, depending on its coverage, between 200 and 270 K. The RAIRS traces in Fig. 7 display peaks at 1339, 1247, 1150, and 1120 cm^{-1}, corresponding to $\delta_S(CH_3)$ in $Pt_3{\equiv}C{-}CH_3$, δ(CH) in $Pt_3{\equiv}C{-}CD_2H$, and/or $Pt_3{\equiv}C{-}CDH_2$, ν(C–C) in $Pt_3{\equiv}C{-}CD_3$, and ν(C–C) in $Pt_3{\equiv}C{-}CH_3$, $Pt_3{\equiv}C{-}CD_2H$, and/or $Pt_3{\equiv}C{-}CDH_2$, respectively (14, 47–51). For the interpretation of the data below, the peaks at 1339, 1247, and 1150 cm^{-1} are here identified with normal ethylidyne ($Pt_3{\equiv}C{-}CH_3$), partially deuterated ethylidyne ($Pt_3{\equiv}C{-}CD_2H$ and $Pt_3{\equiv}C{-}CDH_2$), and per-deuterated ethylidyne ($Pt_3{\equiv}C{-}CD_3$), respectively (14). A further distinction between $Pt_3{\equiv}C{-}CD_2H$ and $Pt_3{\equiv}C{-}CDH_2$ could not be made reliably on the basis of our data, because the listed frequencies for their characteristic modes are too close to be resolved with the resolution of our instrument.

The data displayed in Fig. 7 reveal that partially deuterated ethylidynes are indeed formed on Pt(111) upon thermal activation of C_2D_4 in the presence of hydrogen. In particular, some normal ethylidyne ($Pt_3{\equiv}C{-}CH_3$) is produced at 275 K, indicating that multiple and extensive H/D exchange occurs in that case; the intensity of the 1339 cm^{-1} peak is weak but quite reproducible. A detectable degree of H/D exchange is seen at higher adsorption temperatures as well, but no normal ethylidyne is observed above 300 K, and the relative yield for partially deuterated ethylidyne compared to the amount of per-deuterated ethylene decreases, as inferred from the decrease in the intensity ratio of the RAIRS signals at 1247 and 1150 cm^{-1}.

A different behavior is observed in the case of C_2D_4 coadsorbed with C_2H_4. Figure 8 displays the RAIRS data for the ethylidyne formed after adsorption of 5.0 L of a 1 : 1 mixture of C_2H_4 and C_2D_4 on Pt(111) at temperatures between 275 and 400 K. In this experiment both normal and partially deuterated ethylidyne are also formed, but, in contrast to the experiment with coadsorbed H (Fig. 7), the yield of the partially deuterated ethylidyne increases with adsorption temperature (see the growth of the 1247 cm^{-1} peak at higher temperatures). This result highlights again the fact that it makes a difference for the exchange reaction whether the hydrogen atoms are already present on the surface or have to be produced via the dissociation of chemisorbed ethylene.

Ethylidyne itself can also undergo H/D exchange with surface hydrogen (52, 53). To check if this reaction takes place under the conditions of our experiments, RAIRS data were recorded for submonolayers of ethylidyne (produced by adsorption of 1.0 L of C_2H_4 at 330 K) after being exposed to 5×10^{-8} Torr D_2 for 500 s while keeping the surface at temperatures between 273 and 407 K. The resulting vibrational spectra, displayed in Fig. 9, show that the extent of the H/D exchange increases with temperature, as expected from a typical Arrhenius behavior; note in particular both the decrease in signal intensity in the 1339 cm^{-1} peak and the growth of the 1247 cm^{-1} feature. An additional trace was added to the bottom of Fig. 9 to illustrate the results

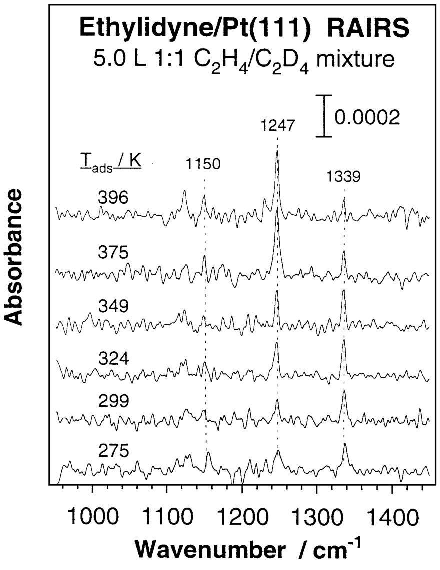

FIG. 8. RAIRS data from the ethylidyne formed by adsorption of 5.0 L of a 1 : 1 C_2H_4/C_2D_4 mixture on Pt(111) at 275, 299, 324, 349, 375, and 396 K. The assignment of the signals is the same as in Fig. 7. In contrast to the data in that graph, however, the relative amount of partially deuterated ethylidyne increases here with reaction temperature.

