

## THE ADSORPTION AND OXIDATION OF ACETIC ACID AND ACETALDEHYDE ON Cu(110)

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Acetic acid adsorbed on Cu(110) at 140 K in a molecular state and XPS showed the double C 1s emission expected for this species. UPS emissions compatible with molecular acetic acid were observed, but the 13a' orbital exhibited a chemisorption bonding shift, indicating that the molecule binds to the surface through the oxygen non-bonding lone-pair orbital of the OH group. Upon heating to 370 K some acetic acid desorbed at 240 K, hydrogen was evolved at 310 K, and the O 1s spectrum narrowed revealing that the remaining tightly bound species possessed identical oxygen atoms. The coverage of the moiety was  $3.5 \times 10^{14} \text{ cm}^{-2}$ . This species appears to be an acetate, and the outermost valence levels in the UPS closely resembled those observed for the formate. The acetate did not decompose until  $\sim 590 \text{ K}$ . The reaction products indicated the formation of another intermediate, acetic anhydride, which decomposed to yield mainly  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{C}_2\text{O}$  (ketene), and carbon fragments. Oxygen preadsorption enhanced acetate formation and resulted in its presence in the photoelectron spectra even at 140 K; the oxygen removed the acid hydrogens to form water at low temperatures. Acetaldehyde adsorbed on the clean surface at 140 K in a molecular state and desorbed without reaction at 200 K. When oxygen was preadsorbed, acetaldehyde reacted with it to form the acetate.

### 1. Introduction

In recent years a new approach has been used by many investigators to gain a basic understanding of catalytic reactions and of adsorption processes taking place at surfaces. This approach involves the logical step of the minimisation of the variables involved in the more classical type of catalytic studies. Crystallographic heterogeneity is avoided by the use of single crystals, and surface cleanliness is maintained by the use of argon bombardment, Auger electron spectroscopy and UHV conditions. By the use of these techniques, unambiguous data relating to reaction mechanisms and surface intermediates involved in such reactions can be obtained. Of course, to obtain the full picture of a catalytic reaction, higher pressure, real system

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studies must be performed in parallel with such investigations to obtain global reaction rates and equilibrium product distributions.

The adsorption and reaction of many simple organic adsorbates have been investigated on several metal surfaces, and the influence of “promoters” and “poisons” on such reaction sequences have been studied [1]. In particular the adsorption and reactions of methanol [2], formaldehyde, and formic acid [3] on the Cu(110) surface have been outlined in previous publications. Here we report the results of a study of the interaction of somewhat more complex species with the Cu(110) plane; *vis*, acetic acid and acetaldehyde. These results will be discussed in the light of other work with formic acid and formaldehyde [3] and with the same reactions carried out on another group 1B metal, Ag(110) [4].

## 2. Experimental

The apparatus used in this study has been described in detail elsewhere [5]. It is a UHV chamber and was operated at a base pressure of  $\sim 5 \times 10^{-10}$  Torr (mostly He). The system contained facilities for LEED, Auger, XPS, UPS and TPRS; the electron analyzer was a double-pass CMA. Photoelectron spectra were stored on a 500 channel multi-channel analyzer and output into an  $x$ - $y$  recorder. He(II) UPS spectra were obtained in 5 min whereas C 1s and O 1s XPS spectra required 20 min each.

The Cu(110) crystal was 5 N purity, oriented to within  $1^\circ$  of the relevant plane. The surface was cleaned by argon bombardment at 600 K. It was found that small amounts of carbon could be removed by dosing with oxygen and heating to 900 K; however more strongly bound C fragments build up after several TPRS experiments with acetic acid and could only be removed with argon bombardment.

## 3. Results

### 3.1. *Acetic acid*

#### 3.1.1. *Adsorption on the clean surface*

Acetic acid was adsorbed on the clean Cu(110) surface at 140 K, and subsequent TPRS yielded the results shown in fig. 1. The main features seen in these spectra are the desorption of acetic acid with peak rate at 240 K, hydrogen evolution at  $\sim 310$  K, and desorption products from a much more strongly bound species at 590 K. There were a variety of masses evolved in this high temperature peak, and these are listed in table 1. The fact that they were desorbed in coincident peaks indicates that they result from the decomposition of a common intermediate species. Furthermore the peak position was independent of initial coverage, indicative of a first order reaction process. From plots of  $\log(\text{rate/coverage})$  versus reciprocal tempera-

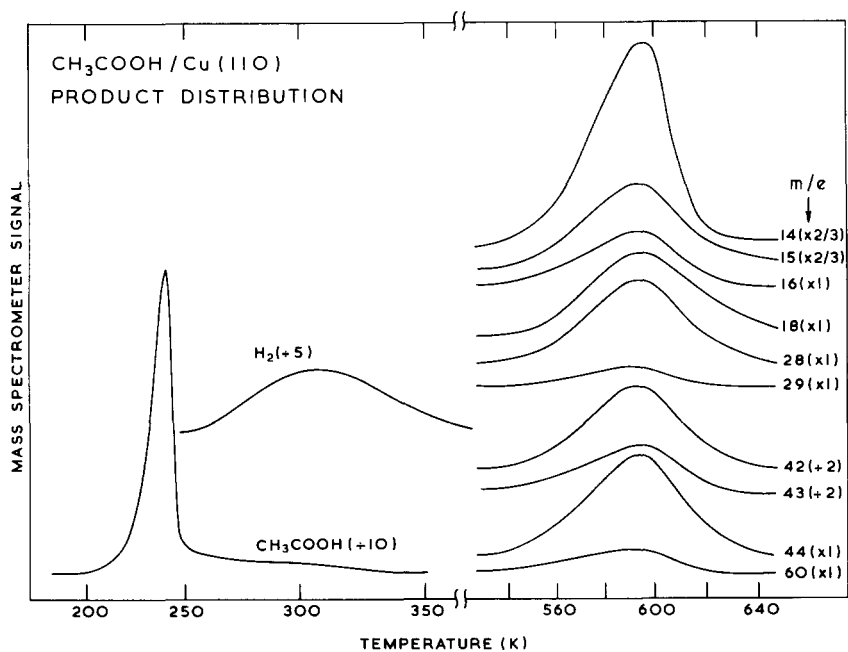


Fig. 1. TPRS product distribution observed for the adsorption of acetic acid on the clean Cu(110) surface at 140 K. The baselines are offset for clarity and the masses observed for the products at 590 K are shown. The dose of acetic acid was 500  $\mu$ s and the heating rate was 4 K  $s^{-1}$ .

