

Kinetics of Propene Desorption from Pd(111) Studied by Thermal Desorption Spectroscopy and Laser-Induced Thermal Desorption with Fourier Transform Mass Spectrometry

Nick A. Thornburg, Ihab M. Abdelrehim, and Donald P. Land*

Department of Chemistry, University of California, Davis, California 95616

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Thermal desorption spectroscopy (TDS) and laser-induced thermal desorption coupled with Fourier transform mass spectrometry (LITD/FTMS) are used to study the interaction of propene on Pd(111). TDS yields the exposure versus coverage dependence for propene adsorbed to Pd(111). A linear uptake from 0.1 to 1 L (corrected for ion gauge sensitivity) implies precursor mediated adsorption. Significant broadening and shifts to lower temperature occur in the TDS above about 0.26 L, which is assumed to be near saturation. Only propene (320 K) and hydrogen (300 and 500 K) desorb after heating a near-saturation exposure of propene. Propene mostly desorbs intact from the Pd(111) surface. TDS shows that no more than 10% of the near-saturation exposure of propene may decompose to surface bound carbon. Isothermal desorption data are acquired using LITD/FTMS at temperatures between 270 and 390 K. Rate constants are extracted from the data, and an Arrhenius plot yielded kinetic parameters (E_a and A): $E_a = 79.2 \pm 0.9$ kJ/mol and, a preexponential, $A = 10^{10.8 \pm 0.3}/s$ (95% confidence level).

I. Introduction

The interactions of hydrocarbons with late transition metals are important in fields of catalysis, waste remediation, and for a fundamental understanding of the reactivity of molecules with surfaces. In particular, there is considerably less data on surface energetics and reactivity for Pd, particularly with higher hydrocarbons, than for Ni, Pt, Fe, or coinage metals.¹ Often, Pd is discussed as if it were a twin with Pt; however, there is little data to support such generalizations. Here we present data on the reactivity of propene on Pd(111). Ethylene is, perhaps, the most studied hydrocarbon since it is the simplest alkene.¹ Ethylene is thought to react to form acetylene on Ni(111)² and ethynylidyne on both Pd(111)³ and Pt(111).⁴ Propene is far less studied but is believed to form propylidyne on Pt(111).^{5–8} Palladium is a uniquely selective catalyst useful for hydrocarbon conversion and often shows decreased C–H bond activation relative to Ni and Pt.⁹ However, no studies have appeared regarding the interactions of propene on clean Pd. Combustion of propene on O/Pd(111)¹⁰ and O/Pd(100)^{11–13} has been reported, as has H–D exchange on Pd(100)-p(1×1) H(D).¹⁴ Propene is the simplest hydrocarbon with both alkene and alkane components. The alkane functionality may lead to sterically decreased π overlap with the surface metal orbitals compared to ethene, causing enhanced desorption and less decomposition. In fact, this is what we observe on Pd(111). Very little decomposition takes place, with at least 90% of a near saturation dose desorbing intact. The details of the kinetic parameters for desorption are difficult to ascertain from thermal desorption spectroscopy (TDS), because preexponential factors cannot be accurately determined due to the presence of multiple, overlapping desorption states.¹⁵ However, laser-induced thermal desorption coupled with Fourier transform mass spectrometry (LITD/FTMS) has emerged as a technique capable of yielding kinetic data for surface catalyzed processes as well as determin-

ing surface molecular composition.^{16,17} We use this technique to measure the desorption activation barrier and preexponential factor for propene on Pd(111). The desorption process follows first-order kinetics. Arrhenius treatment of the rates yields an activation energy of 79.2 ± 0.9 kJ/mol and a preexponential of $10^{10.8 \pm 0.3}/s$ (both 95% confidence level).

II. Methods

Experiments are performed in an ultrahigh vacuum (UHV) chamber (base pressure = 2×10^{-10} Torr) which incorporates Auger electron spectroscopy, low energy electron diffraction, and FTMS. Details of the surface analysis instrument are published elsewhere.¹⁸ A Pd(111) crystal is supported and manipulated by a long motion bellows and rotary feed-through. The sample can be heated resistively and cooled conductively. Temperature is monitored by a type K thermocouple spot-welded to the crystal. Sample cleaning is performed by argon ion sputtering, annealing, and heating in oxygen. Auger electron spectroscopy (retarding field energy analyzer) and low energy electron diffraction are used to verify sample integrity. These methods have been shown to remove surface C by dosing oxygen on the surface at room temperature followed by heating. The presence of remaining surface C is indicated by desorption of CO. A clean surface shows desorption of only O₂.

