

Chemistry of L-proline on Pd(1 1 1): Temperature-programmed desorption and X-ray photoelectron spectroscopic study

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Abstract

The surface chemistry of proline is explored on Pd(1 1 1) using a combination of temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy. Proline adsorbs on Pd(1 1 1) at temperatures of 250 K and below into second and subsequent layers prior to the saturation of the first layer, where approximately 70% of the adsorbed proline is present in its zwitterionic form. Molecular proline desorbs between ~ 315 K and ~ 333 K depending on coverage. When adsorbed at ~ 300 K, only the first monolayer is formed, and the proline is present as zwitterions, oriented such that all of the carbons are detected equally by XPS. Proline decomposes by scission of the C–COO bond, where the carboxylate moiety desorbs as carbon monoxide and carbon dioxide, while the nitrogen-containing moiety desorbs as to HCN, and evolves pyrrole at ~ 390 K, pyrrolidine at ~ 410 K, and final species that desorbs at ~ 450 K that cannot be unequivocally assigned but may be 2-butenitrile ($\text{CH}_3\text{--CH=CH--CN}$), 3-butenitrile ($\text{CH}_2\text{=CH--CH}_2\text{--CN}$), 2-methyl-2-propenenitrile ($\text{CH}_2\text{=C(CH}_3\text{)--CN}$) or cyclopropanecarbonitrile.

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1. Introduction

It has been demonstrated that enantioselective chemisorption occurs on Pd(1 1 1) in ultrahigh vacuum (UHV) when the surface is chirally modified by R- or S-2-butanol, where enhanced chemisorption of propylene oxide of the same chirality as the modifier is found over a narrow 2-butanol coverage range [1]. More recently, similar behavior was found on Pt(1 1 1) [2]. This effect was also observed on a surface modified by chiral 2-amino butanoic acid, while no enantioselectivity was detected when using 2-methyl butanoate. It was suggested that the freer azimuthal rotation of the chiral center in 2-methyl butanoate results in a loss of enantioselectivity, while an amino group anchors

the chiral center to the surface, thus restoring enantioselectivity [3]. In order to better understand the adsorption of α -amino acids on Pd(1 1 1) and probe their chemical stability, we have recently studied the adsorption, desorption and thermal dissociation of the simplest (non chiral) amino acid, glycine [4] and the simplest chiral amino acid, alanine [5], on Pd(1 1 1). It is found that both molecules adsorb predominantly in their zwitterionic forms on the surface and are stable to just above room temperature, where the major decomposition pathway is via cleavage of the OOC–C bond. The COO moiety further decomposes to desorb CO and CO₂ with approximately the same yields, while a portion of the nitrogen-containing moiety yields methylamine for glycine, and ethylamine for alanine. The remainder of the nitrogen-containing species dissociates further to form CN_(ads) and finally hydrogenates and desorbs as HCN above 400 K. It is expected, therefore, that other more complicated α -amino acids should dissociate in a similar

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manner. However, the existence of a pyrrolidine ring in proline makes it structurally different from other α -amino acids. In order to explore how the presence of a pyrrolidine ring modifies the surface chemistry of the amino acid, the adsorption and dissociation of L-proline is probed using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). L-Proline consists of a five-membered pyrrolidine ring (C_4H_8N-) with a carboxylate bonded to the carbon adjacent to the nitrogen to form $C_4H_8N-COOH$, thereby creating a chiral carbon in the ring.

2. Experimental

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber operating at a base pressure of 8×10^{-11} Torr that has been described in detail elsewhere [6]. The temperature ramp and data collection were controlled using LabView software. This chamber was also equipped with a double-pass cylindrical mirror analyzer for Auger spectroscopy measurements for monitoring sample cleanliness, and an ion-sputtering gun for sample cleaning. X-ray photoelectron spectra (XPS) were collected in another chamber operating at a base pressure of 2×10^{-10} Torr, which was equipped with a Specs X-ray source and double-pass cylindrical mirror analyzer also described elsewhere [4].

The Pd(111) substrate (1 cm diameter, 0.5 mm thick) was cleaned using a standard procedure, which consisted of cycles of argon ion bombardment (2 kV , $1 \mu\text{A}/\text{cm}^2$) and annealing in 4×10^{-8} Torr of O_2 at 1000 K [1]. The cleanliness of the sample was judged using XPS and oxygen titration where O_2 instead of CO desorbs following O_2 adsorption when the sample is carbon free. Following each TPD or XPS experiment, the sample is briefly annealed once again in O_2 to regain its cleanliness.

L-proline was adsorbed on the Pd(111) surface using an evaporation source, which was differentially pumped using a turbo-molecular pump as described elsewhere [4]. L-Proline powder (Aldrich, 99% purity) was stored in a stainless steel vial. The whole evaporation source was warmed by means of a heating tape and temperature was measured by a K-type thermocouple attached to the outer wall of the vial. Proline was typically outgassed for at least two hours at 350 K before adsorption. ^{13}CO (ISOTECH, $\geq 99\%$ ^{13}C) was used as received.