Table 1  
TPRS products

$m/e$	Experimental products	Literature cracking patterns			
		H <sub>2</sub> C <sub>2</sub> O	CH <sub>3</sub> COOH	CO <sub>2(a)</sub>	CH <sub>4</sub>
60	15		60		
45	36		91		
44	52			100	
43	56		100		
42	80	94	16		
29	8	7	13		
28	42	11	7	6	
18	40				
16	40		7	7	100
15	60		45		85
14	100	100	13		16

a) Experimentally the 16 and 28 signals were found to be much bigger in the UTI mass spectrometer – they were 25% of the 44 signal.

ture the activation energy barrier for this decomposition was found to be  $180 \text{ kJ mol}^{-1}$  with a pre-exponential factor of  $2 \times 10^{15} \text{ s}^{-1}$ .

Unlike other simple organic molecules on this surface [2,3] XPS showed that a considerable amount ( $\sim 5\%$  of a monolayer) of carbon was left on the surface after such a TPRS experiment. Most of this carbon could be removed by dosing the surface with oxygen and heating to 900 K to desorb CO near 850 K. However, some more strongly bound carbon fragments remained after such treatment. Because of the lengthy procedure of argon bombardment it was impracticable to clean the surface in this way after every TPRS run (one run was needed per mass fraction analyzed), and bombardment was carried out only after the strongly bound C species built up to  $\sim 10\%$  of a monolayer. As a result the cracking fraction distribution was not completely reproducible, and the exact stoichiometry of the surface species involved in this decomposition was difficult to obtain. Nevertheless the mass evolution at 590 K shown in fig. 1 is typical of that obtained from the Cu(110) with  $< 10\%$  monolayer of C impurity. From the mass distribution it is clear that several products were desorbed from the surface. Large mass 14 and 12 signals are indicative of ketene while the presence of 43, 45 and 60 indicate acetic acid (all postulated products and their cracking fractions are shown in table 1).

Fig. 2 shows the UP spectra obtained for acetic acid adsorption on the Cu(110) surface. The assignment of orbitals is given in the same figure and the gas phase orbital positions are taken from the work of Carnovale et al. [6]. Unfortunately, the latter work only gives orbitals up to the  $9a'$  in I.P. The energies of the final two emissions in the spectrum are thus not known. The two envelopes of orbitals peaking at 8.0 and 10.2 eV agree well with those of Carnovale, including relative intensities, though in the gas phase spectrum the  $9a'$  ( $\sigma_{\text{OH}}$  bonding) gives a distinct emission of its own; it may account for the tail in the range 11–12.5 eV. However the most important feature of the spectrum of adsorbed acetic acid is the single emission peak below 6 eV binding energy instead of the two expected for the  $13a'$  and  $3a''$  (oxygen non-bonding and  $\pi$  orbitals, respectively). The simplest explanation is that the molecule is bonded to the surface primarily through the oxygen lone pair orbital, which then shows a chemisorption bonding shift of  $\sim 1.2 \text{ eV}$ . This is completely compatible with results for other simple organic molecules on this surface, including methanol [2], formaldehyde and, particularly, the  $\text{C}_1$  carboxylic acid, formic acid [3]. The latter showed exactly the same effect, and the chemisorption shift was the same. There may also be small shifts for other orbitals (particularly the  $12a'$  which involves oxygen non-bonding orbitals), but they cannot be deconvoluted in these spectra; the main shift is certainly the  $13a'$ . By analogy with other molecules it is likely that the most tightly bound orbital in the spectrum will show some shift to lower binding energies, and thus we can attempt to *approximate* the positions in which the final two emissions would be expected in the gas phase. This estimate is shown in the gas phase spectrum in fig. 2. The assignment we have given for the spectrum of adsorbed acetic acid shows the molecule suffers an extra-molecular relaxation/polarisation shift (ERPS) of 2.4 eV by comparison of the ionization