FTMS is performed using a 5 cm cubic cell in a 0.5 T magnetic field. Impulse excitation¹⁹ or RF excitation²⁰ is used to accelerate the ions trapped in the FTMS cell. Data are acquired and processed by an IonSpec OMEGA/486 data system. The FTMS was tuned to propene gas (Matheson) at 5×10^{-9} Torr using electron impact ionization (70 eV, 1–20 μ A, 10 ms duration) and a trapping voltage of 3.50 V (± 0.7 V). The acceleration voltage and transmitter plate voltages were adjusted to maximize the reproducibility of the transient signal and mass spectra. The fragmentation pattern of propene was compared with a library mass spectrum to ensure purity.²¹

For the TDS studies, the clean Pd(111) crystal is cooled to 130 K and exposed to propene. The sample is positioned 1 mm

* To whom correspondence is addressed. tel: (916) 752–5260; fax: (916) 752–8995; e-mail: dpland@ucdavis.edu.

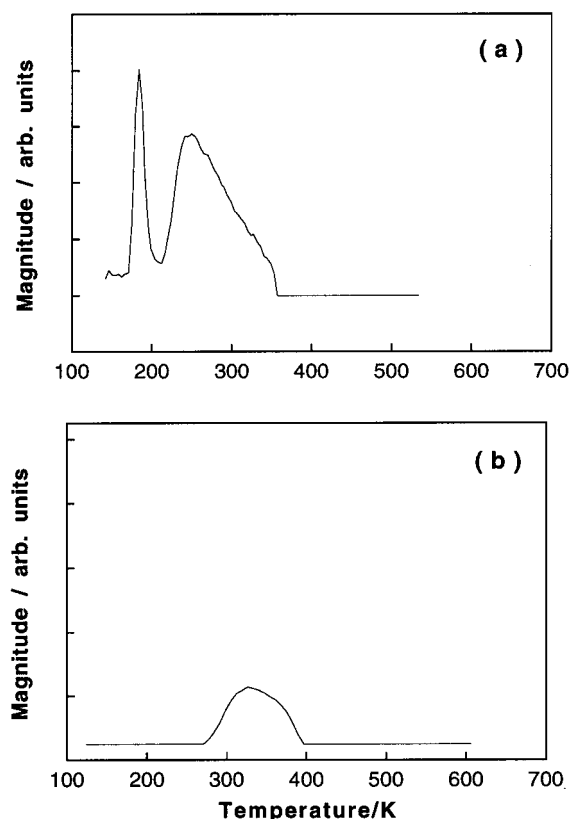


Figure 1. TDS of propene on Pd(111) thermal desorption spectra of m/z 41 for (a) 0.4 L and (b) 0.26 L of propene on Pd(111). The lower exposure shows only one peak at 327 K indicative of only a subsaturation coverage which desorbs between 270 and 390 K. Exposures above 0.26 L lead to broadening and shifting of the peak to lower temperature. Exposures of about 0.4 L start to show a peak at ~ 180 K, likely resulting from multilayers.

from an aperture in the mass spectrometer cell. The sample is then heated at a rate of 2.5 K/s (± 0.5 K/s), while mass spectra are acquired at 0.5 Hz. Because FTMS is used to detect the desorbing species, a complete mass spectrum is obtained at each temperature. Several TDS were performed using coverages between 0.1 and 1.0 L (L = Langmuir = 10^{-6} Torr·s). All exposures were corrected for ion gauge sensitivity (3.06 for propene and 0.46 for hydrogen).²² Figure 1 shows two TDS traces for m/z 41, the most intense propene mass peak, versus temperature. All other ions (principally m/z 39, 40, 42) showed the same behavior. Figure 1(a) is from a 0.4 L exposure, and Figure 1(b) is from a 0.26 L propene exposure. Only one desorption peak is observed in the TDS at 0.26 L. Exposures greater than 0.26 L result in significant broadening and shifting of this peak to lower temperatures. Just below 0.4 L, one starts to observe an additional thermal desorption peak growing in at 180 K, likely corresponding to multilayers of propene.