obtained from similar experiments with a saturated layer of ethylidyne (produced by dosing 5.0 L C_2H_4 (14)); no detectable exchange is seen in that case even at 324 K. These data indicate that the H/D exchange between ethylidyne and surface hydrogen is important only at relatively high temperatures (above about 400 K) and low ethylidyne coverages.

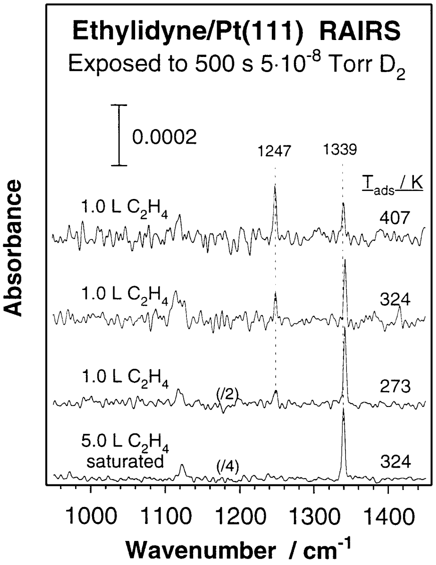

FIG. 9. RAIRS data from nondeuterated ethylidyne on Pt(111) after exposure to an atmosphere of 5×10^{-8} Torr of D_2 at 273, 324, and 407 K for 500 s. The top three traces correspond to a submonolayer coverage of ethylidyne (0.10 ML, or 40% of saturation) produced by adsorption of 1.0 L of C_2H_4 at 320 K, while the bottom trace was obtained after adsorption of 5.0 L of C_2H_4 at 324 K to produce a saturated layer (0.25 ML). The signals at 1247 and 1339 cm^{-1}, associated with the presence of partially and nondeuterated ethylidyne, respectively, provide a measure of the degree of H/D exchange between the original nondeuterated ethylidyne and deuterium. The data show that this reaction occurs only at high temperatures and for submonolayer coverages of ethylidyne.

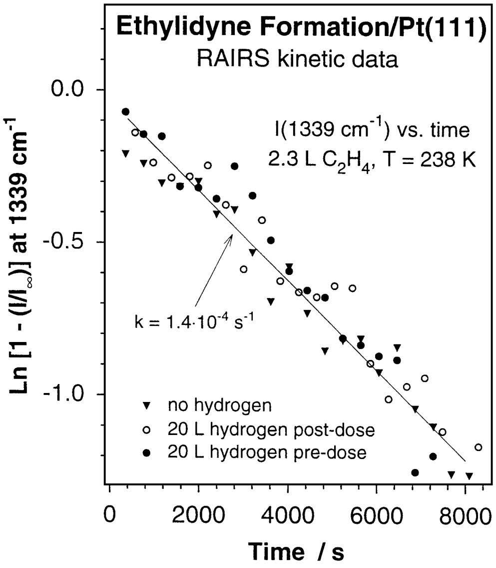

FIG. 10. Kinetic measurements for ethylidyne formation on Pt(111) at 238 K after adsorption of 2.3 L of C_2H_4 on Pt(111) surfaces clean (solid triangles) and after 20 L H_2 post- (open circles) or pre- (filled circles) doses. The conversion was determined by dividing the integrated intensity of the RAIRS signal at 1339 cm^{-1} (which corresponds to the $\delta_s(CH_3)$ mode of ethylidyne) in a given spectrum by that obtained after flashing to 330 K, which forces the reaction to completion. These data clearly show that the rate of ethylidyne formation is independent of the hydrogen coverage. Moreover, the linearity of the semi-logarithmic plots indicate that the reaction is first order; a rate constant of $1.4 \pm 0.1 \times 10^{-4}\ s^{-1}$ was determined at this temperature.