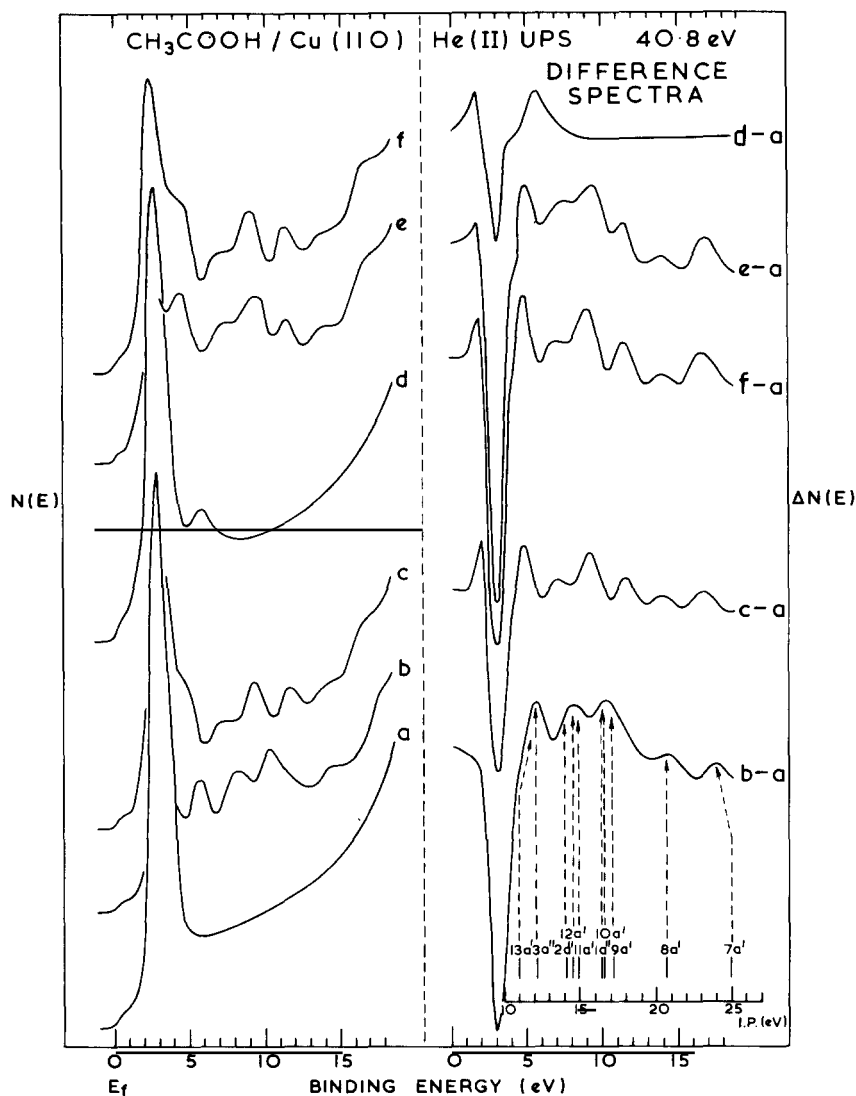


Fig. 2. Ultra-violet photoelectron spectra and difference spectra for acetic acid adsorption on Cu(110); the full d-band emission is not shown on all the spectra for clarity. Spectrum (a) is that from the clean surface, (b) after  $\text{CH}_3\text{COOH}$  adsorption at 140 K, and (c) layer of (b) heated to 375 K. Spectrum (d) was obtained after adsorption of 0.25 monolayer of oxygen at 300 K while (e) is that layer after subsequent adsorption of  $\text{CH}_3\text{COOH}$  at 140 K and (f) is the spectrum after heating to 370 K.

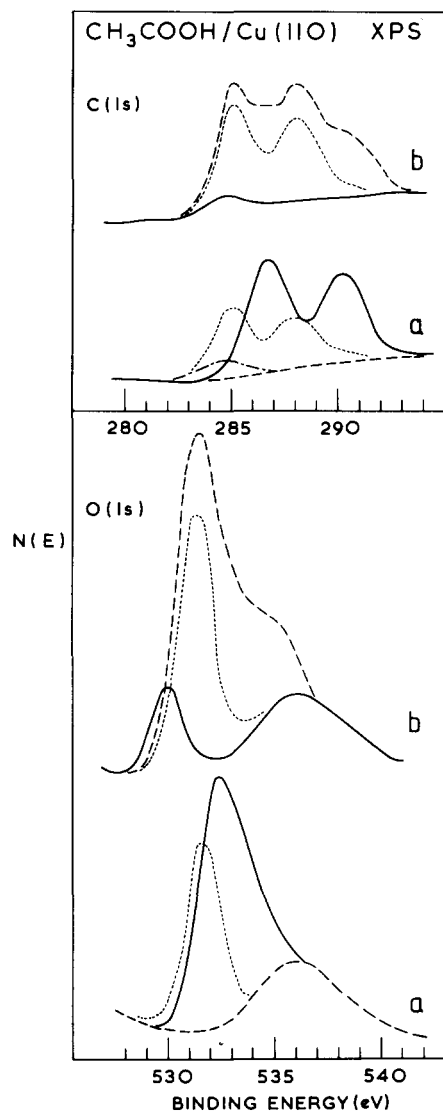


Fig. 3. X-ray photoelectron spectra for acetic acid adsorption on Cu(110). Spectra (a) were obtained for adsorption on the clean surface, (---) is the emission from the clean surface, while (—) are the spectra after acetic acid adsorption at 140 K (dose of 500  $\mu$ s) and (...) is the same layer heated to 370 K. The spectrum shown as (-.-.-) shows carbon remaining on the surface after heating to 650 K. Spectra (b) were obtained from the oxygen dosed surface; (—) is the O 1s spectrum after adsorption of 0.25 monolayer of oxygen, (---) is that after subsequent adsorption of acetic acid at 140 K, while (...) is the spectrum after heating that layer to 370 K and (—) in the C 1s spectrum indicates some carbon remaining on the surface after heating to 650 K.

potentials of gas phase and adsorbed species (which includes the additional term of the surface work function with adsorbate present). The change in width of the He(I) spectrum [7] after the adsorption of acetic acid of 140 K gives a work function decrease of 1.2 eV.

Upon heating the surface to 375 K the work function of the surface increased again to only 0.25 eV below the clean value. The He(II) spectrum became that shown in fig. 2c (difference spectrum (c-a)). The major orbitals seen for the low temperature species were still observed, but there was a general decrease in intensity; a shifting of around 0.9 eV occurred of all orbitals to lower binding energy relative to the Fermi energy and, most importantly, an apparently new emission emerged at 11.5 eV. The shift in orbital energies was the result of measuring the binding energies relative to the Fermi level. The ionisation potential is the same as for spectrum 2b, when corrected for work function differences. This spectrum is almost identical to that found for a surface formate [3]. The only difference was the presence of the two emissions above 13 eV binding energy which are mainly associated with the additional carbon atom. The relative intensities of the first four bands were also very similar to those in the formate; the position of the fourth band is more than 1 eV lower than that in the formate.