3. Results

3.1. Proline coverage measurements

It has been shown previously that at 250 K and below, glycine and alanine adsorb sufficiently strongly into second and subsequent layers that multilayer condensation commences onto a partially covered first layer [4,5]. In this case, the bare surface coverage Θ_0 is given by

$$\Theta_0 = \exp(-FSt)$$

where F is the incident flux, S the sticking probability, and t the dosing time. The total coverage Θ_{tot} is then given by

$$\Theta_{\text{tot}} = FS t.$$

Here it is assumed that the sticking probabilities on the clean and covered portions of the surface are identical and that the amino acid is not mobile during adsorption at low temperatures [4,5]. The results for glycine reveal that, at the point at which the monolayer saturates, a total of approximately 3 ML has been deposited onto the surface [4]. The data shown below suggest that proline grows in the same manner. The coverage of the bare surface was measured by titrating it using CO, where isotopically labeled ^{13}CO was used to distinguish it from the small amount of ^{12}CO formed by proline decomposition. Fig. 1 displays a series of 29 amu (^{13}CO) TPD traces collected after various proline dosing times onto initially clean Pd(111) held at 250 K, using an evaporation source temperature of ~ 350 K. The resulting peak areas are integrated and fit to an exponential decay (data not shown). This yields a value of $FS = 0.15 \pm 0.01$ ML/min. This enables the dosing time to be converted directly into proline coverage using the equation above and all subsequent data are labeled with the proline coverage determined in this way.

3.2. Low-temperature adsorption of proline: XPS measurements

XPS spectra were collected for proline adsorbed onto Pd(111) at a sample temperature of ~ 80 K, using a source

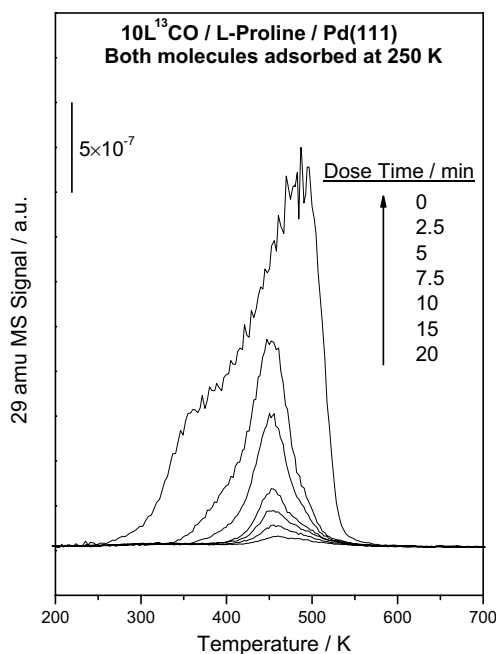


Fig. 1. ^{13}CO (29 amu) temperature-programmed desorption profiles collected following exposure of Pd(111) surfaces dosed with alanine to 10 L ($1 \text{ L} = 1 \times 10^{-6}$ Torr s) as a function of L-proline dose in minutes for a source temperature of ~ 350 K.

temperature of ~ 350 K. The sticking probability of proline does not vary as long as the Pd(111) substrate is kept at or below 250 K so that the above-derived dosing rate at a temperature of 250 K is applicable here. Fig. 2a displays the C 1s region of the spectrum following the adsorption of 3 ML of proline on the surface at 80 K and subsequently annealed to 340 and 400 K. The spectrum of the as-deposited proline displays two features at ~ 288.4 eV assigned to the COO carbon [7,8] and a more intense feature at

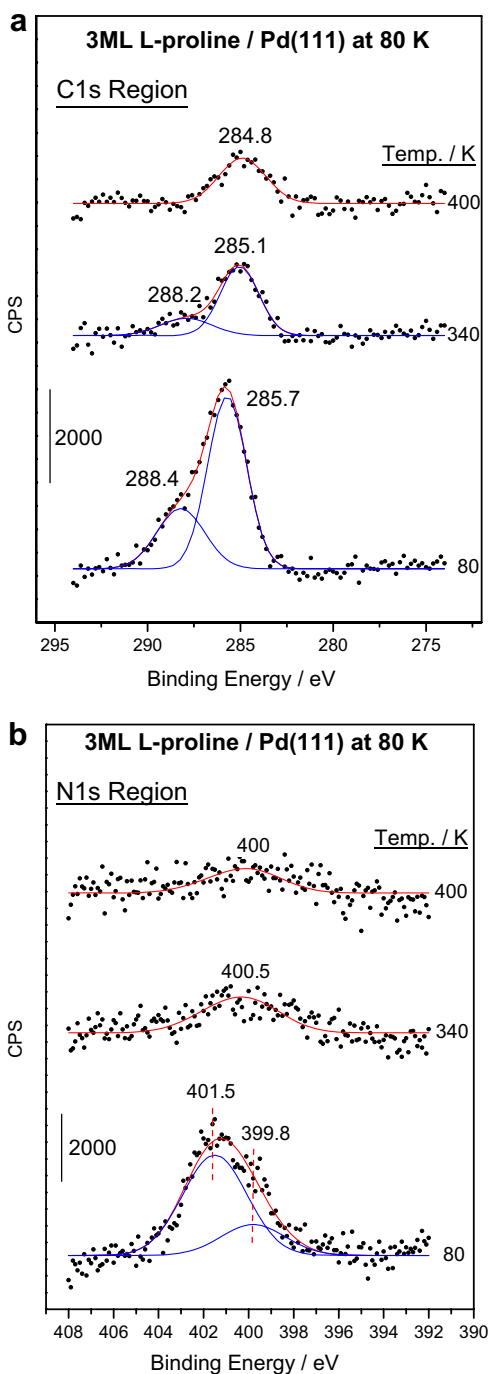


Fig. 2. (a) C 1s and (b) N 1s photoelectron spectra for 3 ML L-proline adsorbed at 80 K and subsequently annealed to 340 and 400 K.

285.7 eV due to carbons within the pyrrolidine ring. Lorentzian profiles are shown fitted to these features. The integrated intensity ratio of the ring-carbon to the COO feature is $\sim 2.5:1$, while the stoichiometry suggests that it should be 4:1. This is different from observations for both glycine and alanine on Pd(111) [4,5] and will be discussed in greater detail below. Upon annealing to 340 K, both the COO and ring-carbon signal intensities decrease, together with slight binding energy shifts to lower values. As will be shown below, this is due primarily to desorption from the multilayer and also to some degree of decomposition. After annealing to 400 K, the COO carbon signal completely disappears, indicating that proline has completely decomposed. The species remaining on the surface at this temperature display a C 1s feature at 284.8 eV.

