The surface chemistry of acetic acid on Pd{111}

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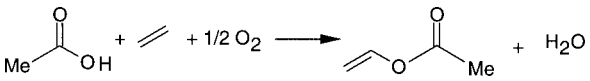
XPS, temperature-programmed reaction and HREELS have been used to study the adsorption and reactions of acetic acid on Pd{111}. At 170 K the adsorbed monolayer contains intact and dissociated acetic acid molecules, the latter consisting of a mixture of bidentate acetate and another species tentatively identified as monodentate acetate. The monodentate acetate appears to resemble closely the acetate species observed under reaction conditions at the surface of a pure palladium vinyl acetate synthesis catalyst. Thermal decomposition of the adsorbate yields CO_2, H_2O, CO, H_2 and carbon. The associated processes may be rationalised in terms of two reaction channels, one due to the monodentate and the other due to the bidentate acetate.

KEY WORDS: acetic acid; palladium; adsorption; HREELS; XPS; TPR; monodentate acetate; bidentate acetate

1. Introduction

Interest in the surface chemistry of carboxylic acids on transition metal surfaces partly stems from the fact that the associated species are important either as reaction intermediates or as products in catalytic oxidation reactions. See, for example [1–4]. The acetic acid/palladium system is of particular importance with respect to the selective oxidation of ethene to vinyl acetate, according to the overall process



Aas and Bowker [5] used XPS to examine acetic acid adsorption on Pd{110}, concluding that an acetate species was formed at 325 K. Davis and Barteau studied acetic acid adsorption on Pd{111} and on Pd{111} 2 × 2-O [6,7] by HREELS and TPR as part of a wider investigation which included formic and propanoic acids. In the case of acetic acid, they found that the acetate decomposed to yield CO_2 and H_2 at 350 and 375 K, accompanied by deposition of methyl groups, which decomposed further to yield adsorbed carbon and H atoms. Co-adsorbed oxygen stabilised the acetate, resulting in an autocatalytic decomposition at higher temperatures.

Here we report on an investigation by XPS, HREELS and TPR of the behaviour of the Pd{111}/CH_3COOH system in the absence and presence of co-adsorbed oxygen. New information is presented and erroneous conclusions reached in earlier work are corrected.

2. Experimental

Experiments were performed in two different vacuum chambers, described in detail elsewhere [8]. Both operated at a base pressure of $\sim 10^{-10}$ mbar; one was used for LEED, Auger and TPR measurements, the other for HREELS and XPS. The TPR measurements were carried out with the front face of the sample positioned 0.5 cm from a collimator positioned immediately in front of the mass spectrometer ioniser. In this configuration, under appropriate conditions, the TPR spectra were almost entirely due to species desorbing from the sample front face and free from artefacts (*e.g.*, due to desorption from the sample supports). Control experiments were carried out in which one of the sample support rods was deliberately positioned in front of the collimator. These confirmed that in the acetic acid spectra a large peak appearing at an apparent sample temperature of ∼350 K was in fact due to desorption from the sample supports. This is of importance, as will become apparent below. The Pd{111} sample was cleaned by Ar^+ sputtering (5 μA/cm^2, 700 eV, 850 K) and by heating in oxygen (800 K, 4×10^{-7} mbar) until the Auger, XP and thermal desorption spectra indicated freedom from contamination.

Glacial CH_3COOH (Aldrich, >99.99% purity) was further purified by means of freeze–pump–thaw cycles and admitted to the sample *via* a leak valve/tube doser assembly; a similar arrangement was used for oxygen dosing. Adsorption was carried out over a range of temperatures, as indicated, but the HREEL and XP spectra were all recorded at 140 K.