For LITD/FTMS the sample is cleaned, cooled to 130 K, and exposed to 0.26 L of propene. The sample is positioned in front of the mass spectrometer cell as described above. A Nd:YAG laser (1064 nm, 5 ns pulse width, ~ 20 mJ/pulse) is focused through a fused silica lens to a 1.0 mm diameter spot on the sample, yielding $\sim 10^9$ W/cm² at normal incidence. Under these conditions, there is complete removal of propene from the surface as neutrals, yet no Pd ablation. Subsequent laser pulses at the same spot within 1–2 s show less than 10% of the signal observed from the first laser pulse at a spot. The neutrals effuse into the FTMS cell where they are positionized by an electron beam. The ions are trapped and excited to larger cyclotron radii,

and an image current is detected and amplified. Fourier transformation yields a mass (frequency) spectrum. For the isothermal studies, the sample is heated to the desired temperature (270–390 K), and the IonSpec OMEGA system begins triggering the laser and acquiring mass spectra at up to 1 Hz. The position of the laser beam on the sample is changed after each laser pulse by a computer controlled movable mirror, allowing sampling from 43 nonoverlapping spots. Thus, each laser pulse results in a complete mass spectrum from an unperturbed area of the sample. Spectra are gathered using a 10 ms electron beam width and 16, 32, or 64 K time-domain data points. Under these conditions no signal is observed unless the laser is allowed to strike the sample.

III. Results and Discussion

A. Propene Adsorption. Because each Nd:YAG laser pulse hits a different area of the Pd(111) crystal face during the LITD/FTMS sequence, it was crucial to determine if a consistent FTMS signal could be obtained over the entire sample. Several experiments were performed in which an exposure of propene was dosed on the crystal at 100 K. The dosed crystal was oriented in front of the FTMS cell, and LITD/FTMS was performed at 43 different spots on the sample while it was maintained at 100 K. (No desorption or reaction is evident at 100 K.) It was observed that there was less than 10% fluctuation in the magnitudes of the propene signals: the average absolute ion intensity for m/z 41 was 11.58 with a variance of 0.85.

The uptake of propene was observed by following the increase in the LITD/FTMS signal. The sample was cleaned, cooled to 100 K, and positioned in front of the FTMS cell. Propene was leaked into the chamber at a constant pressure (2×10^{-9} Torr), and the uptake of propene by the sample was monitored by observing the magnitude of the propene laser-desorbed from the surface. A 10 ms electron beam was utilized so that gas-phase propene would not be detected. The uptake of propene was linear with time over the range of exposures included in these experiments. This is indicative of extrinsic precursor state behavior.²³

B. Desorption vs Decomposition. Two experiments were conducted to determine the amount of desorption versus decomposition on the Pd(111) surface. AES is not sensitive to the carbon adsorbed to the palladium surface since the C and Pd lines overlap; no difference in the carbon (272 eV) peak was observed when 2.0 L propene was adsorbed to the surface under conditions similar to those used for LITD/FTMS, so AES could not be used to quantify adsorbed C. Instead, 1.5 L of propene was desorbed from Pd(111): heating was applied at 3 K/s, the sample was cooled to 130 K, a 2 L-exposure of O₂ was adsorbed onto the Pd(111), and TDS was performed using a heating rate of 3 K/s. CO (m/z 28) would be detected by TDS if significant decomposition occurred; the surface bound carbon species would react with the adsorbed oxygen to form CO. A similar experiment was conducted on an unexposed sample as a blank. No differences were observed in the CO desorption yields from these two experiments. Thus, we estimate from a comparison of the magnitude of propene to the magnitude of CO/noise, at most, 15% of the propene may react and leave hydrocarbon fragments on the surface.

Hydrogen was also monitored during TDS after dosing with propene. Surface hydrogen recombines and desorbs in a second-order process, such that the desorption peak shifts to lower temperatures with increasing hydrogen coverage. The small amounts of hydrogen produced here lead to a desorption feature peaking at 400 K, corresponding to a very low hydrogen

