Structure and decomposition pathways of vinyl acetate on Pd(111)

Florecia Calaza a, Dario Stacchiola a, M. Neurock b, Wilfred T. Tysoe a,*

a Department of Chemistry and Biochemistry, Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
b Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904-4741, USA

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Abstract

The surface chemistry of vinyl acetate on clean Pd(111) is explored experimentally in ultrahigh vacuum using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) combined with density functional theory (DFT) calculations. The relative intensities of the vibrational features of a vinyl acetate overlayer are in good agreement with the structure calculated by DFT. Furthermore, the calculated heat of adsorption of vinyl acetate (63.4 kJ/mol) is in excellent agreement with the measured desorption activation energy (65 ± 7 kJ/mol). The thermal decomposition pathways of adsorbed vinyl acetate are relatively complex involving initial cleavage of the O-acetyl or O-vinyl bonds to form either vinyloxy and acetyl, or acetate and vinyl species, respectively on the surface. The acetate thermally decomposes to desorb methane at ~260 K, while the acetyl and vinyloxy species isomerize and react to form acetaldehyde or methane. Ethylidyne is formed, and adsorbed CO either desorbs or oxidizes to CO2 at ~450 K.

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1. Introduction

Several million tones of vinyl acetate monomer (VAM) are produced annually to provide a feedstock for the manufacture of adhesives, paints and textiles. The palladium-catalyzed synthesis of vinyl acetate monomer (VAM) from acetic acid, ethylene and oxygen was discovered some thirty years ago [1]. It has been shown that vinyl acetate is formed on clean Pd(111) by reaction between adsorbed ethylene and acetate species [2]. The reaction proceeds via ethylene insertion into the

* Corresponding author. Tel.: +1 414 229 5222; fax: +1 414 229 5036.
E-mail address: wtt@uwm.edu (W.T. Tysoe).
adsorbed acetate species to form an acetoxyethyl-palladium intermediate, which decomposes via β-hydride elimination to yield vinyl acetate [3, 4]. Despite its commercial interest, there have been no previous studies of the chemistry of vinyl acetate itself on clean palladium surfaces. We experimentally examine the adsorption mode, structure, and energy of vinyl acetate along with its thermal decomposition pathways over the Pd(111) surface herein using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) to help provide insight into the reaction pathways of VAM. The selectivity to vinyl acetate is a central issue for the catalytic reaction, where total combustion products, CO₂ and water, can arise from combustion of ethylene [5–7], acetic acid [8] or vinyl acetate. Understanding the chemistry of vinyl acetate on Pd(111) will provide insights into the latter chemistry.

It is, in principle, possible to obtain adsorbate geometries using group theory and by exploiting the infrared surface selection rules [9]. However, given the relatively large size of vinyl acetate and its inherently low symmetry, this task is facilitated by using density functional theory (DFT) calculations to obtain proposed adsorption sites and structures along with simulated vibrational frequencies for comparison with infrared spectra. Temperature-programmed desorption (TPD) is used to estimate the heat of adsorption of vinyl acetate on the palladium surface in order to compare with values calculated by DFT and provide further corroboration of the proposed surface structure. The thermal decomposition pathways are also studied using a combination of TPD to monitor decomposition products and RAIRS to identify the nature of the surface intermediates.

2. Experimental methods

Infrared data were collected using a system that has been described previously [10]. Briefly, a palladium single crystal was mounted in a modified 2 3/4" six-way cross, equipped with infrared-transparent, KBr windows. It could be resistively heated to 1200 K, or cooled to 80 K using liquid nitrogen. Infrared spectra were collected using a Bruker Equinox infrared spectrometer and a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO₂-free air. Data were typically collected for 1000 scans at 4 cm⁻¹ resolution.

Temperature-programmed desorption (TPD) data were collected in another ultrahigh vacuum chamber that has been described in detail elsewhere [11] using a heating rate of 3 K/s, were desorbing species were detected using a Dichor quadrupole mass spectrometer placed in line of sight of the crystal.

The Pd(111) sample was cleaned using a standard procedure that consisted of heating to 1000 K in ~4 × 10⁻⁸ Torr of oxygen and then annealing at 1200 K in vacuo to remove any remaining oxygen. Since a strong palladium peak effectively obscures the carbon KLL Auger feature, Auger spectroscopy is insensitive to the presence of small amounts of surface carbon. A sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly. The complete absence of carbon is indicated by desorption of only O₂.