3. Results and discussion

3.1. Temperature-programmed reaction

TPD measurements showed that adsorption <170 K resulted in formation of multilayers. Therefore, acetic acid was dosed at 170 K in order to selectively populate the first monolayer. Figure 1 shows the TPD spectra of molecular

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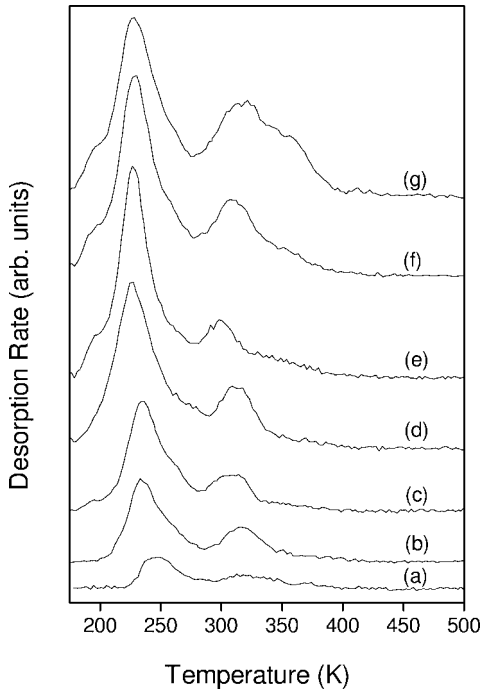

Figure 1. Desorption spectra of CH_3COOH following different initial exposures to Pd{111} at 170 K: (a) 0.05, (b) 0.1, (c) 0.3, (d) 0.5, (e) 1.0, (f) 2.0 and (g) 5.0 L.

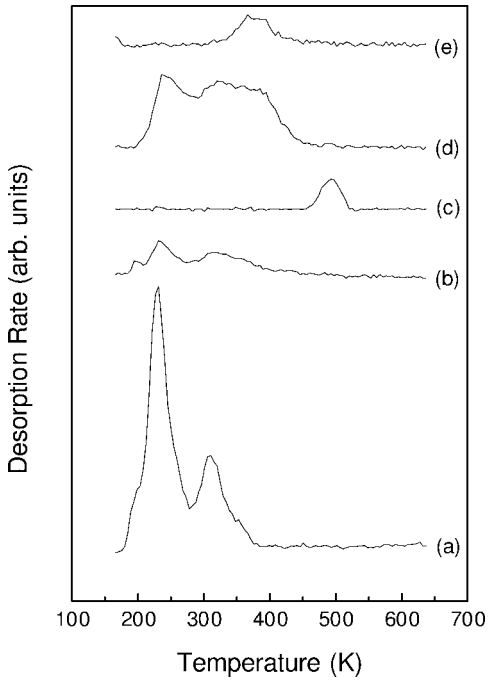

Figure 2. TPR spectra for monolayer coverage of CH_3COOH on Pd{111} at 170 K: (a) CH_3COOH, (b) H_2O, (c) CO, (d) CO_2 and (e) H_2.

acetic acid from Pd{111} as a function of increasing initial acid dose; it is clear that several desorption features evolve as the surface coverage increases, until monolayer saturation was reached at a dose of 2 L. Control experiments showed that even with our favourable detection geometry, acid exposures >2 L introduced artefacts due to significant desorption from the sample support assembly. This effect is illustrated by the 5 L desorption trace (figure 1(g)): the high temperature feature at ∼350 K increased continuously with further increases in acid exposure. No LEED patterns other than the (1 × 1) pattern due to the Pd{111} surface were observed under any conditions.

Figure 2 shows a set of TPR spectra for monolayer acid coverage (2 L exposure) dosed at 170 K. CH_3COOH desorption occurs over a range temperatures, producing a TPR spectrum consisting of multiple overlapping peaks. However, two major peaks at 230 and 310 K are well resolved. A variety of reactions also occur, yielding CO_2, CO, H_2O and H_2, and inspection of figure 2 reveals that CH_3COOH desorption is correlated with some of the decomposition reactions. Specifically, for CO_2 and H_2O formation, there appear to be two reaction channels in the temperature regimes 200–275 K and 275–375 K which are broadly coincident with the principal CH_3COOH desorption peaks.

