

A STUDY OF THE INTERACTION OF FORMIC ACID AND PROPIONIC ACID WITH OXIDISED LEAD AND COPPER SURFACES BY PHOTOELECTRON SPECTROSCOPY AND LEED

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The interaction of formic acid with oxidized Pb(100) and Cu(100) single crystal surfaces has been studied by electron spectroscopy (XPS and UPS) and LEED. At 80 K formic acid is adsorbed without decomposition, but on warming to 190 K the reaction $M-O + HCOOH \rightarrow M(OH)_{ads}(HCOO^-)_{ads}$ occurs. Further exposure of the Pb(OH)(HCOO⁻) surface to formic acid at 298 K leads to regeneration of the clean lead (100) surface, as evidenced by both electron spectroscopy and LEED. The overall reaction is therefore $PbO(s) + 2 HCOOH(g) \rightarrow Pb(s) + H_2(g) + 2 CO_2(g) + H_2O(g)$. The clean Pb(100) surface does not react with formic acid at 298 K. The Cu(OH)(HCOO⁻) surface can not be reduced by formic acid at 298 K, but heating in vacuum to 520 K again regenerates the clean metal surface. When copper has been oxidised beyond the monolayer and exposed to formic acid, only the surface is reduced by subsequent heating in vacuum. Propionic acid adsorbs with decomposition into the propionate ion on both clean copper and oxidized copper at $T \geq 190$ K. Heating the Cu(OH)(CH₃·CH₂·COO⁻) surface in vacuum at 500 K results in removal of all surface oxygen, although some elemental carbon remains.

1. Introduction

We have previously carried out a detailed study of the interaction of several metals with formic acid, using X-ray and ultra-violet photoelectron spectroscopy [1]. At 80 K spectra resembled those of gas phase formic acid, although evidence of hydrogen bonding was noted in the condensed phase. Between 120 and 190 K the acid decomposed into adsorbed formate ions and protons. Breakdown appeared to occur in three stages: (i) cleavage of hydrogen bonds in the solid, (ii) reorientation of the molecular skeleton from parallel to perpendicular to the surface plane, and finally (iii) dissociation of the acid. At a higher temperature, the precise temperature depending on the metal, the formate ion decomposed and then desorbed.

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regenerating a clean surface. The activation energies for decomposition of the formate ion agreed with those already reported for the catalytic decomposition of the acid over the metals, to yield carbon dioxide and hydrogen.

Since the catalytic decomposition of formic acid has also been used as a test reaction in the study of oxides, we examine in this paper formic acid interaction with oxide surfaces. Due to the difficulty of obtaining oxide single crystals for structural studies we have studied well ordered thin oxide layers generated at the surfaces of metal single crystals. The surfaces chosen were Pb(100) and Cu(100), where in both cases detailed information of the structure and chemistry of the oxide layers was available [2,3].

There have been a number of studies of the catalytic decomposition of formic acid on oxides, those up to 1959 have been reviewed by Mars [4]. As with metals, dehydrogenation (eq. (1)) and dehydration (eq. (2)) occur and attention has been focussed on factors governing the selectivity of the process. High temperature



(≥ 1100 K) outgassing of the oxide favours dehydrogenation, which also occurs predominantly on the oxides with lower heats of formation [5]. Noto et al. [6,7] have demonstrated the presence of formate ions on both dehydration and dehydrogenation catalysts. With zinc oxide and magnesium oxide, where dehydrogenation occurs exclusively, about fifty layers of metal formate were formed and the generation of metal formates has also been reported by Komarov et al. [8]. Unlike, for example, the catalytic decomposition of nitrous oxide, the decomposition of formic acid can not be simply correlated with the electrical conductivity or semi-conducting behaviour of the catalyst.