The O 1s XPS (fig. 3) showed a broad peak for acetic acid (fwhm of 3.5 eV) adsorbed at 140 K, while in the C 1s region there was the expected doublet emission with peaks for the  $\alpha$  and  $\beta$  carbon atoms at 290 eV and 286.6 eV respectively. It is interesting to note that the higher binding energy  $\alpha$  peak is smaller and broader than the  $\beta$  peak, as also seen in other studies [8]. When this layer was heated to 370 K the O 1s emission narrowed to a single line of instrumental resolution (fwhm 1.8 eV), and the separation of the two C 1s emissions narrowed to 3.1 eV, with both peaks shifting to lower binding energy. When the surface was heated to 650 K all the O 1s intensity was lost, and, as mentioned previously, small amounts of carbon were left on the surface (at a C 1s binding energy of about 285 eV).

### 3.1.2. Oxygen preadsorption

The effect of preadsorbed oxygen on the reaction of acetic acid was to increase the amount of reaction product at 590 K and to completely diminish the hydrogen desorption at 310 K, while showing large amounts of water desorption at low temperatures in a fashion similar to that seen for formic acid [3]. There was also a reduction in the acetic acid desorption by about 50%, though the shape and position of the peak was the same as for the clean surface. An increase in the amount of the more strongly bound species was also seen in the XPS through an increase in total emission. The predosed oxygen showed a binding energy of 530.0 ( $\pm 0.2$ ) eV, but upon adsorption of acetic acid at 140 K, the oxygen was already involved in bonding since the emission at 530 eV was lost, as observed for methanol [2] and formic acid [3]. The O 1s showed a main emission at 531.5 eV with a higher B.E. shoulder which was lost by heating to 370 K and is presumably associated with desorption of the parent acetic acid. In the C 1s spectrum the emissions present in the two

spectra for the clean surface seem to be superimposed to give a rather broad, complex emission. Upon heating, the simpler spectrum due to the species also present on the clean surface at 370 K was observed.

The UPS spectrum of the adsorbed oxygen given in fig. 2d and d—a showed the usual single emission at 5.7 eV binding energy plus the emission peak at around 1.8 eV which is always present for *strongly* bound species chemisorbed through oxygen and seems to be due to increased emission at the top of the metal d-band. When acetic acid was adsorbed on this layer at 140 K, spectrum 2e resulted. This profile is quite similar to that of 2f which was found only after heating the surface to 370 K. However, the most important point about the two spectra is that the 11.5 eV emission was present in both indicating that the more strongly bound species was present at both temperatures when oxygen was preadsorbed.

### 3.2. Acetaldehyde

#### 3.2.1. Adsorption on the clean surface

Acetaldehyde adsorbed on the clean Cu(110) surface at 140 K, but desorbed in-

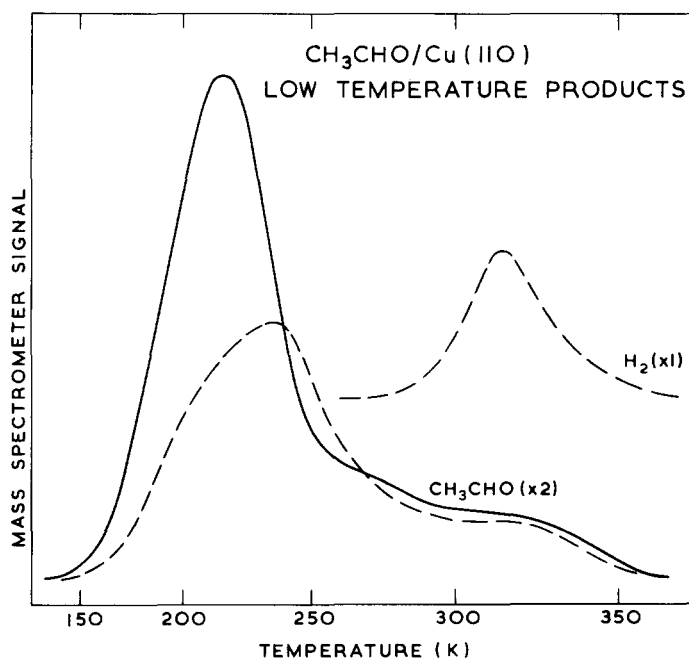


Fig. 4. TPRS product distribution observed for acetaldehyde adsorption on Cu(110). The full line is desorption from the clean surface while the dotted line is the desorption obtained after acetaldehyde adsorption at 140 K on the Cu(110) surface predosed with 0.25 monolayer of oxygen. In each case the dose was 500  $\mu$ s and the heating rate was 4 K  $s^{-1}$ . In the oxygen dosed case the products at 590 K are not shown. They were the same as in fig. 1.



tact during heating, showing no signs of reaction with the surface, (fig. 4). The temperature of the desorption peak shows that this species was fairly weakly bound. Application of Redhead's equation [9] assuming a pre-exponential factor of  $10^{13}$ , indicated a first-order desorption energy of  $56 \text{ kJ mol}^{-1}$ . Fig. 5 shows the UP spec-