Figure 2 shows significant differences when compared to the data reported by Davis and Barteau [6,7]. The present work strongly suggests that the artefact described above by which high acid exposures lead to subsequent desorption from the sample support assembly has erroneously been ascribed by Davis and Barteau to desorption from the Pd{111} surface itself. That is, the true high temperature acetic acid desorption peak at 310 K overlaps with a "ghost" peak due to the sample support assembly. In addition, Davis and Barteau showed only partial TPR profiles for the various products, *i.e.*, the individual spectra, unlike ours, did not encompass the entire temperature range. For this reason, a complete comparison between their data and ours is not possible.

The associative desorption of acetate with H(a) to yield acetic acid might be expected to follow second-order kinetics and therefore symmetrical TPR peak shapes would be expected. Figure 2 suggests that such is indeed the case, with two or three overlapping CH_3COOH desorption peaks in the temperature interval 200–340 K. The small shoulder at ∼190 K is assigned to associatively chemisorbed acetic acid that is also present in the first monolayer. This assignment is supported by XPS and HREELS evidence presented below. Increasing acid exposures at 170 K gave TPR spectra in which the 190 K shoulder developed into an asymmetric peak that increased continuously with CH_3COOH dose. This is consistent with development of physisorbed multilayers on top of the chemisorbed monolayer. According to Davis and Barteau [6] monolayer formation requires an acetic acid exposure of 20 L at 170 K. According to our findings, such an exposure would produce multilayers rather than a monolayer. Therefore it is suggested that the acetic TPD data acquired by these authors may have been interpreted incorrectly to the extent that the reported low temperature peak at 205 K includes an important contribution due to multilayer acid desorption.

3.2. X-ray photoelectron spectroscopy

Complementary XPS spectra were recorded in order to gain additional insight. Figure 3 shows corrected C_{1s} XP

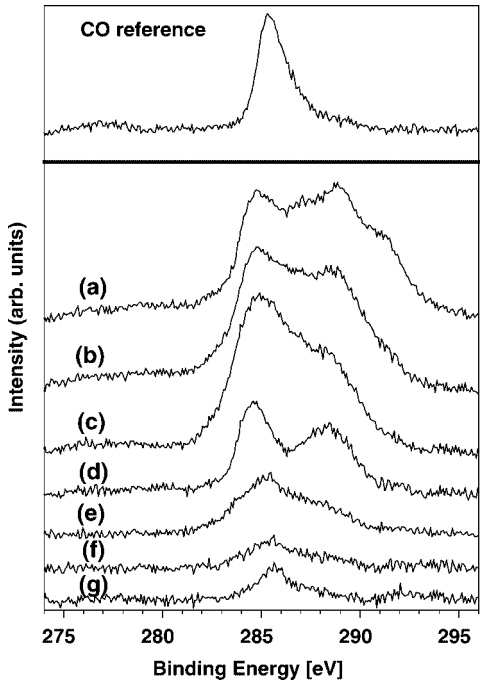

Figure 3. Background corrected C_{1s} XP spectra for CH_3COOH on Pd{111} following various treatments: (a) 10 L at 140 K, (b) annealed to 170 K, (c) annealed to 190 K, (d) 5 L at 190 K, (e) annealed to 230 K, (f) annealed to 250 K and (g) annealed to 350 K.

spectra for acetic acid adsorbed on Pd{111} as a function of temperature; the underlying Pd photoemission has been subtracted and chemical shifts are clearly visible. Dosing 10 L of acetic acid at 140 K produced an XP spectrum that exhibited four peaks corresponding to binding energies of 284.9, 287.2, 289.1 and 291.3 eV (figure 3(a)). According to the TPD results, this should correspond to the onset of multilayer formation on top of the chemisorbed contact layer. The low adsorption temperature was insufficient to cause dissociative adsorption so that acetate formation did not occur.