Vinyl acetate (Aldrich, 99+%)) and d₆-vinyl acetate (Polymer Sources, 98%) were transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers and further purified by several freeze–pump–thaw cycles. The cleanliness of all reactants was monitored mass spectroscopically.

3. Theoretical methods

First-principle periodic density functional theory (DFT) calculations were carried out using the DMol3 code by Delley [12, 13] as implemented in Materials Studios 3.0 [14]. The wavefunction was expanded in terms of numerical basis sets of double numerical quality (DNP) with d-type polarization functions for each atom. The core electrons for the palladium atoms here were mod-
eled using effective core pseudopotentials by Dolg [15] and Bergner [16], which explicitly treat scalar relativistic corrections. The wavefunctions were confined within a 3.5 Å real space cutoff. The density was calculated using a multipolar expansion and integrated using a grid that contains up to 1000 points per atom. All calculations were performed spin unrestricted. The Perdew-Wang 91 form of the generalized gradient approximation (GGA) was used to model the gradient corrections to the correlation and exchange energies. The electronic energies were calculated using a 2 × 2 × 1 k-point grid mesh to sample the first-Brillouin zone. The density was converged within each self-consistent field iteration to within 5 × 10⁻⁴ a.u. To facilitate SCF convergence, Fermi statistics were used to determine the fractional electron occupation around the Fermi level. The energy in each geometry optimization cycle was converged to within 1 × 10⁻⁴ a.u. The gradient was converged to within 2 × 10⁻² Å.

The bulk lattice constant was optimized yielding a value close to the experimental bulk lattice constant of 2.75 Å, which was used in all subsequent calculations. The metal surface was modeled using a 2 × 2 unit cell comprised of four layers of Pd atoms with 10 Å of vacuum, which separates the slab in the z-direction. One adsorbate was used per unit cell thus yielding a 1/4 ML coverage. The top two Pd layers were allowed to relax within the geometry optimization. The lower two were held fixed at their bulk lattice positions. Adsorption energies were calculated by the following expression, which is commonly used:

\[ \Delta E_{\text{Ads}} = E_{\text{VAM/Pd(111)}} - E_{\text{VAM}} - E_{\text{Pd(111)}} \]  

A negative value implies that the adsorption is exothermic. The reported frequencies were calculated using numerical differences with step sizes of 0.01 a.u.

4. Results

The RAIRS spectra of 1.5 L of vinyl acetate adsorbed on Pd(111) at 100 K are displayed in Fig. 1 as a function of exposure, where exposures are marked adjacent to the corresponding spectra, along with the effects of heating to various temperatures. The annealing temperatures are also displayed adjacent to each of the corresponding spectra. These data were obtained by heating the sample to the indicated temperature for 5 s and allowing the sample to cool to 100 K once again, following which the RAIR spectrum was collected. The spectrum obtained at 100 K displays a number of prominent peaks, all of which are due to vinyl acetate itself indicating molecular adsorption at this temperature. The peak positions and their assignments are summarized in Table 1 [17]. The infrared spectrum of the vinyl acetate multilayer is in excellent agreement with that of the liquid. Heating the surface to 156 K results in a diminution of many of the features evident in the spectrum obtained at 100 K. Note, however, that the relative intensities of the features obtained by heating to 156 K are different from those found at lower exposures following adsorption at 100 K, but without substantial differences in vibrational frequencies. As will be shown below, the 100-K spectrum includes first, second, and subsequent layers of vinyl acetate. The multilayer desorbs from the surface at ~137 K (see below) so that the 156-K spectrum is due to the presence of a saturated overlayer of vinyl acetate on the surface. The intensity of the C=O stretching mode (1758 cm⁻¹) of the vinyl acetate monolayer is considerably attenuated compared to that for the multilayer (at 1768 cm⁻¹) indicating that the C=O bond is oriented close to parallel to the surface, while the C=C mode (1649 cm⁻¹) is completely absent, implying that the vinyl C=C bond is parallel to the surface. This is confirmed by the detection of trans-CH (958 cm⁻¹) and =CH₂ (883 cm⁻¹) wagging modes. The methyl asymmetric deformation mode is relatively weaker in the monolayer (1433 cm⁻¹) than the multilayer (1428 cm⁻¹), while the CH₃ rocking (1013 cm⁻¹) mode remains relatively intense, implying that the C-CH₃ bond is oriented close to parallel to the surface. The intense 1245 cm⁻¹ mode (C–C–O stretch) shifts to ~1219 cm⁻¹ so that the 1245 cm⁻¹ mode is assigned to the multilayer, while the 1219 cm⁻¹ mode is due to the vinyl acetate monolayer. This mode is evident as a shoulder in the 100-K RAIRS spectrum. Note also that
there are slight frequency shifts between the monolayer and multilayer spectra indicating interaction with the surface.