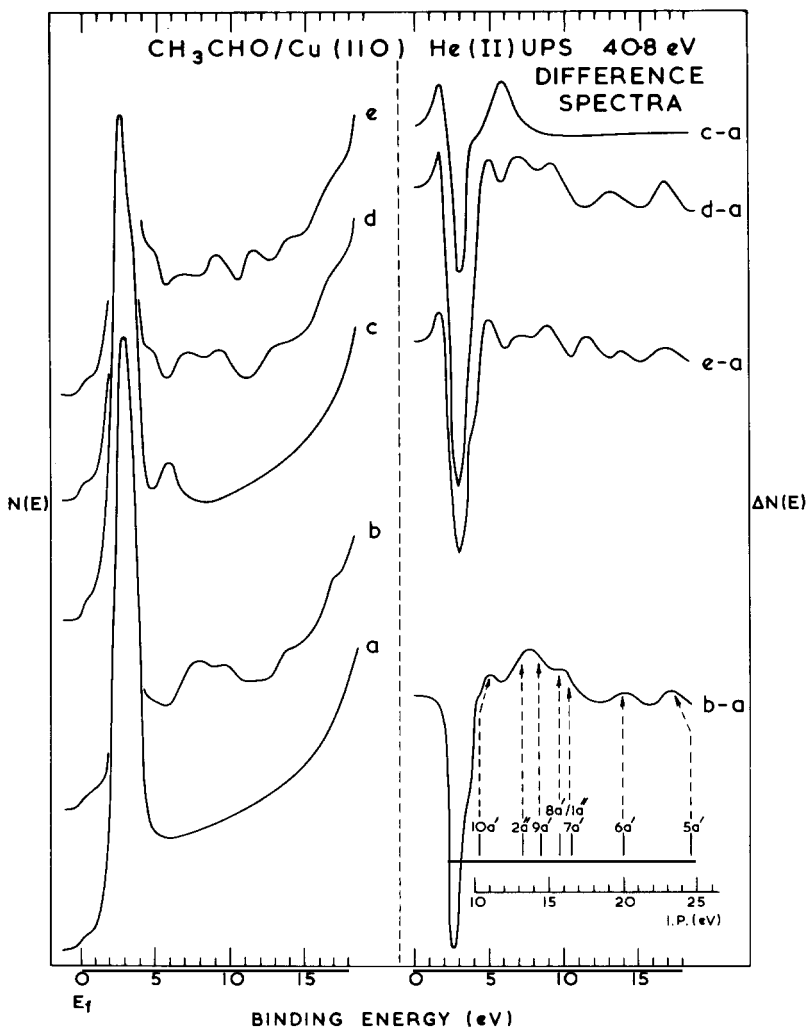


Fig. 5. Ultra-violet photoelectron spectra observed for acetaldehyde adsorption on Cu(110). Spectrum (a) is that from the clean surface, (b) after exposure to  $500 \mu\text{s}$  of  $\text{CH}_3\text{CHO}$  at 140 K, (c) after adsorption of 1/4 monolayer of oxygen at 300 K, (d) after subsequent adsorption of  $\text{CH}_3\text{CHO}$  at 140 K on layer (c), and finally (e) is the spectrum of layer d after heating to 320 K. The gas phase emissions on the lower right are taken from ref. [10].

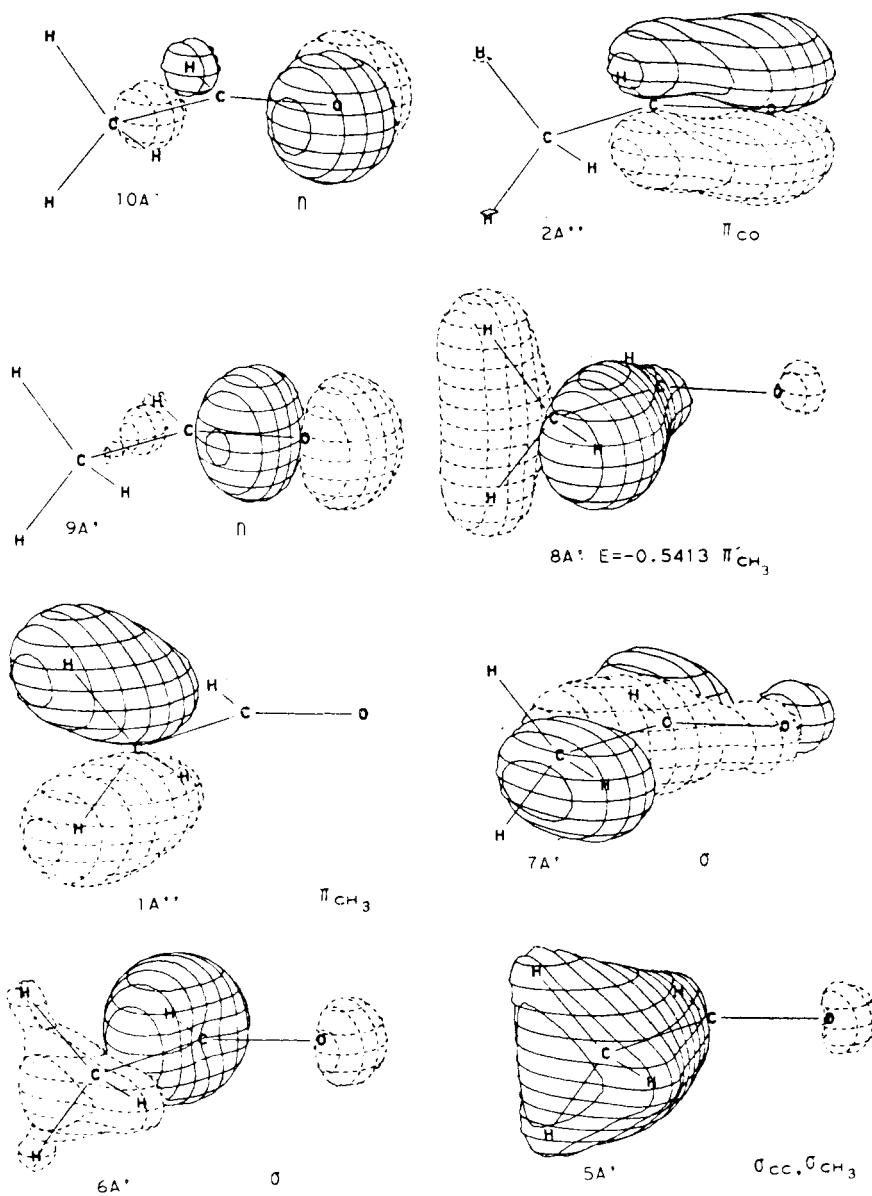


Fig. 6. Electron density contour diagrams for the occupied valence levels of acetaldehyde (from ref. [16]).