How can an adsorbate that contains two chemically distinct carbon atoms (CH_3 and OCO) produce an XP spectrum comprising four peaks? This may be rationalised as follows. The peaks at 284.9 and 289.1 eV can be, respectively, assigned to the CH_3 and OCO carbon atoms of acid molecules that are chemisorbed in the first monolayer. These binding energies are in good agreement with those reported by Aas and Bowker [5] for acetic acid adsorbed on the Pd{110} surface; furthermore, the corresponding peak separation (∼4 eV) is consistent with the data of Smith *et al.* for gaseous acetic acid [9]. The other two peaks at 287.2 and 291.3 eV may be, respectively, assigned to the CH_3 and OCO carbon atoms of acid molecules in the physisorbed multilayers. Again, the ∼4 eV BE difference is consistent with the assignment to acetic acid molecules. The difference in BEs between the two types of molecules is ascribed to final state effects: acid molecules resident in physisorbed layers experience smaller relaxation due to core hole screening by metal valence electrons. Hence the C_{1s} BEs of physisorbed acetic acid peaks are expected to correspond closely to those recorded for gaseous acetic acid, as is indeed the case [9]. This provides strong confirmation of the view that acid exposures in excess of ∼2 L lead to the development of multilayers.

The thermal evolution of the XP spectra at temperatures ⩾170 K may usefully be related to the TPR data. According to the latter, annealing to 190 K should isolate the chemisorbed monolayer which should consist of a mixed adlayer containing dissociatively and non-dissociatively adsorbed acetic acid molecules, and figure 3(c) is the corresponding spectrum. The lowest BE peak at 284.8 eV is relatively well resolved and is assigned to emission from the methyl carbon of both acid and acetate. However, the environment of the OCO carbon atoms in CH_3COO and CH_3COOH is not identical, and somewhat different BEs are to be expected: this is consistent with the broad poorly-resolved higher energy component.

Acetic acid adsorption at 190 K (figure 3(d)) produced a different XP spectrum from that obtained by adsorption at 140 K followed by annealing to 190 K (figure 3(c)). In the latter case the surface coverage was higher, as indicated by the greater intensity of the integrated C_{1s} peaks. In contrast, adsorption at 190 K produced a less intense spectrum comprising two well-resolved peaks of equal intensity at 284.9 and 288.5 eV. The differences between the two may be rationalised as follows. Adsorption at 190 K immediately generates only acetate species by deprotonation of the impinging acid molecules. The two C_{1s} peaks have equal integrated intensities, as each acetate contains two chemically distinct carbon atoms, CH_3COO and CH_3COO. The relatively broad carboxyl emission appears to be an intrinsic characteristic of $CO_2^{\delta-}$ species [10]. No intact acid molecules are present and therefore no photoemission from CH_3COOH carbon atoms is observed. Such CH_3COOH emission (and an increased net coverage) does result if adsorption is carried out at 140 K followed by annealing to 190 K, as discussed above.

Annealing to 230 K resulted in a decrease in intensity of both the CH_3COO and CH_3COO emission, together with a shift to lower and higher BE, respectively (figure 3(e)). The decrease in intensity is due to desorption (*cf.* figure 2). The peak shifts are principally a consequence of acetate decomposition with release of CO molecules to the surface, again consistent with the TPR results. As shown in figure 3, the C_{1s} BE of CO on Pd{111} lies between the two C_{1s} emissions from acetate. Hence, superposition of the three C_{1s} peaks should generate the XP spectrum displayed in figure 3(e). According to the TPR data, annealing in the range 250–350 K completes the desorption and decomposition of remaining acetate species, leaving CO and carbon to the surface. The XP spectra shown in figure 3 (f) and (g) support this: the CH_3COO and CH_3COO C_{1s} emission disappeared leaving only that due to CO and C(a) emission.