Further heating of the monolayer-covered surface induces additional changes to the infrared spectra. All of the features due to adsorbed vinyl...
acetate decrease in intensity on heating to 208 (Fig. 1) and 237 (Fig. 2) K, while the C\text@symbol@O stretching mode disappears completely, suggesting that the C\text@symbol@O bond is completely parallel to the surface. An additional feature, however, appears at 1402 cm\textsuperscript{-1} when the surface is heated to 208 K, which intensifies at 237 K. Drastic changes occur on heating to 290 K. First, all vinyl acetate features are absent indicating that all of the vinyl acetate has desorbed or decomposed by this temperature. In addition, the intermediate yielding a feature at 1402 cm\textsuperscript{-1} has also disappeared. The spectrum now exhibits distinct features at 1087 and 1767 cm\textsuperscript{-1}, and some intensity at 1578 cm\textsuperscript{-1}, and a very weak feature at \~1333 cm\textsuperscript{-1}. The feature at 1767 cm\textsuperscript{-1} indicates the continued presence of C\text@symbol@O-containing species at this temperature. These species remain on heating to 354 K where the 1087 cm\textsuperscript{-1} peaks shifts slightly to 1079 cm\textsuperscript{-1} and decreases substantially in intensity and the 1578 cm\textsuperscript{-1} feature intensifies and shifts slightly to 1587 cm\textsuperscript{-1}. These modes disappear completely when the sample is heated to 373 K (Fig. 1). The C\text@symbol@O stretching mode shifts to above \~1800 cm\textsuperscript{-1} when the sample temperature exceeds 354 K, indicative of carbon monoxide formation and the carbon monoxide feature almost disappears on heating to 490 K. Accompanying these changes is the growth of a feature at \~1333 cm\textsuperscript{-1}, which reaches its maximum intensity on heating to 373 and 417 K, and completely disappears at 490 K.

The corresponding spectra for d\textsubscript{6}-vinyl acetate are shown in Fig. 2 and the assignments for a perdeuterated vinyl acetate monolayer are summarized in Table 1. The infrared spectra for d\textsubscript{6}-VAM (Fig. 2) shows similar drastic changes on heating. At 237 K, the majority of the features are due to the continued presence of a small amount of VAM on the surface and the growth of an intense feature at 1401 cm\textsuperscript{-1}, corresponding to the 1402 cm\textsuperscript{-1} peak found for normal VAM (Fig. 1), indicating that the vibrational normal mode does not involve hydrogen, which is assigned to an acetate species [2,3,18]. Heating the surface to 290 K diminishes the intensity of the acetate mode and yields additional features at \~1565, 1092 and 960 cm\textsuperscript{-1}, a shift of the CO stretching mode to \~1790 cm\textsuperscript{-1} and a shift in the feature at \~1565 cm\textsuperscript{-1} to 1587 cm\textsuperscript{-1}. Heating to 390 K and above causes these features to disappear, and CO is formed on the surface as indicated by the intense peak above 1800 cm\textsuperscript{-1}. Further heating to \~490 K caused the CO vibrational features to disappear (not shown), as found in Fig. 1.

Fig. 3 displays the temperature-programmed desorption spectra of 1.5 L of vinyl acetate adsorbed onto Pd(111) at 90 K collected using a heating rate of 3 K/s. An intense desorption state

### Table 1

<table>
<thead>
<tr>
<th>Experimental frequency/cm\textsuperscript{-1}</th>
<th>Calculated frequency/cm\textsuperscript{-1}\textsuperscript{(a)}</th>
<th>Assignment [17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal VAM</td>
<td>d\textsubscript{6}-VAM</td>
<td></td>
</tr>
<tr>
<td>1768</td>
<td>1762</td>
<td>1771, 1745</td>
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<td>1727</td>
<td>–</td>
<td>1726, 1711</td>
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<tr>
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<td>1582</td>
<td>1627, 1687</td>
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<tr>
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<td>–</td>
<td>1456</td>
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<tr>
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<td>–</td>
<td>1284</td>
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<td>1017, 1011</td>
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<tr>
<td>958</td>
<td>–</td>
<td>946</td>
</tr>
<tr>
<td>883</td>
<td>–</td>
<td>818</td>
</tr>
</tbody>
</table>