trum observed for this species; it is compared with positions of orbital energies observed for acetaldehyde in the gas phase [10]. Because we do not have a spectrum of the condensed species the alignment is not unambiguous, but that shown in fig. 5 seems the most reasonable. This assignment leaves the  $6a'$  orbital unaffected by any chemisorption shift, as is to be expected for an orbital composed of mainly C  $2s$  type orbitals [10]. Then the  $2a''$ ,  $9a'$ ,  $8a'$  and  $1a''$  (which are close in energy and overlap in gas phase photoelectron spectra) and  $7a'$  orbitals are contained within the envelope between 6–11 eV. Furthermore, there appeared to be a chemisorption bonding shift of the  $10a'$  orbital, the oxygen in plane non-bonding orbital (see fig. 6), of 0.8 eV, which is compatible with other results for the chemisorption of organic molecules on metal surfaces [2,3,11]. In particular, formaldehyde exhibited a very similar chemisorption bonding shift of 0.7 eV on this same surface [3]. This assignment gives a shift of  $\sim 1$  eV to lower binding energies for the  $5a'$  orbital, and this effect has also been observed for the higher binding energy valence orbitals of formaldehyde [3,11,12], acetaldehyde [11] and other molecules [2]. The extra-molecular relaxation polarisation shift given by the alignment of fig. 5 is 1.8 eV, the work function change being  $-1.1$  eV.

In fig. 7 the XPS spectrum for acetaldehyde adsorbed on the Cu(110) surface is shown. The O  $1s$  spectrum is a broad peak at 533.4, while two separate peaks are seen in the C  $1s$  spectrum for the  $\beta$  and  $\alpha$  carbons at 284.9 eV and 287.1 eV respectively. Upon heating the surface to 370 K, XPS showed no signs of any C or O species remaining on the surface.

### 3.2.2. Oxygen preadsorption

When oxygen was predosed onto the Cu(110) surface and acetaldehyde was subsequently dosed, the TPRS showed quite different features; examples of the low temperature product distribution seen when approximately 0.25 monolayer of oxygen was preadsorbed are shown in fig. 4. Acetaldehyde was desorbed at 240 K, 20 K higher than on the clean surface, but the amount desorbed was decreased. However, most notably, there were products desorbed from a much more tightly bound species at 590 K, and the products observed were similar to these seen for acetic acid adsorption described above; again, as for acetic acid, hydrogen was evolved at 310 K.

The UPS spectrum of oxygen on the copper (110) surface is shown in fig. 5c; 5d shows the spectrum after acetaldehyde adsorption on that layer. Spectrum 5d seems similar to a spectrum anticipated simply from oxygen plus acetaldehyde although the third band is somewhat more intense than that band in acetaldehyde alone. Spectrum 5e shows the surface plus adsorbate after heating to 320 K, and clearly the spectrum has changed, most noticeably showing a new orbital at 11.5 eV and a shift of the  $9a'$  orbital to higher binding energy. These points will be discussed in the following section.

In the XPS (fig. 7) adsorbed oxygen shows a peak at 530 eV, characteristic of chemisorbed oxygen atoms. Upon adsorption of acetaldehyde at 140 K, this peak

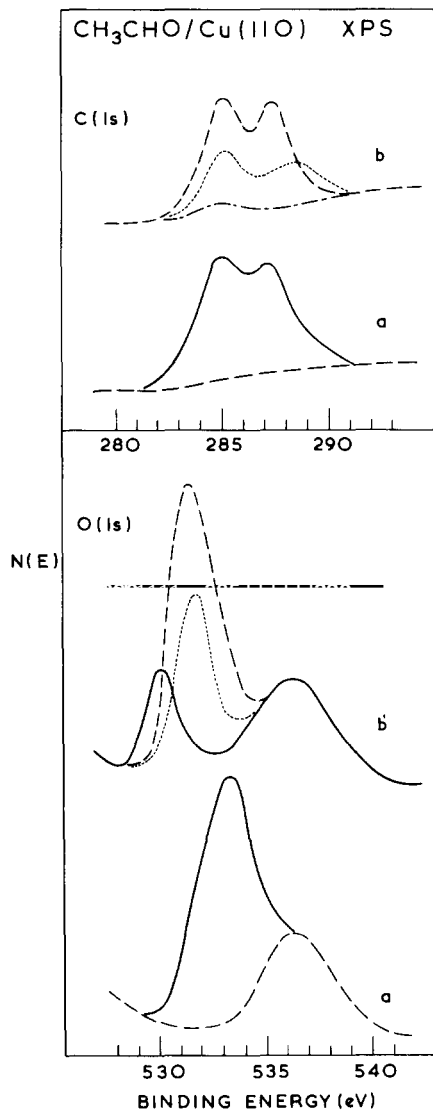


Fig. 7. X-ray photoelectron spectra found for acetaldehyde adsorption on Cu(110). Spectra (a) were obtained after acetaldehyde adsorption at 140 K (—) on the clean surface (---). Spectra (b): (—) after oxygen adsorption at 300 K to 1/4 monolayer coverage, (---) after the subsequent adsorption of  $\text{CH}_3\text{CHO}$  at 140 K, (...) after heating to 390 K and (-.-.-) shows carbon remaining on the surface after heating to 650 K.

Table 2  
Results summary

Adsorbed species	Coverage (species cm <sup>-2</sup> × 10 <sup>-14</sup> ) a)	TPRS	Δφ (eV) (± 0.05 eV)	E <sub>FO</sub> 1s (eV) ± 0.2	E <sub>FC</sub> 1s (eV) ± 0.2	UPS features
O	2.8	Stable to > 900 K	+0.05	530.0 (singlet)	—	Single emission at 5.8 eV
CH <sub>3</sub> COOH	6.8	Half desorbs half dissociates	-1.2	532.4 (broad)	α290.1 β286.6	Peaks characteristic of molecular acid chemisorption shift of 13a' orbital of 1.2 eV
CH <sub>3</sub> CHO	10.2	Desorbs at 220 K	-1.1	533.4 (broad)	α287.1 β284.9	As molecular peaks, but chemisorption shift of 10a' orbital of 0.8 eV
CH <sub>3</sub> CHOO	2.8	Formed between 140 and 240 K Decomposes to CH <sub>3</sub> COO + H at < 240 K	—	—	—	—
CH <sub>3</sub> COO	3.5 5.2 b) 2.8 c)	Reacts further to acetic anhydride on the surface Then decomposes at 590 K to produce mainly acetic acid, ketene, CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O	0.30 0.40 0.25	531.6 (singlet)	α288.2 β285.0	Four emissions below 12 eV, very sim- ilar to the formates [3]

a) Measured by XPS relative to p(2 × 1)O as 5.5 × 10<sup>14</sup> atoms cm<sup>-2</sup>, coverage uncertainty estimated at 20%.