The corresponding spectra for the N 1s region are displayed in Fig. 2b. The spectrum at 80 K displays two features, one at ~ 401.5 eV binding energy, assigned to NH_2^+ species due to the presence of zwitterionic proline, and the second at 399.8 eV assigned to $-\text{NH}-$ groups of neutral proline. Measurement of the peak areas suggests that $\sim 70\%$ of the proline is present in the zwitterionic form. Annealing to 340 K causes a significant signal intensity decrease in accord with Fig. 2a, due mainly to multilayer desorption. In this case the signal can no longer be separated into two components. A Lorentzian fit reveals a single feature centered at ~ 400.5 eV. Further annealing to 400 K causes further intensity and binding energy decreases of this feature.

3.3. Desorption and decomposition of adsorbed proline: temperature-programmed desorption

The decomposition and desorption of proline was explored in greater detail using temperature-programmed desorption (TPD). The mass spectrometer used in this study is capable of detecting masses from 1 to 100 amu so that the parent mass (at 115 amu) could not be monitored. However, 70 amu (due to the pyrrolidine ring fragment) can be used for this purpose, especially since this is the most intense fragment of proline [9]. Fig. 3 displays the desorption profiles at 70 amu as a function of proline coverage. At the lowest coverage (0.39 ML), molecular proline desorbs at 315 K, but the peak shifts slightly to higher temperatures at higher coverages. At a coverage of 4.5 ML, a desorption peak maximum is found at 333 K. Note that the high-temperature tails of these profiles extend up to ~ 500 K, suggesting some high-temperature desorption product(s) have fragments at 70 amu.

As has been described in the introduction section, both glycine and alanine decompose predominately through C–C bond cleavage to generate COO and nitrogen-containing species. In order to explore whether proline decomposes in a similar manner, additional masses were monitored. Fig. 4 displays desorption from 25 to 28 amu as a function of proline coverage. These show very similar behavior to glycine

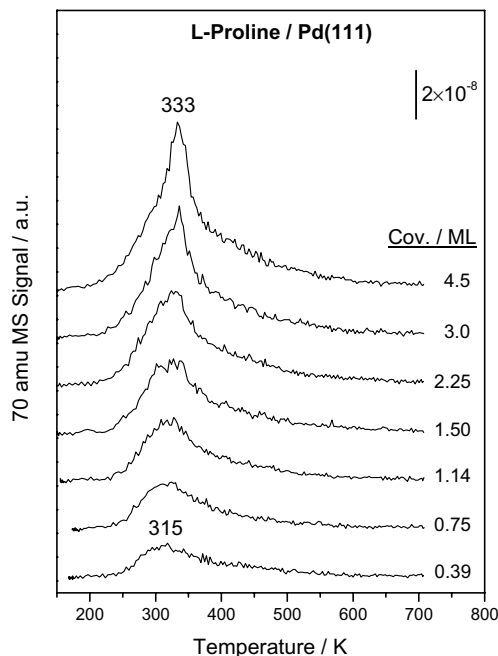


Fig. 3. Temperature-programmed desorption profiles (70 amu) for various coverages of L-proline on Pd(111) collected using a heating rate of 6.5 K/s, where the proline coverages are displayed adjacent to the corresponding spectrum.

and alanine [4,5]. CO (28 amu) desorbs at ~ 500 K at the lowest proline coverage, shifting to ~ 465 K at the highest coverage. A single desorption state is found at 26 and 27 amu for a proline coverage of 0.3 ML centered at 805 K. Starting from a coverage of 0.6 ML, a second

desorption state appears at ~ 560 K. These desorption states only occur at 26 and 27 amu confirming their assignment to HCN. The high-temperature desorption of HCN broadly resembles that found for glycine and alanine on Pd(111). However, in addition to these two desorption states, glycine has a sharp HCN desorption state at ~ 430 K [4], while alanine has a corresponding state at ~ 460 K [5].

Additional spectra were collected at 29, 30, 38, 39 and 40 amu and are displayed in Fig. 5. Both the 29 and 30 amu signals only display desorption intensity at 325 K. By comparing with the desorption profile at 70 amu (Fig. 3), it is evident that these are due to fragmentation of molecular proline. For masses at 38–40 amu, besides molecular desorption contributions, additional features are detected at 390 K. Fig. 6 presents the desorption profiles between 41 and 45 amu. The 41 amu signals resemble those from 38 to 40 amu, indicating that these are fragments of the same desorption product while the dominant component at 42 amu is due to fragmentation of molecular proline. However, weaker components are also found at 390 and 430 K. For desorption from 43 to 45 amu, besides fragmentation of molecular proline (at 325 K), strong features are found at 410 K at these three masses. Although these coincidentally desorb at the same temperature, their origins are vastly different. As will be shown below, desorption at 44 amu is due predominately to CO_2 , while desorption at 43 and 45 amu due to nitrogen-containing molecules.