\textsuperscript{(a)} VAM vibrational frequencies calculated using DFT as indicated in the text.
is detected at \( \sim 137 \) K with significant intensity at 44, 43, 29, 27, and 26 amu. A very weak signal is detected at 45 amu (note that the 45-amu trace is multiplied by a factor of 10), which, together with intensity at 43 amu, would have indicated desorption of acetic acid. The relative intensities of the features observed at \( \sim 137 \) K are in good agreement with the mass spectrometer ionizer fragmentation pattern of pure vinyl acetate measured using the same mass spectrometer. This feature
continues to grow with increasing vinyl acetate dose and is therefore assigned to desorption of second and subsequent layers of molecular vinyl acetate. The desorption temperature is also in accord
with the infrared spectra, which indicate that the vinyl acetate multilayer is removed by heating to 156 K (Figs. 1 and 2). A peak is also detected at 262 K with a fragmentation pattern corresponding to molecular vinyl acetate and is assigned to desorption of vinyl acetate from the palladium surface in accord with the infrared data (Figs. 1 and 2) showing that the vinyl acetate on the surface is completely removed by heating to 290 K. Assuming that the desorption pre-exponential factor lies between $1 \times 10^{11}$ and $1 \times 10^{14}$ s$^{-1}$, and using the experimental heating rate of 3 K/s yields a desorption activation energy of vinyl acetate from Pd(111) of 65 ± 7 kJ/mol [19].

Several additional desorption states are detected at higher temperatures due to vinyl acetate decomposition products. A broad hydrogen (2 amu) desorption state is detected centered at 335 K, where hydrogen desorption commences at ~270 K indicating that a small amount of vinyl
acetate decomposition is underway coincident with monolayer desorption. A much weaker 2-amu desorption state is also observed at \( \sim 450 \text{ K} \).

Sharp features are detected at \( \sim 282 \text{ K} \) with fragments at 15 and 16 amu assigned to some methane desorption. A broad desorption state is observed centered at \( \sim 310 \text{ K} \) with intensity at 26, 27, 28, 29, 43 and 44 amu, with the 29 amu (CHO) feature being the most intense, but with no intensity at higher masses. Based on the relative desorption intensities at various masses, this is assigned to acetaldehyde desorption from the surface. A broad, intense feature centered at \( \sim 336 \text{ K} \) is also detected with intensity at 15 and 16 amu, again assigned to methane desorption. The trailing edges of both the acetaldehyde and methane desorption states coincide with the trailing edge of the most intense, 330-K hydrogen desorption state implying that they arise from the hydrogenation of adsorbed species from the decomposition of vinyl acetate.

Higher-temperature desorption states are detected at \( \sim 460 \text{ K} \) at 27 and 29 amu, where the trailing edges, in this case, coincide with the high-temperature hydrogen (2 amu) desorption state, again implying that these arise from the hydrogenation of surface species. There may be some desorption intensity at 28 amu associated with this desorption state, however, this is obscured by the intense CO (28 amu) desorption state centered at \( \sim 470 \text{ K} \). The infrared spectrum indicates that the surface contains predominantly CO on heating to 390 K (Fig. 1) and this desorbs as either CO at \( \sim 470 \text{ K} \) or is oxidized to \( \text{CO}_2 \) to desorb at \( \sim 450 \text{ K} \).

The optimized structure for a 1/4 ML coverage of vinyl acetate on Pd(111) was calculated by using DFT. Various different configurations for the adsorption of VAM were explored as a result of how the ethylene and acetate groups bind to the surface. We examined ethylene in both di-\( \sigma \) and \( \pi \)-bonded configurations and acetate bound with its molecular plane parallel and perpendicular to the surface. The most stable configuration was one in which ethylene binds in the di-\( \sigma \) configuration and acetate binds in a configuration where it is slightly tilted off of the parallel and oriented away from the surface. The more perpendicular configuration of acetate was found to be 42 kJ/mol less stable. The most stable structure predicted from theory is shown in Fig. 4. The vinyl group here is somewhat rehybridized and the carbon–carbon bond is oriented approximately parallel to the surface. This adsorption geometry constrains the OCO group to be oriented close to parallel to the surface with both the C=O and the C–CH\(_3\) bonds being oriented only slightly away from the surface. The acetate group itself remains planar. The heat of adsorption of vinyl acetate, calculated from the difference in energy between the adsorbate-covered surface and the clean surface plus gas-phase vinyl acetate (Eq. (1)), for the adsorbed species depicted in Fig. 4, is 63.4 kJ/mol.