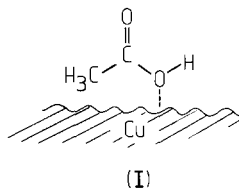
b) Acetate formed from acetic acid on surface predosed with 1/4 monolayer oxygen.

c) Acetate formed from acetaldehyde on surface predosed with 1/4 monolayer of oxygen.

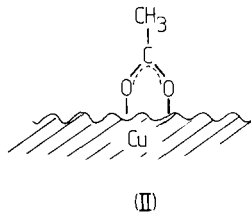
disappears, and a new one emerges at 531.4 eV which diminishes on warming to 300 K and also shifts slightly to 531.7 eV. The C 1s spectrum shows  $\alpha$  and  $\beta$  carbons as for the adsorbate on the clean surface, but warming to 390 K results in the separation of 2.3 eV increasing to 3.2 eV. When the surface is heated above 650 K, the C 1s shows some residual carbon when the crystal is cooled and analyzed. The coverages typically found in such spectra are listed in table 2.

#### 4. Discussion

From the results presented in the previous section it is clear that acetic acid adsorbed efficiently on the clean Cu(110) surface. The broad O 1s peak in the XPS and the large separation of the C 1s peaks indicate that the species present after adsorption at 140 K is very like the gas phase species; that is, it is adsorbed in a molecular form. The He(II) UPS spectra also show this, but further reveal that the acetic acid molecule is bonded to the surface via the oxygen of the hydroxyl group as in structure I below.



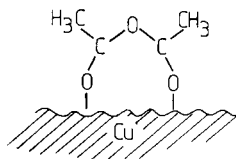
In this respect there appears to be some difference between acetic and formic acid. Formic acid shows almost exactly the same UPS spectrum for the low temperature species as for the dissociated form, the formate; this was proposed as being due to a partial dissociation or certainly a weakening of the O—H bond even while the formic acid was only bonded through one oxygen [3]. Since the spectra of acetic acid are different it is quite reasonable to assert that the O—H bond is not so much affected at low temperatures, especially since acetic acid is a weaker acid than formic acid and is therefore less likely to dissociate. The data shows that the acetic acid is dissociated at 300 K, since the O 1s peak is narrow and the separation of C 1s peaks diminishes to  $\sim 3.1$  eV. These effects are consistent with results for formic acid and indicate that the two oxygen atoms in the molecule become completely equivalent, probably due to the formation of a bidentate acetate species (structure II). The de-



crease in separation of the two C 1s peaks is due to a relative shift in the higher binding energy peak which must be associated with the carbonyl carbon. This drop in binding energy is presumably due to an increase in electron density at the carbon as the surface complex reverts from species I to II. The change of binding energy of the  $\alpha$  carbon is very similar for both acids at around 2 eV. From measurements of the changes in the XPS and UPS spectra at various temperatures the conversion of acetic acid to acetate occurs near 230 K, which is about the temperature at which the acetic acid desorbs.

A further important difference between the spectra of the acetic acid and acetate species is the apparent shift of both C 1s peaks in the acetic acid molecule to higher binding energies (by around 1.5 eV) than would normally be expected;  $\text{CH}_3$  groups always appear in the region around 285 eV and have been seen in this position for methanol [2] and higher alcohols [17] on this surface. It is difficult to find a satisfactory explanation for this apparent shift. It is unlikely to be the result of charging effects since in spectrum of fig. 7b the methyl group for the acetate appears in the usual place. Initial state bonding effects are not likely to affect both carbons similarly. A lessening of the final state extra-atomic relaxation terms for  $\text{CH}_3\text{COOH}$  also seems to be eliminated, since the density of near neighbour atoms is similar in the acetate and acid. Thus the origin of this phenomenon remains a mystery and seems to be only applicable to the carboxylic acids bonded to this surface (the carboxylic carbon in formic acid shows about the same shift as for acetic acid when converting to the carboxylate).

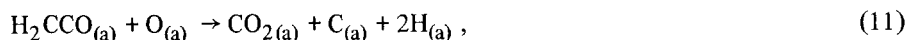
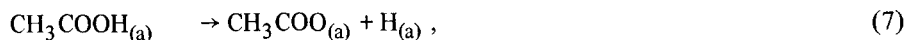
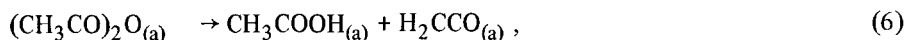
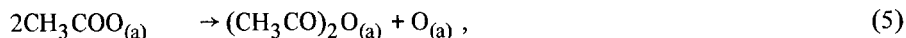
The main change observed in the UPS spectrum with heating is the appearance of a distinct peak at 11.5 eV binding energy, and the spectrum up to 12 eV becomes very similar to that for the formate. Furthermore, after the loss of some molecular acetic acid from the surface at 240 K, TPRS shows  $\text{H}_2$  evolution at 310 K which is due to the recombination of hydrogen atoms formed in the dissociation of the acetic acid molecule at a lower temperature; this  $\text{H}_2$  evolution is desorption limited [13]. At this stage, as mentioned previously, the photoelectron spectra indicate the presence of the carboxylate (II) on the surface. The decomposition of this spe-



(III)

cies was, however, quite different from the simple decomposition behaviour for the formate. In fact, this intermediate was the most strongly bound entity observed for a range of simple organic molecules on the Cu(110) surface. Furthermore the complex pattern of products evolved at 590 K appears to indicate further reaction between acetate species to produce the acetic anhydride intermediate (III). The surest evidence for this is the desorption of acetic acid and ketene, both of which are seen

as the major products of the gas phase decomposition of acetic anhydride [14]. Thus the complete mechanism for the adsorption and reaction of acetic acid with Cu(110) can be written as follows:



Steps (1)–(4) have already been outlined. Step (5) presumably takes place close to the desorption temperature and is perhaps part of a concerted decomposition; the evidence for this is again the narrow width of the O 1s spectrum seen up to 540 K – the anhydride would be expected to have a broadened peak due to the bridging oxygen atom.