Additional masses were monitored at a proline coverage of 3 ML to gain more information on the surface chemistry, especially the detailed reaction mechanism of pyrroli-

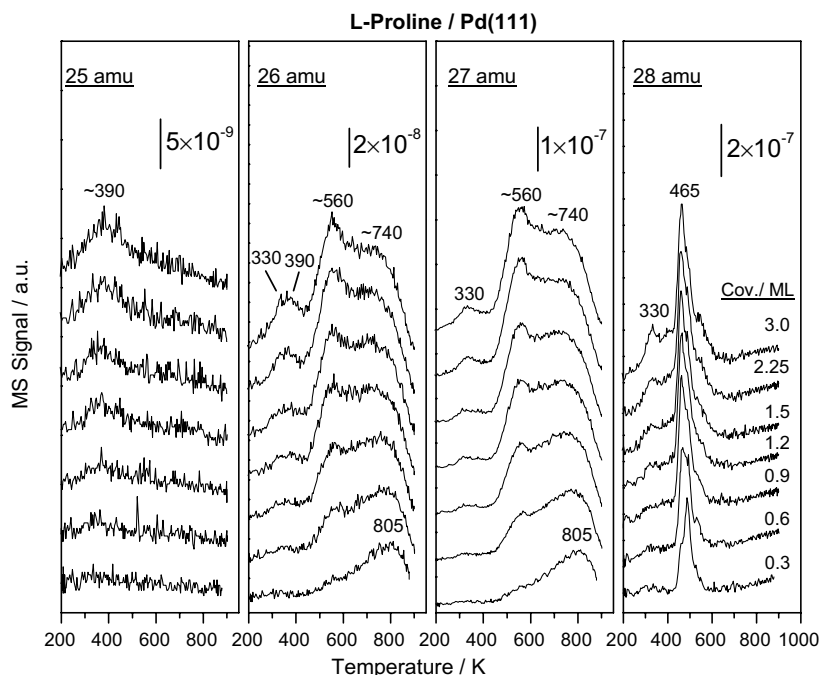


Fig. 4. Temperature-programmed desorption profiles (25, 26, 27 and 28 amu) for various coverages of L-proline on Pd(111) collected using a heating rate of 10.5 K/s, where the proline coverages are displayed adjacent to the corresponding spectrum.

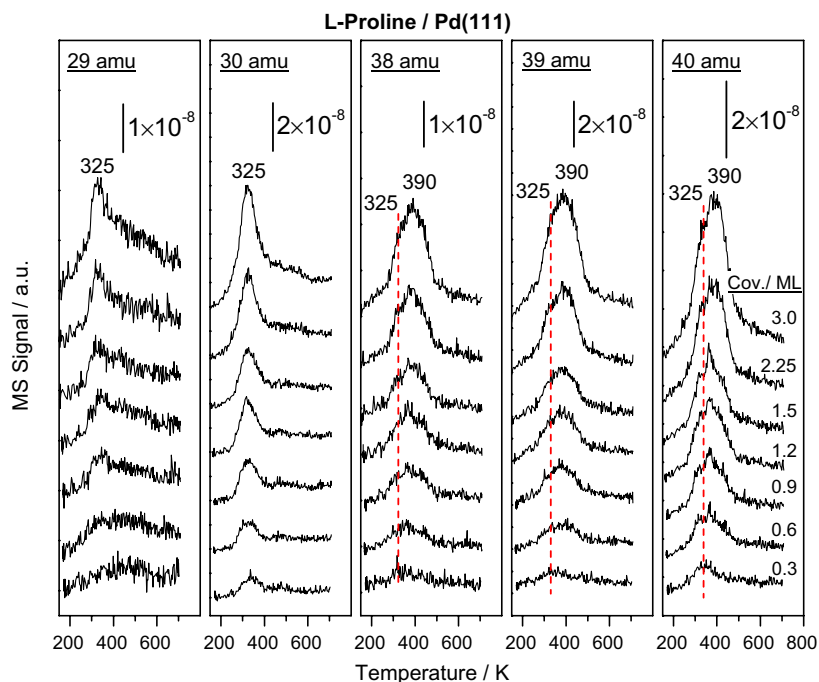


Fig. 5. Temperature-programmed desorption profiles (29, 30, 38, 39 and 40 amu) for various coverages of L-proline on Pd(111) collected using a heating rate of 6.5 K/s, where the proline coverages are displayed adjacent to the corresponding spectrum.

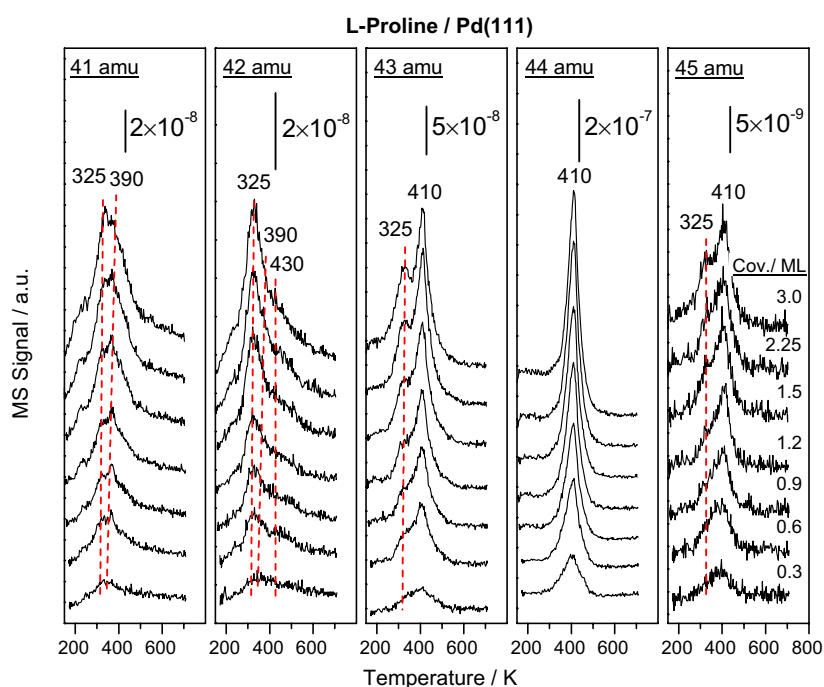


Fig. 6. Temperature-programmed desorption profiles (41, 42, 43, 44 and 45 amu) for various coverages of L-proline on Pd(111) collected using a heating rate of 6.5 K/s, where the proline coverages are displayed adjacent to the corresponding spectrum.

dine ring dissociation. Fig. 7 displays desorption of masses from 31 to 67 amu, except masses already displayed in previous figures. Fig. 8 presents desorption from 78 to 73 amu. A detailed assignment of these masses will be given below.