Finally, as mentioned above, one of the processes that could account for the discrepancy between the decrease in the 32 amu signal intensity and the concomitant development of the 31 amu peak in the experiments shown in Fig. 4 is the decomposition of ethylene into ethylidyne. It has already been shown earlier that in the absence of surface hydrogen the rate of ethylidyne formation follows a first-order rate law (4, 16, 20, 25, 46, 54), but for both the LITD and the RAIRS experiments presented above it is important to determine whether coadsorbed hydrogen affects the rate of ethylidyne formation or not. To examine this point, the intensity of the $Pt_3{\equiv}C{-}CH_3$ RAIRS signal at 1339 cm^{-1} was followed for about 8000 s after adsorption of 2.3 L of C_2H_4 at 238 K both in the absence of coadsorbed hydrogen and with 20 L H_2 post- and predoses; the results are displayed in Fig. 10. The initial ethylene coverage in these experiments was determined from the integrated absorbance at 1339 cm^{-1} (by assuming a 1 : 1 conversion from ethylene to ethylidyne) to be about 0.15 ± 0.02 ML (50–70% of saturation), and the extent of its conversion was calculated by the $I(t)/I_\infty$ ratio, where I(t) is the integrated absorbance at 1339 cm^{-1} at a certain point in time and I_∞ that after 100% conversion to ethylidyne (obtained by flashing the sample to 330 K). The data in Fig. 10 clearly show that there is no significant difference in the rate of formation of ethylidyne among the three experiments reported there; a rate constant of $(1.4 \pm 0.1) \cdot 10^{-4}\ s^{-1}$ was found for all cases. This indicates that dosing hydrogen on the surface either before or after ethylene adsorption does not affect the decomposition of ethylene to ethylidyne in any significant way. Also, the value of the rate constant measured here is in excellent agreement with that calculated for the same temperature by using the kinetic parameters published by Erley *et al.* (16), but somewhat lower than those derived from the data published by Zaera (25) and by Mohsin (46).

4. DISCUSSION

The LITD and RAIRS data presented above lead to specific conclusions on the mechanism of the conversion of ethylene on Pt(111) surfaces. As explained in the previous section, the formation of partially deuterated ethylene is the result of H/D exchange reactions between surface