Step (6) is then typical of decomposition of acetic anhydride in the gas phase. Both the products then have two alternative pathways to follow on the surface – desorption and decomposition – and they appear to be approximately 50% selective in the route they choose. The desorption route yields those molecules shown in fig. 1 as products in the gas phase. The decomposition mechanism is not, of course,

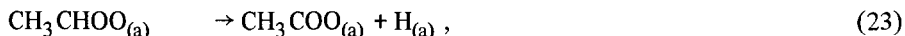


completely clear, but steps (9)–(19) are proposed as a reasonable pathway to explain the products observed. The ketene product is a highly reactive molecule and it appears to suffer nucleophilic attack by the oxygen produced in step (5) at the carbon–carbon double bond. Such reactions have been observed for several molecules on copper and silver surfaces (1)–(4). This process is shown as step (11) in the above scheme and is likely to result in carbon deposition on the surface.  $\text{CO}_2$  and methane are produced mainly from acetic acid decomposition at these elevated surface temperatures. Not all the carbon produced is consumed by step (12) since the XPS shows some residue always present on the surface.

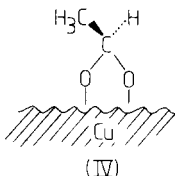
The desorption of acetaldehyde from the clean Cu(110) surface is very similar to that seen for formaldehyde [3] and is close to the same peak temperature. However, the O 1s spectrum is quite broad, whereas for formaldehyde it was a single line. There is no obvious explanation for this apparent anomaly – multiple adsorption states for the molecule would be expected to show up as more than one desorption peak, and none are evident (although there is some distortion on the high temperature side of the peak). As for acetic acid the separation of the peaks in the C 1s spectrum is slightly less than that in the gas phase ( $\sim 2.4$  versus  $2.7$  [15]) mainly due to a decrease in the binding energy of the  $\alpha\text{C}$  1s electron, indicating a small change on the carbon due to adsorption and consequent weakening of the  $\text{C}=\text{O}$  bond (lower bond order).

When oxygen was preadsorbed, the acetaldehyde desorption behaved much the same way as formaldehyde, producing a decrease in amount desorbed and a distortion of the main peak to higher temperature, though with an indication of the presence of more than one peak. However, the XPS was considerably different from that of formaldehyde, which showed the presence of two distinct species at low temperatures, namely  $\text{H}_2\text{COO}$  and  $\text{H}_2\text{CO}$  [3]. Although the distinct oxygen moiety has disappeared in fig. 7b there is only one main oxygen peak (although it is fairly broad). The C 1s appears similar to that for unreacted acetaldehyde, as does the UPS (spectrum in fig. 5d). It is possible that the acetaldehyde is interacting with the adsorbed oxygen, but is remaining essentially intact, which is in contrast to the formaldehyde when reaction was observed to have taken place at 140 K. It is likely that the hydrogenated acetate species (IV) is formed in transit to the acetate, but its temperature range of stability seems to be so narrow that it was not observed and the acetate was already formed by 240 K. It must be emphasized, however, that no studies were made by XPS or UPS between 140 and 240 K where species IV might be stable. On Ag(110) the decomposition of the hydrogenated acetate was established to take place at 240 K (heating rate  $24\text{ K s}^{-1}$ ), since on that surface hydrogen evolution was decomposition limited [4].

The situation above 240 K is much clearer; the UPS and both XPS spectra show the presence of the acetate (II) on the surface. The subsequent TPRS is very like that for acetic acid, showing the same decomposition products. Thus the overall mechanism for acetaldehyde reaction with the clean and oxidised Cu(110) surfaces is as follows:



Steps (21) and (23) have occurred by 240 K, and step (22) is seen in TPRS at that temperature. The hydrogen is relatively strongly adsorbed and does not desorb until 310 K (step (24)). The remaining acetate then decomposes in the manner shown in steps (5)–(19). This mechanism is exactly the same as for acetaldehyde adsorption on the oxygen dosed Ag(110) surface [4], though the acetate decomposition seemed to result in higher yields of  $\text{CO}_2$  and  $\text{CH}_4$  in the latter case.



## 5. Conclusions

The adsorption and reactions of acetic acid and acetaldehyde confirm the general chemistry observed for formic acid and formaldehyde presented in an earlier paper [3]. The acids adsorb intact, apparently binding to the surface through the hydroxyl oxygen, though due to its more acidic nature, the formic acid OH bond is shown by UPS to be strongly perturbed. Upon heating, the acids dissociate completely below 240 K to leave a strongly bound carboxylate species ( $\text{RCOO}$ ) and adsorbed hydrogen. TPRS shows hydrogen recombination and desorption around room temperature and decomposition of the carboxylates at 480 K and 590 K respectively, for formate and acetate. In this sense the acetate species is the most strongly bound organic entity adsorbed on Cu(110) observed in this laboratory. The aldehydes adsorb only weakly on the clean surface and are lost by heating the surface above 240 K. When oxygen is adsorbed it acts as a strong nucleophile, attacks the carbonyl carbon atom and results in hydrogenated carboxylate formation; this species decomposes at  $< 240$  K to yield the carboxylate and adsorbed hydrogen. In the case of acid adsorption the preadsorbed oxygen acts as a strong base inducing the acids to dissociate even at 140 K and resulting in water formation.

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