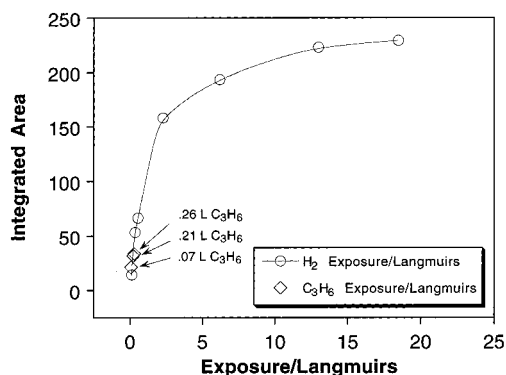


Figure 2. Hydrogen desorption from Pd(111) integrated areas for TD spectra of desorbed H_2 are plotted along with areas for TD spectra of desorbed hydrogen desorbed from Pd(111) after exposure to propene. Both hydrogen and propene exposures use the same X-axis. A 0.26 L exposure of propene decomposed to hydrogen which was equivalent to 15% of hydrogen saturation and <10% propene decomposition.

coverage. Additionally, the quantity of hydrogen evolved from the decomposition of propene, detected by TDS, showed that propene decomposed to yield an amount of hydrogen equivalent to 15% of a saturated H_2 exposure on Pd(111) cooled to 130 K. Assuming saturation H coverage to be 1:1 (H: Pd) and accounting for 6 H's per propene, less than 3% of a monolayer of propene decomposes. It has been shown that a saturation coverage of ethylene comprises 25% of a monolayer on Pt(111).¹⁷ Assuming propene saturation on Pd(111) does not exceed that, then the amount of hydrogen observed is less than 10% of the initial propene adsorbed.

Hydrogen (H_2) desorption was detected by FTMS by reducing the magnetic field to 0.1 T (T) so that mass 2 had a cyclotron frequency < 1 MHz. Typically, the magnetic field is held at 0.5 T; a 0.5 T magnetic field and a 2 MHz ADC allows a minimum $m/z > 10$ to be detected. A calibration curve of H_2 exposures—0.1 L to 65 L—was generated by integrating the area under each thermal desorption spectrum's curve. Figure 2 displays the integrated areas for TDS of hydrogen evolved from the decomposition of three propene exposures (0.07, 0.21, and 0.26 L) on Pd(111) compared to those of a H_2 calibration curve. Again, a 0.26 L exposure of propene decomposed to yield 15% of a H_2 -saturation exposure. Several blank TDS experiments were run to determine the amount of background hydrogen which adsorbed to the cooled sample during the time period of a TDS preparation and acquisition; the integrated areas were modified to reflect the amount of adsorbed background hydrogen.

Propene (0.26 L exposure) was coadsorbed with several hydrogen exposures (0.17–1.0 L), and TD spectra were acquired. The integrated areas for the m/z 2 TD spectra were compared to areas for H_2 -only exposures, as shown in Figure 3. The fitted lines are parallel but offset by an amount which is equivalent to the amount of hydrogen decomposed from 0.26 L of propene, indicating that the adsorbed hydrogen does not affect the dehydrogenation of propene on Pd(111).

C. Desorption Kinetics. Desorption of propene was monitored by observing the loss of signal in LITD/FTMS as a function of time under isothermal conditions near the desorption temperature for propene. A complete set of LITD/FTMS data was acquired for each isotherm (287 K, 290 K, 295 K, 299 K, 2 @ 311 K, 2 @ 322 K, 2 @ 330 K, 2 @ 336 K). These are well below the H_2 desorption temperature. Plots of m/z 39, 41, and 42 magnitude (propene's primary fragments) versus time for each isotherm were made. The data were fit to first- and

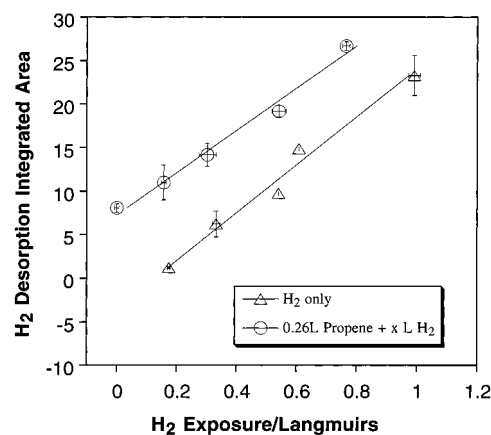


Figure 3. Integrated areas for H_2 desorption from coadsorbed H_2 and C_3H_6 on Pd(111) integrated areas for TD spectra of H_2 from Pd(111) after the adsorption of H_2 alone are compared to areas for the desorption of H_2 from Pd(111) after the coadsorption of 0.26 L C_3H_6 and various exposures of H_2 (0.17–1.0 L). Lines fit to both sets of areas are parallel but offset by an integrated area for H_2 equivalent to that obtained from 0.26 L of propene.