By using the XP spectrum of the CO-saturated surface as a calibration point (c(4 × 2); 7.6×10^{14} molecules/cm^2) one may estimate the adsorbate loadings associated with each of figures 3 (a)–(g) as follows: 11.9, 11.6, 11.0, 5.2, 3.4, 1.5, 1.2×10^{14} acid molecules/cm^2, respectively. The relatively small change in going from figure 3 (a) (onset of

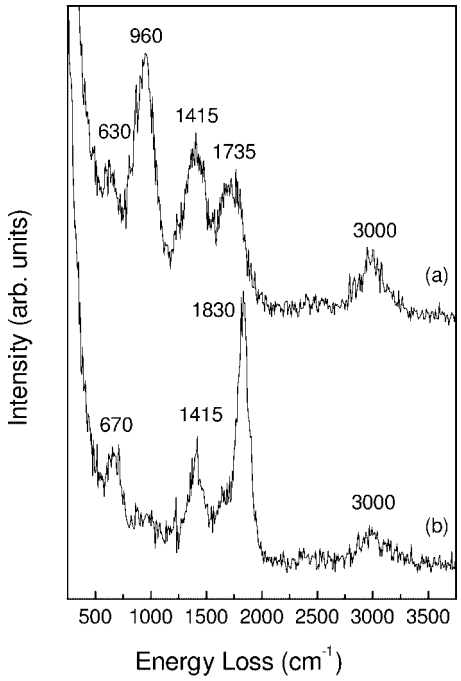

Figure 4. HREEL spectra for 5 L CH_3COOH adsorbed on Pd{111} at 140 K: annealed to (a) 190 and (b) 230 K.

multilayer growth) to (c) (nominal monolayer of acid and acetate) suggests that molecules in the contact layer are considerably more densely packed than physisorbed molecules. This seems reasonable, especially as many of the former are present as "standing-up" bidentate acetate species.

3.3. HREEL spectra

Although the XP and TPR spectra may be successfully correlated and used to rationalise aspects of the surface chemistry, XPS is inadequate for more detailed characterisation of the adsorbed species. In particular, it cannot be used to investigate whether bidentate acetate is present in both bridging and chelating forms, as suggested for example in the case of Ru{0001} [10]. In addition, with respect to vinyl acetate synthesis, the possible formation of *monodentate* acetate is of interest. HREELS analysis was therefore used to address these issues.

Figure 4(a) illustrates the HREEL spectrum for 5 L of acetic acid dosed at 140 K and annealed to 190 K and table 1 lists the energy loss assignments which can be ascribed to both dissociatively and non-dissociatively adsorbed acetic acid. The presence of molecular acetic acid is primarily indicated by the intense γO–H bending mode at 960 cm^{-1} [6] and the 1415 cm^{-1} loss is a ν_sOCO symmetric stretch, diagnostic of a bidentate acetate species [6,11,12]. The other prominent losses can be assigned to δOCO deformation (630 cm^{-1}), νC=O stretching (1735 cm^{-1}) and $\nu_s CH_3$ symmetric stretching of methyl hydrogens (3000 cm^{-1}). Losses associated with the methyl group ($\nu_s CH_3$ and $\delta_s CH_3$) and the δOCO deformation are to be expected for acetic acid and for various acetate configurations and cannot therefore be used to discriminate between these different species. The νC=O stretching vibration corresponds to the presence of molecular acetic acid and/or monodentate acetate, but not bidentate acetate.

Table 1
Vibrational assignments for CH_3COOH adsorbed on Pd{111} compared with those for CH_3COOH in the solid, liquid and gaseoous phases.

Mode assignment	Vibrational assignments[a] (cm^{-1})				
	(a) Pd{111}	(b) Pd{111}	(c) Monomer	(d) Dimer	(e) Solid
$\nu_s CH_3$	3000	2965	2997, 2961	3030	
νOH		2525	3577	3193	2875
νC=O	1735	1685	1799	1683	1648
$\delta_s CH_3$	1415	1425	1401, 1340	1431, 1371	1448, 1356
νC–O		1310	1279	1255	1284
γOH	960	955	1192	944	923
C–C		955	846	898	908
δOCO	630	685	654	623	635
ν_sOCO	1415	1415			

[a] (a) figure 4, (b) [6], (c) [14], (d) [14,15] and (e) [13].