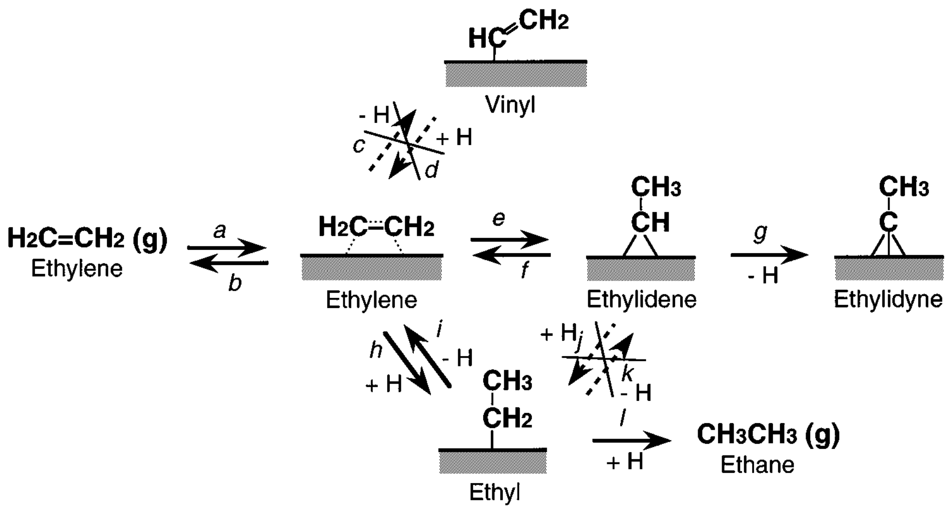

FIG. 11. Reaction scheme proposed for the chemistry of ethylene adsorbed on Pt(111) surfaces. The following reactions are shown: ethylene adsorption (*a*) and desorption (*b*), dehydrogenation of adsorbed ethylene to vinyl (*c*), hydrogenation of vinyl to ethylene (*d*) 1,2-H shift in ethylene to ethylidene (*e*), 1,2-H shift in ethylidene back to ethylene (*f*), α-H elimination from ethylidene to ethylidyne (*g*), hydrogenation of ethylene to ethyl (*h*), β-H elimination from ethyl to ethylene (*i*), hydrogenation of ethylidene to ethyl (*j*), α-H elimination from ethyl to ethylidene (*k*), hydrogenation of ethyl to ethane (*l*). H/D exchange in chemisorbed ethylene is proposed to go via an ethylene–ethyl interconversion (steps *h* and *i*), while ethylidyne formation is believed to involve an ethylidene group instead (and follow steps *e*, *f*, and *g*). The elementary steps indicated with dashed arrows do not appear to occur on the Pt(111) surface.

hydrogen and ethylene. The H/D exchange takes place at temperatures well below those required for ethylene decomposition, and its activation barrier, determined to be 11 ± 2 kcal/mol (Fig. 5), is noticeably lower than that for the decomposition of ethylene to ethylidyne (15–18 kcal/mol) (16, 25, 46). These results strongly suggest that the H/D exchange and ethylidyne formation reactions do not share a common rate-limiting step.

The mechanisms of the different reactions observed for ethylene on Pt(111) will be discussed below in terms of the reaction scheme displayed in Fig. 11. The two most probable reaction paths for H/D exchange in adsorbed ethylene are (1) an initial decomposition of ethylene to a vinyl moiety, followed by the hydrogenation of that moiety back to ethylene (steps *c* and *d*), and (2) an initial hydrogenation to ethyl followed by β-H elimination from the ethyl back to ethylene (steps *h* and *i*). Ethyl moieties could in principle also be formed via an ethylidene intermediate (steps *e* and *j*), but in that case an α-H elimination step (step *k*) would be needed to convert the ethyl back to ethylene (because of the principle of detailed balance), and that reaction has been shown not to occur to a significant extent below 600 K (41, 55, 56). A vinyl intermediate (path 1 above) can also be ruled out, since the data in Fig. 2 prove that H/D exchange takes place before any ethylene dehydrogenation is possible. Furthermore, the reverse conversion of vinyl moieties to ethylene is complex and involves at least two isolatable intermediates (15), while the β-H elimination from ethyl to ethylene is direct and has a low activation barrier (<6 kcal/mol) (40). We therefore conclude that the H/D exchange reaction reported here must involve the reversible interconversion between ethylene and ethyl. Furthermore, given that the activation barrier measured for the H/D exchange is low but still higher than that for the β-H elimination step in ethyl, the hydrogenation from ethylene to ethyl is likely to be the rate-limiting step in the former process. This means that at higher temperatures, when both reactions are fast, an equilibrium shifted towards the ethylene side is expected. This agrees well with the fact that no significant amounts of ethyl moieties have ever been detected during ethylene conversion. Ethyl intermediates in the H/D exchange between ethylene and surface hydrogen have been proposed earlier (14, 21), but the LITD data presented here provide a better argument to support this conclusion.

Our LITD and RAIRS data also indicate that the H/D exchange reaction is more complicated than what the scheme in Fig. 11 suggests. The data in Figs. 2, 6, 7, and 8 show that the exchange is sensitive both to the way the surface is prepared (H_2 postdose or predose) and to the source of the hydrogen atoms (H_2 or C_2H_4). A couple of reasons for this complex kinetic behavior can be tracked back to the sequential nature of the H/D exchange steps and, under certain circumstances, to the occurrence of side reactions which affect the hydrogen and ethylene coverages, e.g., ethylene and hydrogen desorption, ethylene hydrogenation, and ethylidyne formation. In addition, recent experiments have revealed that between 200 and 250 K chemisorbed ethylene can exist in both a strongly bound (presumably di-σ bonded) and a weakly bound (presumably π bonded) chemisorbed states, and that those species have different reactivities towards hydrogen (7, 16, 20). Finally, ethylene forms islands on the Pt(111) surfaces, as indicated by STM experiments (18), and such an inhomogeneous distribution may also affect the kinetic behavior of the conversion reactions.