2. Experimental

The apparatus has been described previously [3] and consisted of a diffusion pumped stainless steel system, ultimate vacuum $\approx 5 \times 10^{-9}$ Pa, equipped for ultraviolet and X-ray photoelectron spectroscopy and low energy electron diffraction. Crystal preparation and specimen cleaning, using argon ion bombardment, have also been described [2,3], as has the preparation of formic acid [1]. Binding energies were referred to the Fermi level [14] and calculated using the following clean surface binding energies:

$$\text{Cu } 2p_{3/2} = 932.8 \text{ eV [11]}, \quad \text{Pb } 4f_{7/2} = 137.1 \text{ eV [2]}.$$

Coverages were calculated from the following peak area ratios:

$$\text{O } 1s/\text{Cu } 2p_{3/2} = 0.020 \text{ for the oxygen } - (\sqrt{2} \times \sqrt{2})R45^\circ \text{ monolayer on Cu(100)} \equiv 8 \times 10^{14} \text{ atoms cm}^{-2} \text{ [3];}$$

O 1s/Pb 4f_{7/2} = 0.045 for the Pb O(100) monlayer [2] on Pb (100) $\cong 8 \times 10^{14}$ atoms cm⁻².

3. Results

3.1. The oxidation of Pb(100)

The clean lead surface before oxidation showed no carbon or oxygen XPS features and had a well ordered LEED pattern. It was exposed, at 295 K to molecular oxygen at $\approx 10^{-3}$ Pa pressure for 20 min, a total exposure of $\approx 12\,000$ Langmuirs*. The detailed results of the oxidation of Pb(100) have been published [2] and are summarised as follows:

(i) A well ordered monolayer of orthorhombic lead (II) oxide, coverage $\approx 8 \times 10^{14}$ oxygen atoms cm⁻², is formed at this oxygen exposure. The surface structure is Pb O(100), the unit cell being $a = 0.46$ nm, $b = 0.54$ nm, $\alpha = 89^\circ$, orientated with a at $\pm 43^\circ$ and b at $\pm 42^\circ$ to the vectors of the primitive Pb(100) unit cell.

(ii) The O (1s) binding energy is 529.5 eV and the Pb (4f) binding energy 138.0 eV; the latter is shifted by about 1 eV to higher binding energy with respect to the Pb (4f) metal peak at 137.1 eV.

(iii) The He I spectrum of the PbO surface resembled that reported for the oxidation of polycrystalline lead [10].

3.2. Interaction of PbO (100) with formic acid

The surface was cooled to 80 K and exposed to formic acid for 10 min at $\approx 10^{-5}$ Pa (≈ 60 L). The formic acid in the gas phase was pumped away and the O (1s), Pb (4f) and ultra-violet photoelectron spectra which were observed are shown (figs. 1–3). Binding energies are given in table 1. Exposure to formic acid caused the disappearance of all diffraction features, leaving only a high background intensity. The surface was allowed to warm slowly to 295 K in vacuo ($\approx 10^{-7}$ Pa) while monitoring the photoelectron spectra (figs. 1–3). The diffraction pattern remained diffuse, indicating a disordered adlayer. Although marked changes occurred in the spectra during warming to 295 K no further differences were noted on heating the surface to 400 K in vacuo.

The PbO(100) surface, in a separate experiment was exposed to formic acid at 295 K, and the results are shown in figs. 3 (curve 4) 4 (O (1s) spectra) and 5 (Pb (4f) spectra). Fig. 6 shows the change in the surface oxygen concentration as a function of formic acid exposure. At exposures < 1000 L the diffraction pattern remained unchanged, although the background intensity had increased. Between exposures of 1000 and 2000 L the oxide diffraction pattern gave way to that of the

* 1 Langmuir = 10^{-6} Torr s = 1.33×10^{-4} Pa s.

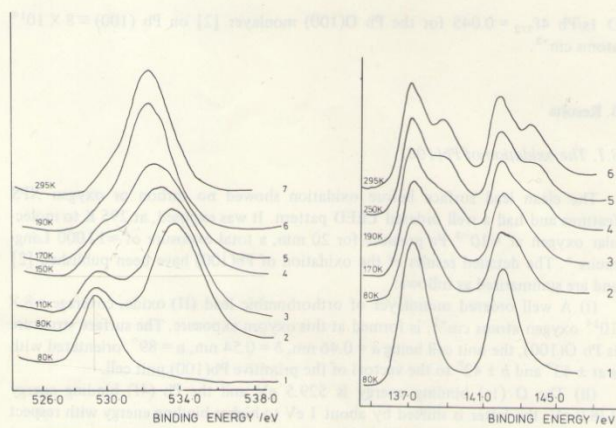


Fig. 1. XPS of Pb(100), O (1s) region. Curve 1: After oxidation at 295 K and cooling to 80 K in vacuum. Curve 2, as 1, after exposure to 60 L of formic acid at 80 K. Curves 3–7, as 2, after warming in vacuum to the temperatures shown.