Thus the 190 K HREEL spectrum supports the TPRS and XPS data which are consistent with the co-existence of molecular acetic acid and acetate in a mixed chemisorbed layer. It provides clear evidence for the existence of molecular acetic acid and bidentate acetate, but the presence of monodentate acetate can neither be proved nor disproved.

Davis and Barteau [6] recorded HREEL spectra of acetic acid adlayers adsorbed on Pd{111} at 170 K and after annealing to 200 K and in several important respects our results are in agreement with theirs, although our 190 K spectrum shows no clear evidence for hydrogen bonded networks of acid molecules that they observed at 170 K (characterised by a broad νOH loss at $\sim$2550 cm^{-1} [6,13]). The absence of the νOH mode in the 200 K spectrum of Davis and Barteau accords with our interpretation of the 190 K spectrum presented in figure 4.

Acetic acid forms dimers in both the liquid phase and in the gas phase [14,15]. The 190 K spectrum provides no evidence for such species as there is no loss at $\sim$3200 cm^{-1}, which is characteristic of acetic acid dimers. This too is in agreement with the work of Davis and Barteau [6]. Our results provide good evidence for the existence of adsorbed acetic acid molecules in the chemisorbed layer. This fact, and the absence of dimers and catemers, indicates that the Pd{111} surface accommodates acetic acid monomers at 190 K. This conclusion is at variance with [6] in which the authors reported that they never detect the presence of acetic acid monomers. However, as noted above, their 200 K spectrum does indeed provide evidence for the existence of acetic acid monomers, in agreement with our 190 K spectrum. Isolating the acid monomer can be difficult because the correct coverage has to be achieved. If the coverage is too low then only acetate is formed; if it is too high then catemerisation and/or multilayer formation occurs. As already suggested, it seems likely that the second possibility occurred in the experiments carried out at 170 K by Davis and Barteau.

Gaseous monomeric acetic acid exhibits a νC=O stretching vibration close to 1800 cm^{-1} [14], whereas liquid

phase dimers and solid state catemers have νC=O stretching modes near 1680 [14,15] and 1650 cm^{-1} [13], respectively (table 1), these latter being close to losses observed by Davis and Barteau at the higher coverages they used, though not observed by us. Instead (figure 4(a)) we observe an intense νC=O stretching mode at 1735 cm^{-1}, intermediate between gaseous monomer and the dimer. In this connection, the results of Augustine and Blitz [17] are of relevance. They used DRIFTS to study the Pd-catalysed vapour phase synthesis of vinyl acetate and detected $Pd(OOCCH_3)_2$, consistent with our observations.

Most interestingly, Augustine and Blitz also observed an absorption at 1735 cm^{-1} and were able to exclude the possibility that this band was due to physisorbed or condensed acetic acid. Instead, they concluded that the species responsible was a "Pd-ester" distinct from bidentate acetate. If correct, this assignment corresponds formally to identification of a monodentate acetate. Given the close match in frequencies between their work and ours, we therefore tentatively assign our 1735 cm^{-1} band to a monodentate acetate. Although this frequency is somewhat high for a monodentate acetate, two points are consistent with the proposed assignment. First, since monodentate acetate lacks an –OH function, it is incapable of forming hydrogen bonds. This would account for the complete absence from our data of spectral features associated with H-bonded acetic acid structures. Second, the apparent absence of the associated C–O stretch at ~1390 cm^{-1} is understandable because this mode is expected to be weak.

Whatever the case, it seems likely that our "1735 species" is the same as the "1735 species" observed by Augustine and Blitz under reaction conditions. The question remains as to whether this species is actually a reaction intermediate; work on Au/Pd model catalysts suggests that it may indeed be [19].

The conclusion, therefore, is that our 190 K spectrum probably corresponds to the presence of acetic acid monomers (too few in number to dimerise or catemerise) bidentate acetate and either monodentate acetate or a closely related species that is also formed under reaction conditions.