Considering the kinetic aspects of the H/D exchange reaction mentioned above, several reasons can be given for why the C_2D_4 disappears faster and the H/D exchange steps take place to a larger extent (leading to more multiple substitution) in the hydrogen predosing experiments (Fig. 6). First, a higher hydrogen coverage (and H/C_2D_4 ratio) can be expected from dosing hydrogen before ethylene, since that way the hydrogen adsorption sites are not blocked by ethylene, and second, the hydrogen and ethylene may be better intermixed on the surface in that case as well. This can be explained as follows: when ethylene is dosed on a clean Pt(111) surface, islands are formed (18) and hydrogen can only adsorb outside those ethylene patches; the likely result from this situation is thus a surface with separate ethylene and hydrogen phases. On the other hand, ethylene adsorption on a hydrogen-covered Pt(111) surface does occur readily, and consequently, a more homogeneous mixing of the two reactants can be expected in that case. An additional reason for the faster decay of the C_2D_4 in the hydrogen-predosing experiments is the fact that adsorbed hydrogen enhances the formation of weakly bound chemisorbed ethylene (7, 8, 14). For one, this may lead to a larger contribution from ethylene desorption to the decay of the C_2D_4 coverage, but in addition, the low binding energy of the π-bonded species may favor its hydrogenation. Isothermal kinetic experiments have shown that the weakly bound state of ethylene is hydrogenated to ethane more easily than the di-σ counterpart (7, 8). No ethane was detected in the experiments presented here, but, since both ethane formation and H/D exchange reactions go through the same rate-limiting ethyl-formation step, it can be speculated that the H/D exchange between surface hydrogen (deuterium) and ethylene is also faster with the π-bonded species.

A noteworthy observation from the LITD experiments is the fact that the production of C_2D_3H seems to saturate after about 1000 s of reaction at a level which depends on the reaction temperature, as indicated by the time evolution of the 31 amu LITD signals in Fig. 4. Since the initial surface concentration of hydrogen and ethylene were more or less the same in all those experiments (as inferred from the initial intensities of the 32 amu signals in Fig. 4), the saturation levels cannot be associated with global changes in surface coverages. It is possible, however, that the reaction requires specific ethylene + hydrogen ensembles on the surface, and that it only takes place at the edge of ethylene islands, perhaps because the mobility of the hydrogen atoms inside the ethylene islands is limited. Unfortunately, the data available to date are insufficient to confirm this hypothesis.

The complex kinetic behavior of the H/D exchange reaction also manifests itself in the opposite trends seen in the relative amounts of partially deuterated ethylidyne produced from coadsorbed C_2D_4/H_2 versus C_2H_4/C_2D_4 mixtures with increasing reaction temperature (Figs. 7 and 8). This may be explained by a change in the behavior of the hydrogen coverage with temperature in those experiments. In the former case the hydrogen coverage is determined by the adsorption–desorption equilibrium of H_2, and that leads to a lower hydrogen surface concentration at higher temperatures. Hence, the production of partially deuterated ethylene slows down, and the selectivity in ethylidyne formation shifts toward the per-deuterated compound. In the C_2H_4/C_2D_4 mixture, on the other hand, the hydrogen atoms are supplied by the decomposition of C_2H_4, and since that reaction is accelerated by higher temperatures, higher steady-state hydrogen coverages are obtained in those cases. Consequently, there is a shift in selectivity toward partially deuterated ethylidyne with increasing reaction temperatures. Note that even though in the RAIRS experiments the H/D exchange in adsorbed ethylene was probed by analyzing the isotopic composition of the ethylidyne resulting from its thermal activation, the direct H/D exchange between ethylidyne and surface hydrogen is negligible under the conditions used in those experiments and, therefore, does not cloud the conclusions reached above. The data in Fig. 9 show that such a reaction is important only at higher temperatures and lower ethylene coverages.

One final interesting kinetic feature in the ethylene conversion processes highlighted by the LITD experiments with the 1 : 1.5 C_2H_4/C_2D_4 mixture is the fact that the exchange of hydrogen in C_2D_4 to form C_2D_3H occurs before that between surface D and C_2H_4 (Fig. 6). This difference may be associated with a kinetic isotope effect for ethylene decomposition, which makes the decomposition of C_2D_4 slower (25). Nevertheless, an artifact in the measurements due to hydrogen adsorption from the background cannot be ruled out.