Fig. 2. XPS of Pb(100), Pb (4f) region. Curve 1: After oxidation at 295 K and cooling to 80 K in vacuum. Curve 2, as 1, after exposure to 60 L of formic acid at 80 K. Curves 3–6, as 2, after warming in vacuum to the temperatures shown.

Table 1
Binding energy data (eV w.r.t. Fermi level) on the interaction of oxidized lead with formic acid

	X.P.S.		HeI ^{a)}	
	Pb 4f _{7/2}	O 1s	C 1s	
Clean Pb(100) ^{b)}	137.1	—	—	
Oxidized Pb(100) ^{c)}	137.1, 138.0	529.5	—	9.1
Oxidized Pb(100) + formic acid at 80 K	137.1, 138.0	529.5, 534.0	290.5	6.8, 8.0, 9.5
Oxidized Pb(100) + 850 L formic acid at 295 K	137.1, 138.8	532.0	288.4	4.6, 8.4, 9.7

a) Adsorbate orbitals only.

b) Used for calibration [2].

c) Oxidized by exposure to 1200 L of oxygen at 295 K.

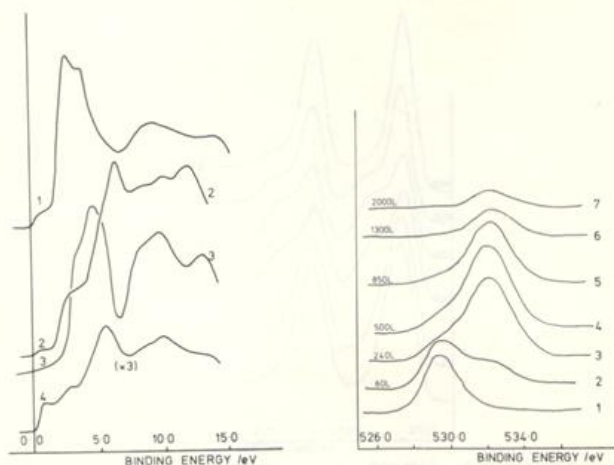


Fig. 3. UPS. (1) He I spectrum of Pb(100) after oxidation at 295 K and cooling to 80 K. (2) as (1), after exposure to 60 L formic acid at 80 K. (3) as (2), after warming to 295 K in vacuum. (4) oxidized lead after exposure to 1300 L of formic acid at 295 K.

Fig. 4. XPS of oxidized lead, O (1s) region. Curve 1: Pb(100) after oxidation at 295 K. Curves 2–7, as 1 after the shown exposure to formic acid at 298 K.

Pb(100) clean surface, while both surface oxygen and carbon coverage decayed markedly. If exposure of the PbO(100) surface to formic acid was limited to 500 L, where significant formic acid adsorption had occurred, no further changes occurred when the surface was heated in vacuum to 400 K.

No adsorption was observed when the clean Pb(100) surface was exposed to formic acid at 295 K (2000 L at $\approx 10^{-4}$ Pa). This is analogous to our earlier studies of the activating role of oxygen in the adsorption of H₂S [2] and more recently the data of Au et al. [9] who studied the H₂O + Cu(111)-O system.

3.3. The oxidation of copper(100)

The clean Cu(100) surface showed no oxygen or carbon XPS features and possessed a well ordered diffraction pattern. The surface was then heated to ≈ 570 K and exposed to oxygen at a pressure of $\approx 1 \times 10^{-4}$ Pa for 30 min. We refer to this as the "oxidized surface". A previous detailed study of the oxidation resulted in the following conclusions [3].