5. Discussion

5.1. Geometry of vinyl acetate on clean Pd(111)

Using the surface selection rules in RAIRS [9], the infrared spectrum of vinyl acetate adsorbed on Pd(111), formed by heating to 156 K (Fig. 1), indicates that the carbon–carbon bond of the vinyl group is very close to parallel to the Pd(111) surface, while the C=O and C–CH\(_3\) bonds of the acetate group are slightly tilted away from the surface. The measured frequencies (Table 1) and orientations are in excellent agreement with the frequencies for the optimized structure calculated using DFT (Table 1 and Fig. 4). There are some additional changes in the relative intensities of the infrared modes due to vinyl acetate on heating to 208 K, as well as an attenuation of all features connoting the desorption of VAM. At this temperature, the C=O stretching mode is completely absent indicating that the C=O bond is completely parallel to the surface. Moreover, the relative intensities of the VAM modes at low exposures (0.6 L) immediately following VAM adsorption at 100 K (Fig. 1) are completely different from those obtained after heating the surface to 156 K. In particular, the relative intensities of the vibrational modes at low coverages are close to those found for the multilayer indicating that metastable, rather randomly adsorbed species are formed at \( \sim 130 \text{ K} \), and that the formation of the most
stable structure depicted in Fig. 4 is slightly activated.

The disappearance of the intense molecular vinyl acetate vibrational features on heating to 156 K (Fig. 1) confirms that the 137 K TPD feature (Fig. 3) is due to multilayer desorption. This assignment is confirmed by the observation that this feature grows continually without showing signs of saturating as the VAM exposure increases. An additional VAM desorption state is found at 262 K (Fig. 3). The attenuation of the features assigned above to VAM adsorbed on the Pd(111) surface on heating to 237 K, and their disappearance after heating to 290 K, confirms that the 262 K feature in TPD is due to chemisorbed vinyl acetate. The desorption activation energy of vinyl acetate adsorbed on the Pd(111) surface is estimated from the Redhead equation [19] to be 65 ± 7 kJ/mol. Since a vinyl acetate multilayer appears after a vinyl acetate dose of only 1.5 L, this implies that the sticking probability of vinyl acetate on Pd(111) is relatively large indicating that adsorption is not strongly activated and suggests that the desorption activation energy should be close to the vinyl acetate heat of adsorption. The measured \( \Delta H_{\text{ads}} \) (vinyl acetate) = 65 ± 7 kJ/mol is in excellent agreement with the heat of adsorption calculated using DFT of 63.4 kJ/mol. This agreement provides additional evidence that the calculated structure is correct.

5.2. Vinyl acetate decomposition pathways

The decomposition pathways of vinyl acetate on Pd(1 1 1) are relatively complex. However, apart from CO and CO\(_2\) desorption at high temperatures, a common feature of the remaining desorption states is that they appear over the range of temperatures at which hydrogen desorption is observed, and the trailing edges of desorption features are coincident with the trailing edges of the hydrogen (2 amu) desorption profiles. This implies that desorption products arise from hydrogenation of the surface fragments formed by vinyl acetate decomposition. Decomposition starts at temperatures close to or slightly higher than the vinyl acetate desorption temperature (~260 K). Three major desorption states are detected between ~250 and 400 K, consisting of methane (282 and 336 K) and acetaldehyde (310 K). Methyl species grafted onto Pd(1 1 1) by reaction with methyl iodide reacts with hydrogen to yield methane at between ~190 and 210 K [20] indicating that methane formation is decomposition- rather than reaction-rate limited. This implies therefore that the two methane desorption states originate from two distinct precursors.