Perhaps the key conclusion from the previous discussion is the fact that H/D reactions in ethylene adsorbed on Pt(111) start with the rate-limiting hydrogenation step that yields ethyl moieties on the surface, and that this reaction is common to the exchange and ethane formation processes. The mechanistic details of this initial hydrogenation, however, have not been well resolved yet. For one, the activation energy for the H/D exchange in ethylene derived here for the H postdosing experiments (11 kcal/mol) matches the value obtained earlier with TPD for both H/D exchange and ethane formation (21), but it is significantly higher than that for ethane production reported by Öfner *et al.* (6 kcal/mol) (7). The reason for this discrepancy appears to be that in the collimated-beam experiments of

Öfner *et al.* (7) the reactive species was a weakly (π) bound ethylene, while in the LITD experiments presented here the exchange reaction involves the strongly (di-σ) bound ethylene instead; the weakly bound species is not stable under the conditions used in the latter study. In this context, the difference in activation energies in ethyl formation can be interpreted as being reflective of the difference in binding energy for the weakly and strongly bound ethylene (8). Reliable heats of adsorption for these two species are needed to settle this issue.

Finally, the fact that the rate of ethylidyne formation does not depend on the surface coverage of hydrogen (Fig. 10) has important consequences for the mechanism of ethylidyne formation; any scheme involving an equilibrium with surface hydrogen can now be excluded, since that would result in a rate that depends on the hydrogen surface concentration. All mechanisms including a preequilibrium between ethylene and either ethyl (steps *h* and *i* of Fig. 11) or vinyl (steps *c* and *d*) before conversion to ethylidyne can therefore be discarded. This leaves ethylidene as the most likely intermediate for ethylidyne formation. The same conclusion was reached earlier based on the fact that ethylidene moieties can be directly converted to ethylidyne via a fast α-H elimination step without producing ethylene (35). From this it is also clear that the ethylidyne formation and H/D exchange reactions follow two different reaction paths and have different rate-limiting steps. This conclusion translates directly into catalytic hydrogenation processes, because there species such as ethylidyne form and cover the surface of the catalyst but appear to act only as spectators during the hydrogen-incorporation steps (4, 30).

5. CONCLUSIONS

Laser-induced thermal desorption (LITD) has been used in combination with Fourier-transform mass spectrometry (FTMS) to study the kinetics of the H/D exchange reaction between ethylene and surface hydrogen (deuterium) on Pt(111). The surface hydrogen was supplied either by direct adsorption of H_2 or by decomposition of C_2H_4. Adsorption of C_2D_4 followed by exposure to H_2 results in the formation of C_2D_3H at temperatures as low as 215 K, indicating that the H/D exchange is quite fast even then; the activation energy and preexponential factor for this case were estimated to be 11 ± 2 kcal/mol and $10^{8\pm1}$ s^{-1}, respectively. No H/D exchange takes place in mixtures of C_2H_4 and C_2D_4 under the same conditions, indicating that the reaction involves surface hydrogen, and does not require the decomposition of ethylene (except to provide the H atoms). This rules out vinyl groups as possible intermediates, and supports a mechanism involving ethyl moieties instead. It was also found that the extent of the exchange is determined both by the actual H/C_2D_4 coverage ratio on the surface and by the dosing order of the reactants; when hydrogen is dosed first, the original ethylene (C_2D_4) disappears faster, and a higher degree of hydrogen substitution per molecule is obtained.

At sufficiently high temperatures the adsorbed ethylene reacts to form ethylidyne, even in the presence of coadsorbed hydrogen. This process was monitored here by RAIRS. It was shown that the deuterium content in the ethylidyne produced by thermal activation of mixed layers of C_2D_4 and either H_2 or C_2H_4 is mainly determined by the previous H/D exchange between ethylene and surface hydrogen, and that direct H/D exchange between ethylidyne and surface hydrogen only occurs at low ethylidyne coverages and significantly higher reaction temperatures. The rate of ethylidyne formation was shown to be independent of the amount of hydrogen on the surface, a result consistent with ethylidene as an intermediate in the conversion of ethylene to ethylidyne. The results presented here agree with the idea of H/D exchange and ethylidyne formation reactions taking place via parallel and independent mechanisms.

ACKNOWLEDGMENTS

The authors thank Dr. H. Öfner for helpful discussion. Financial support for this project was provided by grants of the National Science Foundation (CHE-9530191 and CHE-8913811).

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