3.4. Room temperature adsorption of proline: XPS and TPD measurements

XPS measurement was performed following a 60-min exposure of proline to a Pd(111) sample at a temperature

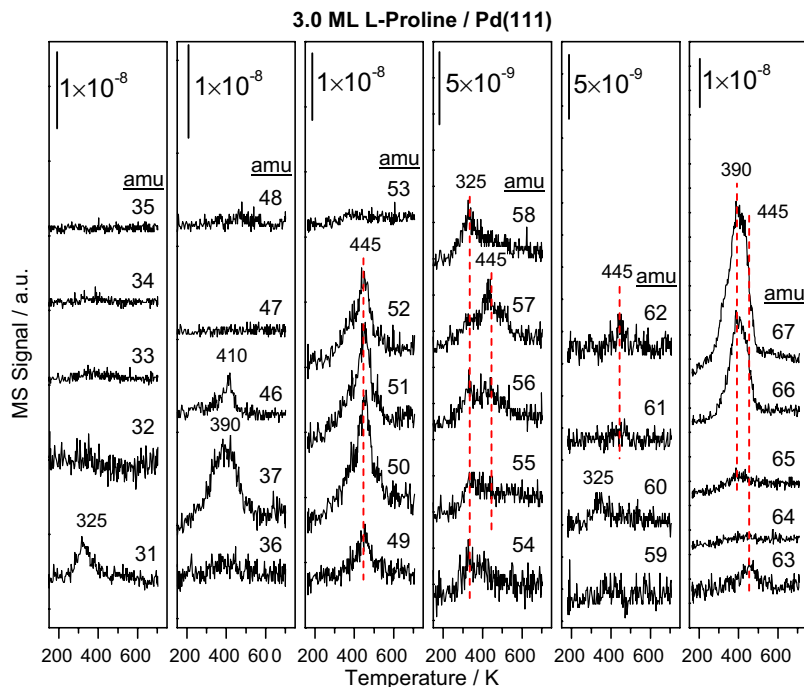


Fig. 7. Temperature-programmed desorption profiles for various masses of 3 ML L-proline on Pd(111) collected using a heating rate of 6.5 K/s, where the masses are displayed adjacent to the corresponding spectrum.

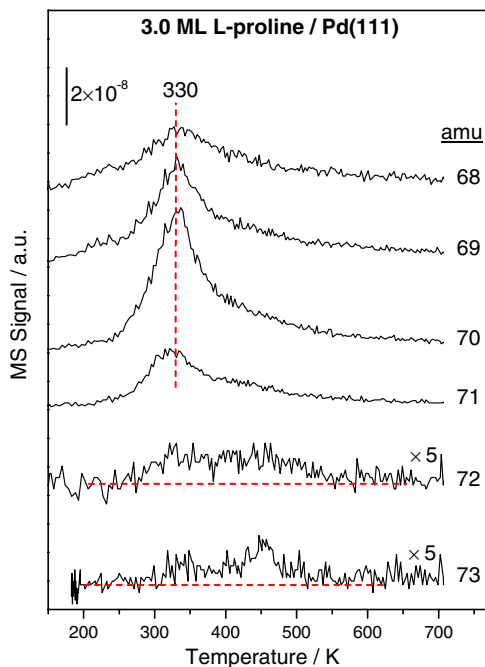


Fig. 8. Temperature-programmed desorption profiles (68, 69, 70, 71, 72 and 73 amu) of 3 ML L-proline on Pd(111) collected using a heating rate of 6.5 K/s, where the masses are displayed adjacent to the corresponding spectrum.

of 300 K. Since hot proline molecules impinge on the Pd surface, the final temperature reached ~ 310 K at the end of this process. Fig. 9a displays the resulting C 1s spectra. The as-deposited film (the bottom spectrum) displays two

features at ~ 288.3 eV assigned to the COO carbon and a more intense feature at 285.1 eV due to carbons within the pyrrolidine ring. Lorentzian profiles are shown fitted to each of these features. This spectrum shows marked differences from that following adsorption at 80 K (Fig. 2a). First, the area ratio of these two features is 1:4, different from the ratio of 1:2.5 shown in Fig. 2a and thus corresponds to the ratio expected from the stoichiometry. Second, the binding energies of these two features are lower than following 3 ML of proline shown in Fig. 2a. Annealing to 340 K decreases the signal intensities of both features suggesting desorption and/or dissociation occurs at this temperature. The COO signal disappears completely at 400 K indicating that by this temperature, proline has completely decomposed.

Fig. 9b presents the corresponding N 1s spectral region, which are again fit to Lorentzian profiles. A weak signal with a binding energy of 400.6 ± 0.4 eV is found following adsorption at 310 K. Note that this is also different from the N 1s spectra shown in Fig. 2b following adsorption at 80 K. This feature shifts to slightly lower binding energies on annealing to 340 and 400 K. Both the C and N 1s spectra obtained by adsorption at room temperature suggest that only the monolayer forms during room temperature adsorption. This is confirmed by increasing the adsorption time and finding no further C or N signal intensity increase (data not shown).