Heating the adlayer to 230 K, produced the HREEL spectrum displayed in figure 4(b). Clearly, this is significantly different to the 190 K spectrum, as would be expected on the basis of the TPRS and XPS data. TPRS shows that the non-dissociatively adsorbed acetic acid monomers desorb by 230 K. In accord with this, the γO–H bending mode at 960 cm^{-1} which is diagnostic of intact acetic acid, disappears. TPRS and XPS data reveal that acetate decomposition reactions commence at 230 K, resulting in a mixed adlayer consisting of acetate species coadsorbed with CO molecules. The ν_sOCO and $\delta_s CH_3$ modes at 1415 cm^{-1}, together with the δOCO (630 cm^{-1}) and $\nu_s CH_3$ (3000 cm^{-1}) modes, confirms that bidentate acetate species are indeed present at this stage. The intensity of the 1735 cm^{-1} loss relative to these features is however significantly reduced, allowing for its substantial overlap with the strong 1830 cm^{-1} loss that now appears (see below). This is consistent with the onset of monodentate removal at ~230 K. Accordingly, the ~230 K acetic acid peak observed in TPR (figure 2) is assigned to desorption of CH_3COOH formed by hydrogenation of the monodentate acetate.

The most intense loss present in the 230 K HREEL spectrum is at 1830 cm^{-1} and is assigned to the νC=O stretch of chemisorbed CO molecules, in excellent agreement with RAIRS studies of the low coverage regime of CO on Pd{111} by Bradshaw and Hoffman [17]. Given that the bidentate acetate is still present at this stage, it is proposed that the monodentate actetate is the source of the CO. That is, at ~230 K the monodentate acetate either reacts with hydrogen to yield acetic acid, or decomposes to yield CO, whereas the bidentate acetate is thermally stable against both of these processes.

Monodentate acetate decomposition yields oxygen and CH_3, in addition to CO. This oxygen may react with the CH_3 to produce the H_2O that is observed (figure 2), or it may react with the CO to produce CO_2. There is also the possibility of the hydrogen atoms combining to evolve as H_2. Finally, we cannot rule out the possibility of decarboxylation of the monodentate acetate species, evolving CO_2 and releasing CH_3 to the surface. Hence monodentate acetate decomposition gives rise to a variety of possible surface reactions that can account for the complicated form of the TPRS.

As noted above, the desorption and decomposition of acetic acid are correlated and there appear to be two main reaction channels. This may now be rationalised in terms of the different thermal stabilities of mono- and bidentate acetate: the former principally accounts for the reactions in the range 200–275 K; the latter mainly accounts for the reactions in the range 275–375 K.

The following scheme is consistent with all the results presented here. (η^1 and η^2 refer to the mono- and bidentate acetate, respectively.)

<170 K	$n CH_3COOH_{(g)} \rightarrow (CH_3COOH)_{n(a)}$
170–190 K	$(CH_3COOH)_{n(a)} \rightarrow CH_3COOH_{(a)}$
	$\rightarrow (\eta^1 + \eta^2)CH_3COO_{(a)} + H_{(a)}$
190 K	$CH_3COOH_{(a)} \rightarrow CH_3COOH_{(g)}$
200–275 K	$\eta^1 CH_3COO_{(a)} + H_{(a)} \rightarrow CH_3COOH_{(g)}$
	$\eta^1 CH_3COO_{(a)} \rightarrow CO_{2(g)} + CH_{3(a)}$
	$\rightarrow CO_{(a)} + CH_3 + O_{(a)}$
	$CO_{(a)} + O_{(a)} \rightarrow CO_{2(g)}$
	$2CH_{3(a)} + 3O_{(a)} \rightarrow 2C_{(a)} + 3H_2O_{(g)}$
275–375 K	$\eta^2 CH_3COO_{(a)} + H_{(a)} \rightarrow CH_3COOH_{(g)}$
	$\eta^2 CH_3COO_{(a)} \rightarrow CO_{2(g)} + CH_{3(a)}$
	$\rightarrow CO_{(a)} + CH_3 + O_{(a)}$
	$CO_{(a)} + O_{(a)} \rightarrow CO_{2(g)}$
	$2CH_{3(a)} + 3O_{(a)} \rightarrow 2C_{(a)} + 3H_2O_{(g)}$
325–425 K	$H_{(a)} + H_{(a)} \rightarrow H_{2(g)}$
470–525 K	$CO_{(a)} \rightarrow CO_{(g)}$