The first methane desorption state is centered at ~282 K, and correlates well with the growth and disappearance of the acetate feature at ~1402 cm\(^{-1}\) (Fig. 1). This frequency is close to that found for acetate species formed from acetic acid on Pd(1 1 1) [18] and this assignment is consistent with the lack of isotope shift when d\(_6\)-VAM is adsorbed on the surface (Fig. 2). However, the acetate mode persists to higher temperatures when formed from d\(_6\)-VAM consistent with a decomposition reaction involving hydrogen abstraction [21,22]. The decomposition temperature is also lower than that found for a saturated overlayer of acetate species on Pd(1 1 1) [18]. However, it has been shown theoretically that the thermal decomposition of acetate species is initiated by a rocking of the OCO plane to allow the methyl hydrogen to access the surface [21,22]. This motion is inhibited when the surface is saturated by acetate species. In this case, acetate species are proposed to form from VAM, much of which desorbs from the surface at ~260 K, leading to a relatively low acetate coverage, which diminishes the extent of crowding and facilitates the thermal decomposition of the acetate. The formation of acetate species is presumably accompanied by the formation of vinyl groups on the surface. Vinyl species on Pd(1 1 1) hydrogenate to ethylene below 300 K [23], but no 28 amu intensity is observed in this temperature range, and also convert to ethyldyne species. The infrared spectrum of vinyl species is extremely weak. However, the appearance of a feature at ~1333 cm\(^{-1}\) at ~290 K, which intensifies with increasing temperature is consistent with the presence of ethyldyne species, which have an intense peak at this frequency [24]. This peak disappears on heating to ~490 K (Fig. 1) and is accompanied by a weak hydrogen desorp-
tion feature at ~460 K, typical of ethyldyne decomposition [24].

An additional vinyl acetate decomposition pathway that occurs at slightly higher temperatures (~290 K) is evidenced by additional features that appear at 1767, ~1578 and 1087 cm\(^{-1}\) from vinyl acetate (Fig. 1) and at 1765, ~1565, 1092 and 960 cm\(^{-1}\) from perdeuterated VAM (Fig. 2). All vinyl acetate has desorbed from the surface by this temperature and no acetylate species remain on a d\(_{0}\)-vinyl acetate pre-covered surface, while some acetate species remain following d\(_{3}\)-VAM exposure due to the isotope effect described above.