^{13}C O titration experiments were performed to measure the adsorption rate at room temperature (data not shown) and the resulting value (0.022 ML/min) is used to convert dosing time to coverages for room temperature TPD exper-

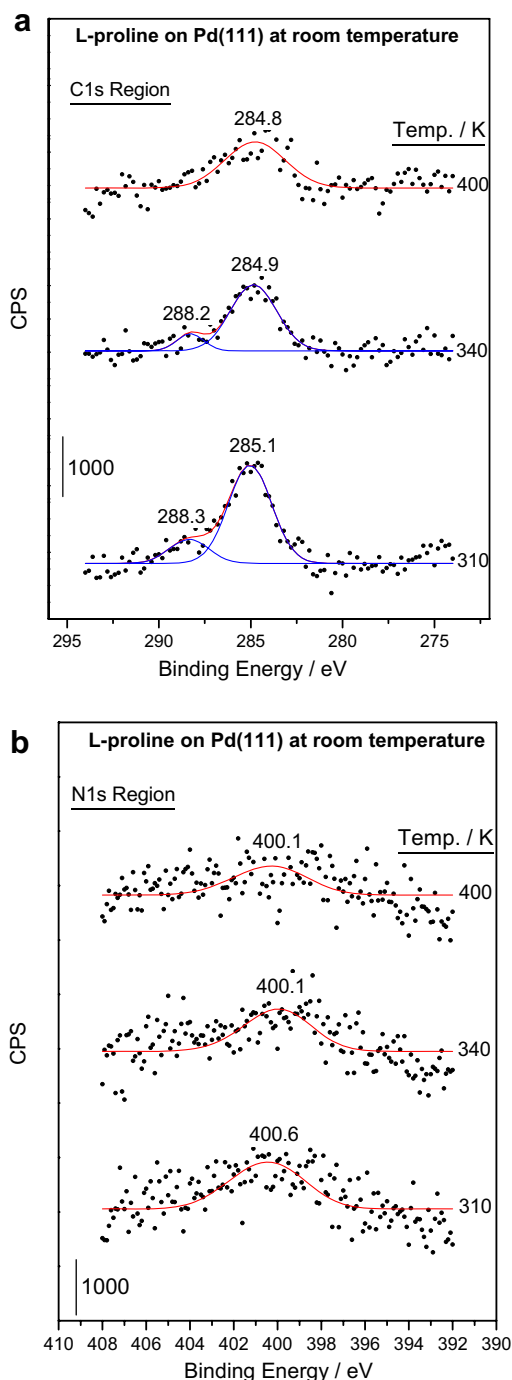


Fig. 9. (a) C 1s and (b) N 1s photoelectron spectra for 1 ML L-proline adsorbed at 310 K and subsequently annealed to 340 and 400 K.

iments. Fig. 10 displays the TPD profiles of selected masses (2, 28, 44 and 70 amu) following room-temperature adsorption of various coverages of proline. 70 amu features are found at ~ 390 K in this case, drastically different from data shown in Fig. 3, further proving that multilayer adsorption is completely excluded. Also note that the yields of H_2 , CO and CO_2 saturate at a coverage of 0.33 ML, indicating no further proline dissociation occurs above this coverage.

4. Discussion

4.1. Adsorption geometry: comparison between adsorption at 80 and 300 K

It is worth emphasizing the difference between low-temperature (below 250 K) and room temperature (~ 310 K) adsorption where mono- and multilayer adsorption occur at low temperatures, while only the first monolayer forms at room temperature. The low-temperature, multilayer growth has been explored in detail for glycine [4] where, at the point at which monolayer saturates, a total of ~ 3 ML has been deposited. ^{13}C O titration demonstrates that proline behaves in the same manner (Fig. 1). There are several pieces of evidence to demonstrate that proline adsorption at room temperature is restricted to only forming the first monolayer. First, increasing the adsorption time does not increase the intensities of C and N 1s signals. Second, a direct comparison between Figs. 3 and 10 at 70 amu (a fragment due predominately to proline) immediately reveals that multilayer growth does not occur in the latter case.

Similar to the behavior found for glycine and alanine on Pd(111), proline is present predominately in its zwitterionic form following adsorption at ~ 80 K. For a 3 ML film of proline adsorbed at 80 K (Fig. 2b), the N 1s feature at ~ 401.5 eV binding energy is assigned to $-\text{NH}_2^+$ species, due to the presence of zwitterionic proline and the signal at 399.8 eV BE is assigned to $-\text{NH}-$ species of neutral proline. The relative intensity ratio of these two features suggests that $\sim 70\%$ of adsorbed proline adsorbs as zwitterions. It is worth pointing out that the binding energies of proline in the multilayer are somewhat higher than those of the monolayer. Such a shift has been observed previously for amino acids on Pt(111) and ascribed to charging effects [7]. However, this would also likely also result in significant broadening and may also be due to final state effects. Based on our previous studies of glycine and alanine on Pd(111) [4,5], the N 1s binding energies of the monolayer features are 0.5–1 eV lower than for a 3 ML film. Assuming the same behavior occurs for proline, the 400.6 eV feature obtained following room temperature adsorption (Fig. 9b) suggests that proline adsorbs exclusively in its zwitterionic form following adsorption at ~ 300 K.