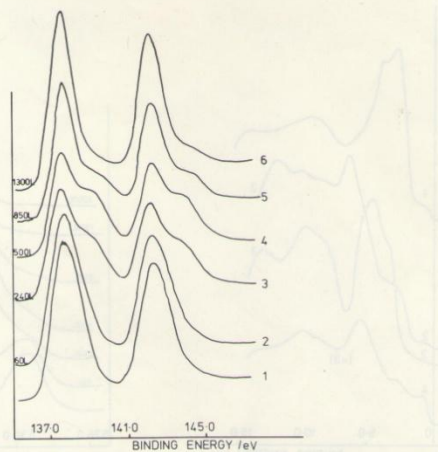


Fig. 5. XPS of oxidized lead, Pb (4f) region. Curve 1: Pb(100) after oxidation at 295 K. Curves 2-6, as 1, after the shown exposure to formic acid at 295 K.

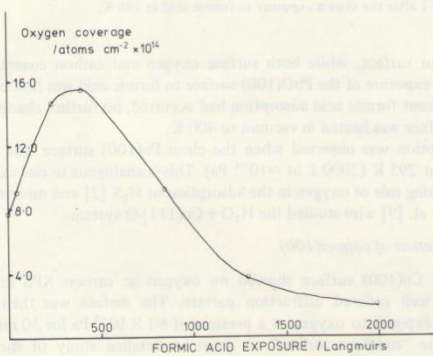


Fig. 6. Surface oxygen concentration during exposure of oxidized lead to formic acid at 295 K.

(i) The surface "oxide layer" is about one monolayer thick, coverage $\approx 1 \times 10^{15}$ atoms cm^{-2} , and its structure can be described as $\text{Cu}(100) - (\sqrt{2} \times 0.460 \text{ nm})R45^\circ - \text{O}$ with a well ordered "coincidence mesh" diffraction pattern. The structure can not be simply related to either of the bulk copper oxides.

(ii) The O (1s) binding energy is 531.0 eV and no changes occur in the copper core level peaks, indicating the absence of copper(II) species. Small changes in the copper Auger spectra suggest the presence of copper(I) species.

We also observed [3] the result of more extensive oxidation of a Cu(100) crystal (100 Pa of oxygen for 1 h at 295 K); the resulting oxide surface is disordered and its thickness is the equivalent of the uptake of at least three monolayers of oxygen. The presence of Cu(I) is now clear from the Auger spectra although no changes occur in the copper 2p core levels. We refer to this as the "heavily oxidized surface".

3.4. Interaction of oxidized copper with formic acid

Some of the changes observed during exposure of the oxidized surface to formic acid were similar to those noted with lead(II) oxide. At 80 K the ultra-violet photoelectron spectra resembled those of gas phase formic acid. On warming to 295 K

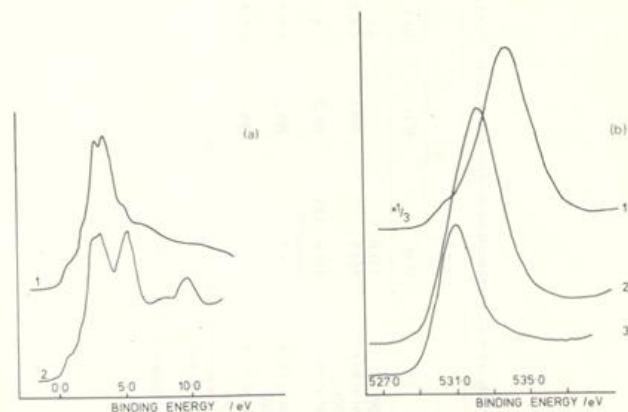


Fig. 7. (a) UPS, He I. Curve 1: Oxidized Cu(100). Curve 2, as 1 after exposure to formic acid at 80 K and warming to 295 K in vacuum. A similar spectrum is observed on exposing oxidized Cu(100) to formic acid at 298 K. (b) XPS, O (1s) region. Curve 1: Oxidized copper after exposure to 100 L of formic acid at 80 K. Curve 2, as 1 after warming to 295 K in vacuum. Curve 3: Oxidized Cu(100).