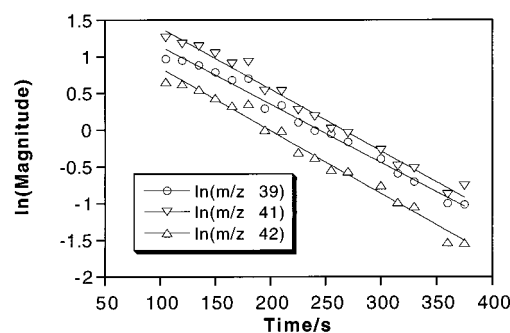


Figure 4. LITD/FTMS data taken at 322 K LITD/FTMS data for m/z 39, 41, and 42 taken at 322 K are displayed as $\ln(\text{magnitude})$ versus time. A linear, first-order fit was applied to each data set yielding the following rates: $k_{d,m/z\,39} = (7.95 \pm 0.23) \times 10^{-3} \text{ s}^{-1}$, $k_{d,m/z\,41} = (8.41 \pm 0.27) \times 10^{-3} \text{ s}^{-1}$, $k_{d,m/z\,42} = (8.56 \pm 0.27) \times 10^{-3} \text{ s}^{-1}$.

second-order models. First-order kinetics are favored over second order at the 90–99% level on comparison of the χ -squared ratio according to the F-distribution.

Figure 4 shows data for m/z 39, 41 and 42 taken at 322 K plotted as $\ln(\text{magnitude})$ versus time and a straight-line fit to the data. The rates of the m/z 41 and 42 desorption are equivalent within error limits: $(8.41 \pm 0.27) \times 10^{-3} \text{ s}^{-1}$ and $(8.56 \pm 0.27) \times 10^{-3} \text{ s}^{-1}$, respectively. The rate of the m/z 39 desorption was slightly different from the others: $(7.95 \pm 0.23) \times 10^{-3} \text{ s}^{-1}$. The m/z 39 species is unlike the m/z 41 and 42 peaks as it can be expected from either adsorbed propene or propylidyne, the likely stable dehydrogenation product. LITD of ethylidyne (CCH_3 , mass 27) on Pt(111) yields only masses 26 and 25.²⁴ LITD of propylidyne (CCH_2CH_3 , mass 41) on Pt(111) yields peaks at mass 40, 39, 26, and 25.²⁵ Peaks at m/z 41 and 42 would only be expected from propene. Hence, the difference in observed rates may indicate a small amount of reaction of propene to propylidyne.

The data in Figure 4 and that for the other temperatures show no curvature that would indicate that the desorption rate constant changes with coverage, at least for these low exposures. The data in Figure 4 represent a change in concentration of approximately 1 order of magnitude, from roughly 0.7 to 0.07 of a saturation monolayer. (Note that, although the initial dose is near a complete saturation monolayer, some desorbs before isothermal conditions are achieved.)

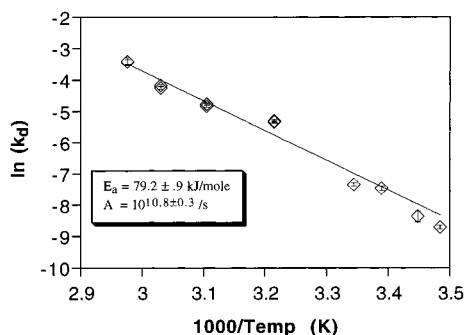


Figure 5. Arrhenius plot an Arrhenius plot of $\ln(k_d)$ versus $1/\text{temperature}$ data for m/z 41 was fit to a weighted least-squares mean fit line. An energy of activation and preexponential were extracted from the plot using the Arrhenius equation: $E_a = 79.2 \pm 0.9$ kJ/mol, $A = 1 \times 10^{10.8 \pm 0.3}/s$.

The effect of the loss of the laser-desorbed material on the observed rates is insignificant. Using a laser spot size of 1 mm and a Pd crystal diameter of 10 mm, each laser pulse removes no more than 1% of the entire surface concentration of adsorbate. This amount of adsorbate removal by the laser is an upper limit; the laser spot size never exceeded 1 mm, and diffusion of adsorbate from the side and back of the sample were not included. Even in the limit of infinitely rapid diffusion, such that the laser-desorption “holes” refilled immediately, and complete removal of all material under the laser beam, the loss of material would not significantly influence the kinetics measurements. Using the experimentally determined rate constant, “corrected” concentrations were calculated for each laser pulse; the corrected concentrations were then used to calculate a corrected rate and compared with the experimentally determined rate, ignoring loss due to removal by the laser. Less than 8% difference was noted between the uncorrected rates and the “LITD-corrected” rates. The rates used throughout are, therefore, those uncorrected for laser removal.