The C 1s XPS data shown in Fig. 9a reveal that, following room temperature adsorption, the signal intensity ratio between the COO carbon and the ring carbon is 1:4. This implies that the molecule is oriented such that all carbon atoms within the proline molecule are sampled equally. However, for low-temperature adsorption, Fig. 2a shows a corresponding 1:2.5 intensity ratio, indicating that proline in the multilayer adopts a different geometry from that in the monolayer. This implies that the pyrrolidine ring must be oriented to obscure the ring carbon atoms. In both cases, proline is predominately in its zwitterionic form (Figs. 2b and 9b) so that the above mentioned ratio

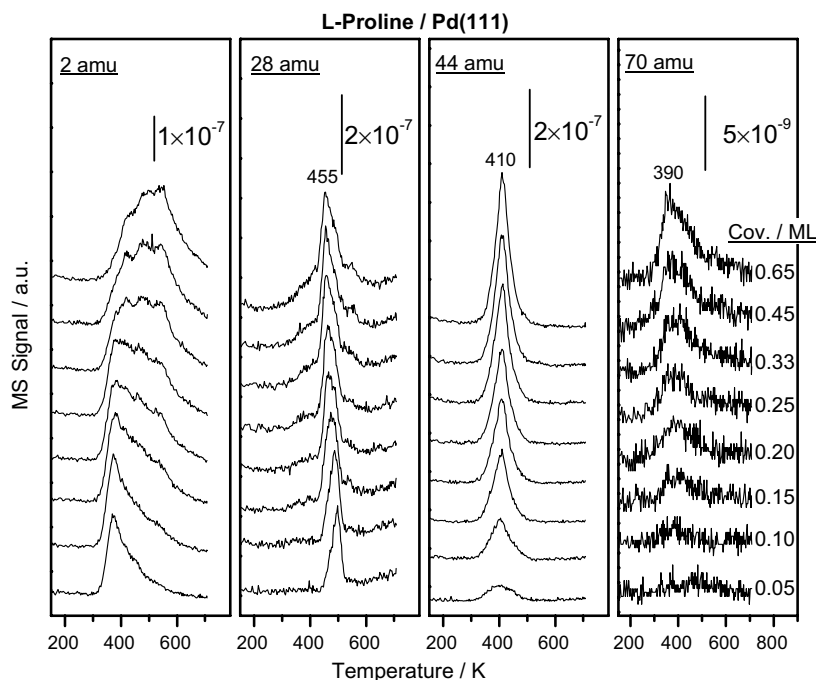


Fig. 10. Temperature-programmed desorption profiles (2, 28, 44 and 70 amu) for various coverages of L-proline adsorbed at room temperature on Pd(111) collected using a heating rate of 6.5 K/s, where the proline coverages are displayed adjacent to the corresponding spectrum.

difference is unlikely due to conformational difference in these two situations so that this effect must derive from the existence of multilayers at low temperatures. Molecular desorption displayed in Fig. 3 suggests the existence of attractive lateral interactions between prolines in different layers, manifest by a desorption temperature increase with increasing coverage. Such an attractive interaction is likely to be due to electrostatic attractions between negatively charged COO^- and the positively charged pyrrolidine ring and be the driving force for different orientations of proline in the monolayer and multilayer. It is of some interest to compare proline with alanine. Room temperature alanine adsorption leads to an intensity ratio of 1:2 between the COO^- and $\alpha\text{-C} + \text{methyl carbon}$, while low-temperature adsorption results in an intensity ratio of 1:3. Apparently, a similar effect occurs in which the COO^- carbon is partially obscured by the $\alpha\text{-C}$ and methyl groups. Similar XPS results have been reported in a recent study for alanine adsorption onto Cu(110) at various temperatures [8], although in this case, adsorption above room temperature leads to the deposition of surface alaninate species.

4.2. Desorption and dissociation of adsorbed proline

Multilayer proline desorbs from the surface between 315 and 333 K (Fig. 3). This observation is consistent with the XPS results (Fig. 2), where extensive C and N 1s signal intensity decreases occur below 340 K. The XPS data of Fig. 9 indicate that a portion of proline in the monolayer also desorbs. The data shown in Fig. 10 reveal that the yields of H_2 , CO and CO_2 saturate at a proline coverage

of ~ 0.33 ML. This proves that no further proline dissociation occurs on the surface above this coverage.

The dissociation of glycine and alanine has been studied recently and it has been demonstrated that the major dissociation pathway involves cleavage of OOC-C bond [4,5]. The COO^- moieties undergo two reaction pathways either to generate gas-phase CO_2 , or form CO and deposit $\text{O}_{(\text{ads})}$ on the surface. For both glycine and alanine, the branching ratio of these two reactions is close to unity. In the case of glycine, the nitrogen-containing species desorb as methylamine and HCN, while for alanine, ethylamine and HCN are generated. Bearing this reaction pathway in mind, proline should dissociate to form CO_2 and CO from $-\text{COO}^-$, and pyrrolidine and HCN from the pyrrolidine ring. As will be shown below, all these products are detected suggesting the validity of this proposal. However, the surface chemistry is more complicated.

A large number of masses were monitored in this study. To gain a clearer picture of various dissociation pathways, Table 1 lists the various detected masses with the corresponding peak desorption temperatures. Apparently, desorption at or below 330 K is due to fragmentation of molecular proline. This demonstrates that proline is stable on the surface to at least this temperature. Intense features are observed at 38–42, 66 and 67 amu for desorption at 390 K. The relative intensities of these masses match well with the cracking pattern of pyrrole [9]. At 410 K, features are detected at 43–46 amu. These are assigned to pyrrolidine formation based on the fragmentation pattern, especially the rather intense signal at 43 amu, which is the strongest fragment of pyrrolidine [9]. Note that the desorp-

Table 1
Mass spectrometer ionizers fragments detected during temperature-programmed desorption over various temperature ranges

Temperature (K)	Masses (amu)
≤330	25, 26, 28, 29, 30, 31, 32, 38, 39, 40, 41, 42, 43, 45, 54, 55, 56, 57, 58, 60, 68, 69, 70, 71
390	25, 26, 37, 38, 39, 40, 41, 42, 65, 66, 67
410	43, 44, 45, 46
445	49, 50, 51, 52, 56, 57, 62, 63, 65, 66, 67
320–600	2
450–500	28
560, 740–810	26, 27
400–500	71, 72, 73

tion profiles at 68–71 amu (Fig. 10) also contain this feature, although not very well resolved. It is worth pointing out that the relative intensity at 44 amu is far too large for a fragment of pyrrolidine, and we assign desorption at this mass to predominately CO₂. Further supporting evidence for this assignment comes from XPS measurements (Figs. 2a and 9a), where the COO feature becomes undetectable at 400 K, in accord with the 410 K desorption feature at 44 amu (Figs. 6 and 10). Similar behavior was found recently for alanine where ethylamine and CO₂ desorb at approximately the same temperatures [5].