Table 2
Binding energy data (eV w.r.t. Fermi level) on the interaction of copper^{a)} and oxidized copper^{b)} with formic acid

	X.P.S.		U.P.S. ^{b)}	
	O 1s	C 1s	He I	He II
Oxidized Cu(100) ^{d)}	531.0	—	6.0	5.9
Cu + formic acid at 80 K ^{c)}	533.8	290.2	6.4, 8.5, 9.8, 11.6	6.8, 8.5, 9.7, 11.8, 16.0
Oxidized Cu(100) + formic acid at 80 K	531.0, 533.8 (shoulder)	290.3	5.8, 7.7, 9.1, 10.8	5.8, 7.7, 9.1, 10.8, 15.1
Cu + formic acid at 295 K ^{c)}	531.7	288.2	4.8, 8.2, 9.8	4.7, 8.1, 9.6, 13.2
Oxidized Cu(100) + formic acid at 295 K	532.2	288.7	4.9, 8.3, 9.7	5.0, 7.4, 9.4, 12.5

a) Binding energies referred to Cu 2p_{3/2} = 932.8 eV for the clean surface [12].

b) Adsorbate orbitals only.

c) From ref. [1].

d) Oxidized by exposure at 570 K to 2000 L of oxygen.

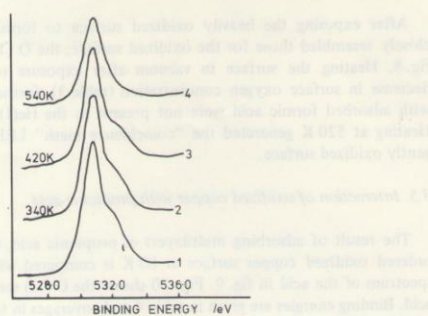


Fig. 8. XPS, O (1s) region. Curve 1: Heavily oxidized copper after exposure to formic acid at 295 K. Curves 2–4, as 1, after heating in vacuum to the temperatures shown.

marked changes occurred and the He(I) spectrum and O (1s) spectrum are shown in fig. 7. In contrast to lead, interaction with formic acid caused no changes in the copper core levels other than a decrease in intensity. Tables 2 and 3 give binding energy and coverage data, and also compare the interactions of formic acid at 295 K with the oxidized and the clean copper surface.

Heating the oxidized crystal in vacuum, after exposure to formic acid at 295 K, resulted in regeneration of the clean copper surface. The surface oxygen and carbon concentrations decreased as a function of temperature, more than 85% being removed at 520 K, and the clean metal LEED pattern reappeared.

Table 3
Surface coverages observed during the interaction of formic acid with copper, oxidized ^{a)} copper and heavily oxidized ^{a)} copper

	Oxygen (atoms cm ⁻² / 10 ¹⁴)	Formic acid (molecules cm ⁻² /10 ¹⁴)
Cu(100) + formic acid at 295 K	—	2 ± 0.5
Oxidized Cu(100)	10 ± 1	—
Oxidized Cu(100) + formic acid at 295 K	10 ± 1	7 ± 1
As above, after heating to 520 K	2.5 ± 1	0 ± 1
Heavily oxidized copper (100)	>30 ± 2	—
Heavily oxidized Cu(100) + formic acid at 295 K	>30 ± 2	6 ± 1
As above, after to 520 K	>23 ± 2	0 ± 1

^{a)} For oxidation conditions see text.

After exposing the heavily oxidized surface to formic acid the UPS results closely resembled those for the oxidized surface; the O (1s) spectrum is shown in fig. 8. Heating the surface in vacuum after exposure to formic acid caused a decrease in surface oxygen concentration (table 3), furthermore, peaks associated with adsorbed formic acid were not present in the He(I) spectrum after heating. Heating at 520 K generated the "coincidence mesh" LEED pattern of the more gently oxidized surface.

3.5. Interaction of oxidized copper with propionic acid

The result of adsorbing multilayers of propionic acid, ($\text{CH}_3\text{CH}_2\text{COOH}$) on the ordered oxidized copper surface at 80 K is compared with the gas phase, He(I) spectrum of the acid in fig. 9. Fig. 10 shows the C (1s) spectrum of the condensed acid. Binding energies are given in table 4 and coverages in table 5.

The surface was allowed to warm to 295 K in vacuum and resultant changes in the photoelectron spectra are also shown in figs. 9 and 10. Condensing propionic acid at 80 K caused the LEED pattern to become diffuse and to remain so during warming to 295 K. Adsorption at 295 K generated the same photoelectron spectra as condensation at 80 K followed by warming in vacuum to 295 K.