Figure 5 is an Arrhenius plot of $\ln(k_d)$ versus $1/\text{temperature}$. A weighted least mean square fit was applied to the data. The data were locally weighted to reflect the relative uncertainty of the rate constant at each temperature (as determined from the linear fit to $\ln(\text{magnitude})$ vs time) and also globally weighted to reflect the logarithmic transformation of the rate constants. Note that, for the four highest temperatures, the experiments were each repeated, and both experimentally determined rate constants are plotted in Figure 5. The data points lie almost directly on top of one another, giving another indication of the reproducibility of the data. Also note that the errors associated with the estimation of the rate constants are indicated by error bars, all of which actually lie within the size of the diamond-shaped symbols used to mark the data on the plot. Using the Polanyi–Wigner equation ($\ln k = \ln A - E_a/RT$) the energy of activation and the preexponential factor were determined: $E_a = 79.2 \pm 0.9$ kJ/mol and $A = 1 \times 10^{10.8 \pm 0.3}/s$. Errors are reported to the 95% confidence level. The energy of activation extracted from the 0.26 L TDS using Redhead’s method (assuming $A = kT/h = 1 \times 10^{12.83}/s$) yielded a value of 85 kJ/mol.²⁶ This value is nearly double the desorption activation energy found for propene on Ag(110).

The value calculated for the preexponential factor is low compared to most preexponential factors for unimolecular desorption processes which typically range from $10^{13}/s$ to $10^{19}/s$.²⁷ Results from Pawela-Crew and Madix indicate that propene adsorbed on Ag(110) experiences repulsive lateral interactions and stronger bonding interactions with the surface than propene.²³ They calculate the preexponential factors for three 2-D

adsorbed states from transition state theory: freely mobile, hindered translational motion, immobile. A freely mobile adsorbed state, a 2-D ideal gas, exhibits a preexponential, $A = 10^{13}/s$, at 300 K. The immobile state, with no degrees of freedom, yields $A = 10^{17}/s$, again at 300 K. The hindered state will have a preexponential between these two extremes. Pawela-Crew and Madix calculated a preexponential, using a TDS leading edge analysis, of $A = 10^{15}/s$, indicating an adsorbed state with hindered translational degrees of freedom.

Clearly, the preexponential factor calculated for propene/Pd-(111) from this work is somewhat lower than even that for a freely mobile adsorbed state. Since the uptake of propene is linear with exposure even at high exposures (i.e., a constant sticking coefficient) indicating precursor mediated adsorption, then it should not be surprising that propene can exist in a 2D gas prior to desorption, as well. Thus, it is not unexpected that the preexponential factor would lie toward the low end of the possibilities. However, a value for first-order desorption that is smaller than kT/h requires a negative entropy of activation—somewhat hard to imagine for desorption. Perhaps the transition state to desorption requires a preferred orientation or occurs from a specific site, such that the propene is more constrained than when it exists solely in the 2D gas. Other explanations for low prefactors might include an unaccounted coverage dependence or the presence of competing processes. However, coverage dependence would show up as a distinct curvature in the $\ln(\text{signal})$ versus time plots, but none is observed. Finally, the system may not follow an Arrhenius behavior in which a single reaction order remains constant and treating it as such could lead to errant results.²⁸ This is especially true of systems in which lateral interactions are strong between adsorbed species. This is unlikely here, since the interaction energies for alkenes are likely to be insignificant relative to the desorption energies measured.

IV. Conclusion

In summary, LITD/FTMS has been used to study the interaction of propene on Pd(111). Desorption of propene is the major process observed. No newly formed organic species were directly detected. Some decomposition was observed (<10%), as evidenced by H_2 evolved from propene during desorption. Rates for the desorption of 0.26 L propene were determined using first-order kinetics, and an Arrhenius plot yielded an activation energy of 79.2 ± 0.9 kJ/mol and a preexponential of $1 \times 10^{10.8 \pm 0.3}/s$.

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