The assignment of the species desorbing at 450 K is more difficult. Note first that this state has a number of masses in common with pyrrole (Table 1) and may imply that this is due to an isomer of pyrrole. The most significant difference is that the 450-K state displays much more intense desorption at 49–52 amu compared to pyrrole. A survey of pyrrole isomers that display relatively strong 49–52 amu features suggest a number of possibilities, including 2-butenitrile (CH₃–CH=CH–CN), 3-butenitrile (CH₂=CH–CH₂–CN), 2-methyl-2-propenenitrile (CH₂=C(CH₃)–CN) and cyclopropanecarbonitrile [9]. All these molecules have identical stoichiometries and rather similar cracking patterns; it is not possible to make more precise assignments. The formation of these nitriles requires opening of the pyrrolidine ring (although ring opening of pyrrole cannot be excluded [10]). This is reasonable since HCN forms at higher temperatures (Fig. 4). The formation of HCN has been studied extensively on Pd(111) from methylamine where it is formed through hydrogenation of CN_(ads) species [11]. In the present study, HCN desorbs at ~560 and 740–810 K (Fig. 4). Recent studies with glycine and alanine also revealed HCN desorption. However, besides these two high-temperature desorption states, glycine has a sharp low-temperature state at ~430 K [4] and alanine has a similar one at ~460 K [5]. The lack of this state for proline suggests that CN_(ads) species only form at ~560 K and above. Additional evidence for pyrrolidine ring opening comes from the desorption profiles at 72 and 73 amu between 400 and 500 K (Fig. 8). These can be assigned to the formation of butanamine so that it might be argued that the 445-K features found at lower masses

are due to fragments of butanamine. However, the extremely small signal intensity at 73 amu, suggests that this is not likely. This is also true for the assignment of 390-K state to pyrrole (which has a parent mass at 67 amu). Since desorption at masses higher than 67 amu is detected (Fig. 8), there is always the possibility that the 67 amu signal (Fig. 7) is actually a fragment of higher molecular weight products. However, all possible higher mass species, namely proline, pyrrolidine and butanamine should not have intensity at 67 amu as large as that displayed in Fig. 7.

CO desorbs at ~500 K at the smallest proline coverages and the desorption temperature decreases to ~450 K at high coverages. As has been suggested previously, CO is formed through decomposition of COO species. CO desorption, however, is desorption-rate limited. The reason that CO desorbs at lower temperatures at higher proline coverages is probably due to repulsive interactions between adsorbates at higher coverages. Hydrogen forms over a rather wide temperature range. There are several reactions that could generate surface hydrogen. First, is the deprotonation of proline, second the dehydrogenation of pyrrolidine to pyrrole and finally, further dissociation of surface species formed through ring opening reactions, so that hydrogen might well be expected to have several desorption states. The data shown in Fig. 10 demonstrate that this is indeed the case. Finally, a broad H₂O desorption state is found between 300 and 600 K (data not shown) where clearly H₂O formation is reaction-rate limited, arising from reaction with oxygen from the COO group where a portion of adsorbed COO dissociates to form CO and leave O_(ads) on the surface, which subsequently reacts with hydrogen to form water. In summary, the initial step of proline dissociation is identical to both glycine and alanine where the C–COO bond cleaves first to generate surface COO and nitrogen-containing species. The complexity of proline decomposition is due mainly to the complex decomposition pathways of the pyrrolidine ring where dehydrogenation, hydrogenation, and ring-opening reactions occur over a rather narrow temperature range.

5. Conclusions

Proline adsorbs on Pd(111) at temperatures below ~250 K into second and subsequent layers prior to the saturation of the first layer, where approximately 70% of the proline adsorbs in its zwitterionic form. Molecular proline desorbs at ~315 K at low coverages, increasing to ~333 K as the coverage increases to ~4.5 ML, indicative of attractive interactions between adsorbed proline molecules. In contrast, adsorption at ~300 K leads to saturation of only the first monolayer, where XPS results indicate that it adsorbs essentially exclusively as the zwitterions, oriented such that all of the carbons are sampled equally by XPS. The decomposition pathway of adsorbed proline resembles that of other amino acids on Pd(111), occurring primarily by

scission of the C–COO bond. The carboxylate moiety desorbs as carbon monoxide and carbon dioxide. In the case of α -amino acids, the nitrogen-containing moiety desorbs as an amine and HCN, while the behavior of proline is more complex. A number of desorption products are detected in addition to HCN, including pyrrole at ~ 390 K, pyrrolidine at ~ 410 K and final species that desorbs at ~ 450 K that cannot be unequivocally assigned but may be 2-butenitrile ($\text{CH}_3\text{-CH=CH-CN}$), 3-butenitrile ($\text{CH}_2\text{=CH-CH}_2\text{-CN}$), 2-methyl-2-propenenitrile ($\text{CH}_2\text{=C(CH}_3\text{)-CN}$) or cyclopropanecarbonitrile.

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