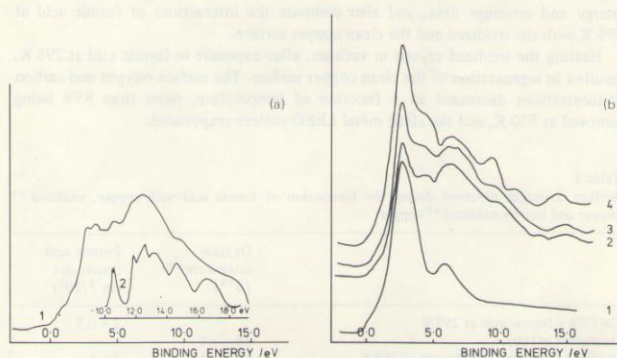


Fig. 9. (a) UPS, He I. Curve 1: Oxidized copper after exposure to propionic acid at 80 K. Curve 2: Propionic acid vapour (from Watanabe et al. [12]). The spectra have been aligned to allow for differences in reference levels. (b) UPS, He II. Curve 1: Oxidized Cu(100). Curve 2: as 1, after exposure to propionic acid at 80 K. Curves 3, 4, as 2, after warming to 128 K (3) and 198 K (4) in vacuum. A similar spectrum to (4) is observed on exposing oxidized copper to propionic acid at 295 K.

Table 4
Binding energy data (eV w.r.t. Fermi level) for the interaction of copper^{a)} and oxidized copper^{b)} with propionic acid

	X.P.S.		U.P.S. b)	
	O 1s	C 1s	He I	He II
Oxidized Cu(100) c) + propionic acid at 80 K	534.0	286.1, 290.3	4.8, 6.8, 9.8	4.6, 6.7, 9.9, 13.2, 15.1
Oxidized Cu(100) + propionic acid at 295 K	532.0	286.0, 288.5	5.0, 7.0, 9.5	4.7, 7.0, 9.5, 11.5, 14.7
Cu(100) + propionic acid at 295 K	532.0	286.0, 288.3	5.0, 7.0, 9.3	4.6, 7.0, 9.5, 11.5, 14.7

a) Binding energies referred to Cu 2p_{3/2} = 932.8 eV for the clean surface [12].

b) Adsorbate orbitals only.

c) Oxidized by exposure at 570 K to \approx 2000 L of oxygen.

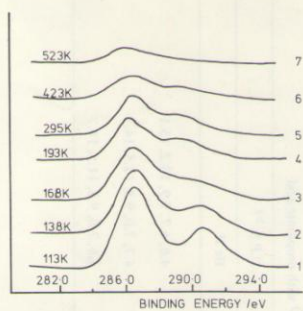


Fig. 10. XPS of oxidized copper, C (1s) region. Curve 1, after exposure to propionic acid at 80 K and warming in vacuum to 113 K. Curves 2–7, as 1, after warming in vacuum to the temperatures shown.

After adsorption of propionic acid on the oxidized surface at 295 K the surface was heated in vacuum. Both O (1s) and C (1s) peak areas decreased sharply, especially above 420 K, as shown in fig. 10. After heating to 520 K the diffraction pattern was typical of the clean Cu(100) surface.

Table 5
Surface coverages observed during the interaction of propionic acid with copper and oxidized copper

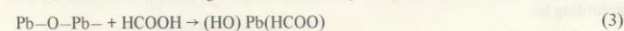
	Oxygen (atoms $\text{cm}^{-2}/10^{14}$)	Carbon (atoms $\text{cm}^{-2}/10^{14}$)	Propionic acid (molecules $\text{cm}^{-2}/10^{14}$)
Cu(100) + propionic acid at 295 K	—	—	8.0 ± 1.0
As above, after heating to 773 K	—	0.8 ± 0.2	0.8 ± 0.2
Oxidized copper	10 ± 2	—	—
Oxidized copper + propionic acid at 298 K	10 ± 2	—	8.0 ± 2
As above, after heating to 520 K	0 ± 0.5	5×10^{14}	0 ± 0.5