Heating a surfaces dosed with d\(_{0}\)-VAM to ~354 K shifts the 1578 cm\(^{-1}\) mode to ~1587 cm\(^{-1}\) and causes the 1767- and 1087 cm\(^{-1}\) modes to diminish significantly in intensity. Heating a d\(_{3}\)-VAM covered surface to ~340 K causes the 1565 cm\(^{-1}\) mode to shift to ~1587 cm\(^{-1}\), the 1765 cm\(^{-1}\) mode to decrease somewhat in intensity and the 1092- and 960 cm\(^{-1}\) modes to be only slightly affected. These surface species form on heating from 237 to 290 K for both normal and perdeuterated VAM, implying that their formation pathway does not involve dehydrogenation. This suggests that they are formed by an acetyl-O bond scission pathway, which would yield isomeric acetyl (CH\(_{3}\)C=O) and vinyloxy (CH\(_{2}\)CHO–) groups. The detection of acetaldehyde desorbing at ~310 K (Fig. 3) is consistent with the presence of acetyl species on the surface. If VAM indeed decomposes by O-acetyl bond scission, the infrared spectrum collected after annealing a VAM-saturated surface to 290 K (Fig. 1) should result in features consistent with a combination of surfacel-bound acetyl and vinyloxy groups. There are no available fingerprint spectra for vinyloxy species on Pd(111) for direct comparison. The feature at 1087 cm\(^{-1}\) is consistent with vinyloxy C–O stretching modes [25,26] and the C=\(^{13}\)C stretching mode of vinyl alcohol has a frequency of ~1628 cm\(^{-1}\) [17,26]. Acetals have been detected on various surfaces where a \(\eta^2\)-(C,\(^{13}\)O) acetyl species exhibits a C–O stretching frequency of 1425 cm\(^{-1}\) and symmetric methyl deformation frequency of 1340 cm\(^{-1}\) [27]. An \(\eta^1\)-acetyl species detected on Pt(111) has a C–O stretching mode at ~1600 cm\(^{-1}\) and a symmetric methyl deformation mode at 1355 cm\(^{-1}\), which shifts to ~1150 cm\(^{-1}\) for CD\(_{3}\)CO [28]. As expected, the C=O stretching frequency is unaffected by deuteration. Acetyl C=O stretching frequencies of ~1595 cm\(^{-1}\) have been measured on Pd(111) [29], and at 1650 cm\(^{-1}\) on sulfur-covered platinum [30]. Thus, the feature at 1087 cm\(^{-1}\) (Fig. 1) can be assigned to the C–O stretching mode of a vinyloxy species and shifts only slightly on deuteration to 1092 cm\(^{-1}\) (Fig. 2). Based on the above discussion, the feature at ~1578 cm\(^{-1}\) at 290 K and 1588 cm\(^{-1}\) at 354 K (Fig. 1) are consistent with both the C=C stretching mode of a vinyloxy (compared with ~1628 cm\(^{-1}\) for vinyl alcohol [26]) and the C=O vibration of a \(\eta^1\)-acetyl species (compared with ~1595 cm\(^{-1}\) on Pd(111) [29]). As noted above, no isotope shift of the acetyl C=O stretching mode is found on deuteration of the methyl group, while the C=C stretching vibration of vinyl alcohol shifts slightly by ~11 cm\(^{-1}\) when CH\(_{2}\) is replaced by CD\(_{2}\) [26]. This suggests that the feature at ~1578 cm\(^{-1}\) formed at ~290 K is due to a vinyloxy species since it shifts to ~1565 cm\(^{-1}\) on deuteration. In contrast, the feature appearing at ~1587 cm\(^{-1}\) when the surface is heated to 354 K (Fig. 1) shows no detectable isotope shift (Fig. 2) implying that it is due to an \(\eta^1\)-acetyl species. This suggests that vinyloxy species can isomerize to form acetyl species at 345 K, consistent with the decrease in intensity of the 1087 cm\(^{-1}\) mode on heating to 354 K. Vinyloxy species have been proposed previously as a product in the Pd(II)-catalyzed decomposition of vinyl acetate [31]. If the vinyloxy species are formed by acetyl-O bond scission at ~290 K, they should be accompanied by the direct formation of acetyl species. The feature at ~1578 cm\(^{-1}\) from normal VAM and at ~1565 cm\(^{-1}\) from d\(_{3}\)-VAM is sufficiently broad that this weak feature is difficult to distinguish. A weak feature is detected at ~1333 cm\(^{-1}\), assigned above to an ethyldyne species suggesting that the acetyl methyl deformation mode is too weak to be detected. The methyl deformation mode shifts to ~1150 cm\(^{-1}\) for CD\(_{3}\)CO on Pt(111), and the feature found at ~960 cm\(^{-1}\) following d\(_{3}\)-VAM adsorption may be due to a methyl deformation
mode. The acetyl species are removed by heating to $\sim$373 K (Fig. 1) and accompanied by the desorption of acetaldehyde and methane (Fig. 3) to deposit CO on the surface.

The origin of the feature at $\sim$1767 cm$^{-1}$ is not clear. It is clearly due to a C=O stretching mode, and its intensity, frequency and the lack of isotope shift on deuteration are consistent with this assignment.

Comparing the maximum absorbance of the acetate feature at $\sim$1402 cm$^{-1}$ (Fig. 1) with that of a saturated overlayer of acetate species on Pd(111) [3,18] indicates that at least $\sim$0.06 monolayers of acetate species are formed from vinyl acetate decomposition. Estimating the initial saturation coverage of chemisorbed vinyl acetate from the structure depicted in Fig. 4 suggests that approximately 50% of the initially adsorbed vinyl acetate decomposes to form acetate and vinyl species. Since TPD (Fig. 3) indicates that a proportion of the initially adsorbed vinyl acetate desorbs intact, this suggests that scission of the vinyl-oxygen bond is the major surface decomposition pathway. The proposed vinyl acetate reaction pathways are summarized in Scheme 1.

6. Conclusions

The relative intensities of the features in the infrared spectrum of a monolayer of vinyl acetate on Pd(111), as well as the heat of adsorption measured using TPD, are in excellent agreement with the predictions of DFT indicating that the carbon–carbon bond of the vinyl group is oriented essentially parallel to the (111) surface in a di-σ configuration and that the OCO plane of the acetate group is slightly tilted with respect to the surface. The thermal decomposition pathways of adsorbed vinyl acetate are relatively complex involving initial cleavage of the O-acetyl and O-vinyl bonds to form either vinyloxy and acetyl, or acetate and vinyl species, respectively, on the surface. The acetate thermally decomposes to desorb methane at $\sim$260 K, while the acetyl and vinyloxy species isomerize and hydrogenate to acetaldehyde or decompose to yield CO and methane.

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