In summary, the above scheme takes account of notable differences between our findings and those of Davies and Barteau, as follows. (i) The low temperature acid desorption peak at ∼205 K is dominated by multilayer desorption. (ii) The true high temperature feature at 310 K can be masked by an artefact due to desorption from the sample supports (iii) The surface species formed are critically dependent on coverage. In particular, both our XPS data and our TPD data confirm that acid multilayers are formed at exposures in excess of ∼2 L. (iv) The contact layer is dominated by dissociated and non-dissociated acetic acid and not by H-bonded species. (v) At ∼190 K a species appears whose vibrational signature very closely resembles that of a molecule formed at the surface of a working Pd vinyl acetate catalyst.

4. Conclusions

(1) At 170 K the first adsorbed monolayer of acetic acid on Pd{111} contains intact and dissociated acetic acid molecules, the latter consisting of a mixture of bidentate acetate and a species tentatively identified as monodentate acetate.

(2) The monodentate acetate forms at high coverages, consistent with its reduced coordination to the surface. It appears to resemble closely the species identified at the surface of a working palladium vinyl acetate catalyst and may be a key reaction intermediate.

(2) Thermal decomposition of the adsorbate yields CO_2, H_2O, CO, H_2 and carbon. The associated processes may be rationalised in terms of two reaction channels, one due to the mono- and the other due to the bidentate acetate.

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References

[1] J.J. Vajo, Y.K. Sun and W.H. Weinberg, Appl. Surf. Sci. 29 (1987) 165.
[2] C.M. Friend and X. Xu, Ann. Rev. Phys. Chem. 42 (1991) 251.
[3] J. Ushio, I. Papai, A. St-Amant and D.R. Salahub, Surf. Sci. 262 (1992) L134.
[4] M.A. Szymanski and M.J. Gillan, Surf. Sci. 367 (1996) 135.
[5] N. Aas and M. Bowker, J. Chem. Soc. Faraday Trans. 89 (1993) 1249.
[6] J.L. Davis and M.A. Barteau, Langmuir 5 (1989) 1299.
[7] J.L. Davis and M.A. Barteau, Surf. Sci. 256 (1991) 50; 260 (1996) 215.
[8] C.J. Baddeley, M. Tikhov, C. Hardacre, J.R. Lomas and R.M. Lambert, J. Phys. Chem. 100 (1996) 2189.
[9] S.R. Smith and T.D. Thomas, J. Am. Chem. Soc. 100 (1978) 5459.
[10] H.J. Freund and M.W. Roberts, Surf. Sci. Rep. 25 (1996) 225.
[11] A.R. Garcia, J.L. da Silva and L.M. Ilharco, Surf. Sci. 415 (1998) 183.
[12] K. Ito and H.J. Bernstein, Canad. J. Chem. 34 (1956) 170.
[13] D.H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 2nd Ed. (McGraw-Hill, London, 1973).
[14] P.F. Krause, J.E. Katon, J.M. Rodgers and D.B. Phillips, Appl. Spectrosc. 31 (1997) 110.
[15] W. Weltner Jr., J. Am. Chem. Soc. 77 (1955) 3941.
[16] S. Kishida and K.J. Nakamoto, J. Chem. Phys. 41 (1964) 1558.
[17] S.M. Augustine and J.P. Blitz, J. Catal. 142 (1993) 312.
[18] G. Socrates, ed., *Infrared Characteristic Group Frequencies* (Wiley, Chichester, 1994) ch. 10.
[19] R.D. Haley, M.S. Tikhov and R.M. Lambert, in preparation.
[20] A.M. Bradshaw and F.M. Hoffman, Surf. Sci. 72 (1978) 513.