4. Discussion

The spectra observed when formic acid is present as multilayers on both oxidized lead and copper at 80 K are very similar to those of gas phase formic acid [11]. Marked differences are observed however, if the surfaces are warmed above ≈ 120 K, or if the oxide is exposed to formic acid at room temperature. In our earlier study, the interpretation of the spectra has been given in detail and in particular we identified the formate ion as a surface species formed above 120 K. The binding energy of the He(I) peaks at ≈ 5.0 eV, 8.3 eV and 9.7 eV and their relative intensity observed in the present investigation are the same as those noted when the formate ion is present at, for example, a copper metal surface. The decrease in the O (1s) binding energy of the oxygen peak from ≈ 534 eV in the "condensed" acid, to about 532 eV was also noted during generation of the formate ion at metal surfaces [1]. Dissociation of the acid also occurs in the same temperature range, 120–190 K.

The results also show the formation of the propionate ion ($\text{CH}_3\text{CH}_2\text{COO}^-$) on oxidized copper, as is most clearly seen by considering the C (1s) spectrum (fig. 10). At 80 K for the condensed acid, this consists of two peaks, intensity ratio 2 : 1, that at ≈ 286 eV binding energy is due to the side chain while that of ≈ 290 eV is due to the carbon of the acid group. Between 150 and 200 K this peak moves to lower binding energy (≈ 288 eV) reflecting increasing negative charge on the atom due to delocalization of charge in the newly formed carboxylate ion. The peak area ratio remains 2 : 1 throughout. As with formic acid, changes in the uv induced spectra also occur.

The spectra also enable us to comment on the fate of the proton formed in the dissociation of formic acid. The results are clearer with the PbO(100) surface, where the O (1s) binding energy of the oxide is quite low (≈ 529.5 eV) although similar molecular events probably occur with copper. Decomposition of the formic acid molecule occurs between 120 K and 190 K, resulting in a decrease in the O (1s) binding energy (fig. 1). There are also marked changes in the oxide O (1s) peak, which shifts to substantially higher binding energy between 170 and 190 K. We consider that this change reflects surface hydroxylation according to eq. (3):



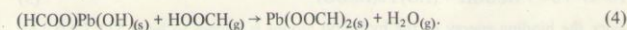
since the binding energy of the hydroxyl groups is known to be at 531.7 ± 0.2 eV [9]. This adds further weight to the mechanism which we proposed for the decomposition of condensed formic acid into the formate ion on metals [1], where release of the proton was suggested to be the last of three stages.

Significant changes also occur during the decomposition process in the lead core level peaks, as shown in fig. 2. Between 170 K and 298 K a peak, shifted by ≈ 1.7 eV from the Pb $4f_{7/2}$ metal peak, clearly emerges. This shift, which is much larger than that noted during interaction with molecular oxygen (≈ 1 eV) indicates increasing positive charge on the surface lead atoms. To decide whether this reflects

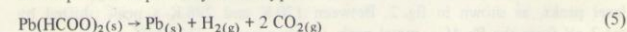
a change in the valence of lead, or is merely due to increased charge transfer of constant valence it is necessary to consider the surface stoichiometry. In the initial oxide layer, represented by fig. 1, curve 1, the oxide thickness is about one monolayer (8×10^4 atoms cm^{-2}), with a surface layer composition PbO. As a result of interaction with formic acid the oxygen coverage increases from 8×10^{14} atoms cm^{-2} to $\approx 2 \times 10^{15}$ atoms cm^{-2} at 150 K (fig. 1, curve 4) a factor of ≈ 2.5 . Completion of reaction 3 would change the stoichiometry from PbO to Pb(OH)(HCOO), with an increase in the O (1s) peak area by a factor of 3. The surface oxygen concentration does not exceed that equivalent to Pb(OH)(HCOO), suggesting that the lead valence does not exceed two. The shift of 1.7 eV may be compared to a similar shift noted by Evans and Thomas [10], who oxidized lead in the presence of surface carbon contamination.

The UPS data firmly establish the existence of formate ions on both oxidized and heavily oxidized copper, the picture is however less clear than for lead. Firstly, as is the case with oxidation, no changes other than of intensity occur in the copper core levels. Secondly, since the O (1s) signal for the oxidized metal (531.0 eV) is much closer in binding energy to that of the formate ion (≈ 532.0 eV) than is the case with lead, there is no clear evidence that surface hydroxyl groups (B.E. ≈ 531.5 eV) are formed.

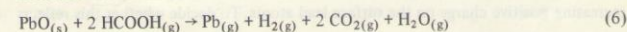
If lead(II) oxide is exposed to 500 L of formic acid at 295 K the spectra closely resemble those noted after exposing the surface to formic acid at 80 K and warming to room temperature in vacuum. The surface is stable in vacuum at 295 K and is also unchanged by heating to 400 K for one hour. If, however, the surface is exposed further to formic acid at 295 K both electron spectroscopy and LEED indicate that reduction of the oxide occurs. The O (1s) peak coverage decreases to $\approx 2 \times 10^{14}$ atoms cm^{-2} , about 25% of that of the original PbO surface, the high binding energy lead peak disappears, and the core level peaks of the clean metal increase in intensity. In UPS the orbitals associated with the formate ion disappear and clean metal features become visible as also does the "clean" LEED pattern of Pb(100). The reduction of the Pb(OH)(HCOO) surface thus requires the presence of formic acid. This suggests that the first steps in the mechanism are the further adsorption of formic acid, as formate ion + hydrogen, and the formation of water, according to:



The result of reactions (3) and (4) is the conversion of oxide to formate with the desorption of water. The metal formate generated in this way is, however, of very low stability, decomposing rapidly to yield a clean metal surface. The nature of the decomposition is probably of the type:



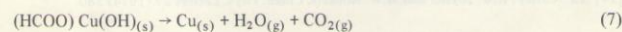
such that the overall reaction is



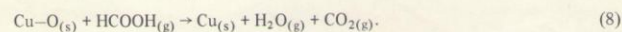
which has $\Delta G_{298}^0 = -179.4 \text{ kJ mol}^{-1}$.

Support for the low stability of the formate ion at the lead metal surface is the inability of Pb(100) to adsorb formic acid at 298 K. In this respect lead resembles gold [1] where the formate ion is stable at the surface only below 200 K.

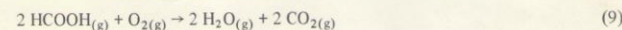
The reduction of the PbO(100) surface by formic acid is more facile than that of oxidised copper, even though the latter reaction is thermodynamically more favourable, ($\Delta G_{298}^0 = -221.7 \text{ kJ mol}^{-1}$, assuming the surface layer to be Cu_2O). There is no evidence for the occurrence with copper, at 295 K, of the analogue of reaction (4) even though the formate ion is stable at the Cu surface [1]. The $(\text{HCOO})\text{Cu}(\text{OH})$ surface is, however, reduced to clean copper by heating to 520 K in vacuum. This reduction is thought to proceed by decomposition of the formate ion, which occurs at this temperature on the clean metal [1]. The result of heating is thus



the overall reaction being:



The coverage data (table 3) support this view since, in the case of both oxidised and heavily oxidised copper, the amount of oxidic oxygen removed by heating in vacuum, after exposure to formic acid at 295 K, is equal to the amount of formic acid originally adsorbed at 298 K. In each case this corresponds to slightly less than the surface monolayer of oxygen atoms. The results suggest that copper, and especially lead, should catalyse the oxidation of formic acid (eq. 9))



which has $\Delta G_{298}^0 = -287.0 \text{ kJ mol}^{-1}$.

It is interesting to note that at 295 K less formic acid ($\approx 2 \times 10^{14}$ molecules cm^{-2}) adsorbs on clean Cu(100) than on the oxidised surface, ($\approx 7 \times 10^{14}$ molecules cm^{-2}). In contrast the amount of propionic acid adsorbed on both surfaces is similar ($\approx 8 \times 10^{14}$ molecules cm^{-2}). Propionic acid desorbs from the clean metal with little decomposition of the side chain, as evidenced by the small residual C (1s) peak at 285 eV. More marked decomposition appears to occur on the oxidized surface, where a larger residual carbon peak is noted (table 5).

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