

The adsorption and reaction of 2-iodoethanol on Ag(111)

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Abstract

Oxametallacycles have been previously grafted onto Ag(110) by adsorbing 2-iodoethanol to mimic possible intermediates in the catalytic epoxidation of ethylene. Since Ag(111) has been shown to be a good model catalyst for this reaction under realistic pressures of ethylene and oxygen, this work was extended to studying the chemistry of 2-iodoethanol on Ag(111) using temperature-programmed desorption and reflection–absorption infrared spectroscopies. It was found that iodoethanol reacts at relatively low temperatures to form 2-hydroxyethyl species and co-adsorbed iodine. Hydroxyethyl species react above ~ 150 K to eliminate water and evolve equimolar amounts of ethylene. The remaining fragment with stoichiometry C_2H_4O reacts with the surface to form predominantly oxametallacycles which thermally decompose at ~ 260 K to yield acetaldehyde. A minority species is also identified which thermally decomposes to yield acetaldehyde at ~ 315 K and may be due to an oxametallacycle which adopts a different orientation as a function of temperature and coverage or a 2-hydroxyethylidene species. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The pathway to the catalytic formation of ethylene oxide from ethylene and oxygen has been studied extensively over the past 20 years [1–4]. The results of this work have demonstrated that a Ag(111) single crystal can catalyze the formation of ethylene oxide with kinetics that resemble those of supported catalysts [5–7]. It has been further shown that the active form of adsorbed oxygen for both selective and total oxidation is adsorbed atomic oxygen, not dioxygen species [5]. Subsurface oxygen, which is also present during the reaction, is also proposed to be a spectator species although

this has been suggested to facilitate the nucleophilic addition of ethylene to adsorbed oxygen [5]. However, the nature of the surface intermediate that is formed from the interaction of ethylene with adsorbed atomic oxygen and which yields ethylene oxide (as well as being proposed to oxidize further forming CO_2 and H_2O) yet remains to be identified. There are two obvious candidates for this intermediate species. The first forms when both p orbitals of the ethylenic π orbital simultaneously interact with adsorbed oxygen to form adsorbed ethylene oxide directly. This either would desorb yielding partial oxidation products or undergo further oxidation on the surface yielding CO_2 and H_2O [5]. Alternatively, the p orbitals can interact with both adsorbed atomic oxygen and the silver surface forming an oxametallacycle [8,9]. This would undergo a reductive elimination to form ethylene oxide.

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Oxametallacycles have been grafted onto Ag(110) by reaction with 2-iodoethanol [8,9]. The chemistry in this case exploits results from previous work on iodoalkanes on silver where they react by removal of the iodine to deposit an alkyl species and adsorbed iodine. Hydrogen abstraction from the hydroxyl species in silver is generally induced by the presence of atomic oxygen [10]. The formation of an oxametallacycle from 2-iodoethanol on Ag(110) was confirmed from its high-resolution electron energy loss (HREELS) spectrum where the fingerprint spectrum was calculated using density functional theory [9]. Interestingly, this was found to decompose yielding ethylene, water, acetaldehyde and ethanol and also dimerized on the surface yielding γ -butyrolactone. However, no ethylene oxide formation was found. Since the majority of the previous mechanistic work has been carried out on Ag(111), the chemistry of 2-iodoethanol is investigated on this surface using a combination of temperature-programmed desorption and reflection-absorption infrared (RAIRS) spectroscopies. It is found that, on clean Ag(111), adsorbed 2-hydroxyethyl species react to evolve equimolar amounts of water and ethylene and form a species with a stoichiometry C_2H_4O . This appears to form two distinct surface species both of which thermally decompose to yield acetaldehyde. One of these is suggested to consist of an oxametallacycle and the other, either an oxametallacycle adopting a different orientation or an adsorbed 2-hydroxyethylidene species.

2. Experimental

The experiments were carried out in a stainless steel, ultrahigh vacuum chamber operating at a base pressure of $\sim 8 \times 10^{-11}$ Torr following bakeout and which has been described in detail elsewhere [11]. Infrared data were collected from an Ag(111) single crystal sample mounted in a modified 2.75 in six-way cross equipped with infrared-transparent KBr windows. The sample could be resistively heated to 1000 K, or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer and is focused onto the sample at an incidence

angle of $\sim 80^\circ$ and the reflected light steered onto the detector of a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path is enclosed and purged with dry, CO_2 -free air. The spectrometer operated at 4 cm^{-1} resolution and data were typically collected for 1000 scans.

The infrared cell was attached to the main 12 in diameter ultrahigh vacuum chamber and the sample could be moved from the cell into the main chamber by means of a transfer rod. This chamber was equipped with a single-pass, cylindrical-mirror analyzer which was used to collect Auger spectra of the sample.

Temperature-programmed desorption data were collected using a heating rate of $\sim 3\text{ K s}^{-1}$ and desorbing species detected using a Dycor quadrupole mass spectrometer located in the main ultrahigh vacuum chamber and interfaced to a PC allowing five masses to be monitored sequentially during the same desorption sweep.

The sample was cleaned using a standard procedure [12,13] which consisted of bombarding with argon ions (1 keV , $2\text{ }\mu\text{A cm}^{-2}$) at 300 K and then annealing to 1000 K in vacuo to remove any remaining surface species. The 2-iodoethanol used for the experiments (Aldrich, 99% purity) was transferred to glass vials, attached to the gas-handling line of the vacuum system, and further purified by repeated freeze-pump-thaw cycles and its cleanness monitored mass spectroscopically.

3. Results

Fig. 1 shows a series of temperature-programmed desorption spectra collected following adsorption of 2-iodoethanol (3 L, $1\text{ L} = 1 \times 10^{-6}$ Torr s) on Ag(111) at 80 K, monitoring various masses. In contrast to the behavior found on Ag(110), no γ -butyrolactone desorption is found. Signals are found at all of the other masses (18, 27, 29, 45 and 31 amu). All of the spectra (except that at 18 amu) exhibit a relatively sharp peak at 205 K. This peak increases in intensity with increasing iodoethanol exposure without saturating and is assigned to multilayer desorption (see Fig. 4). Similar multilayer desorption was found

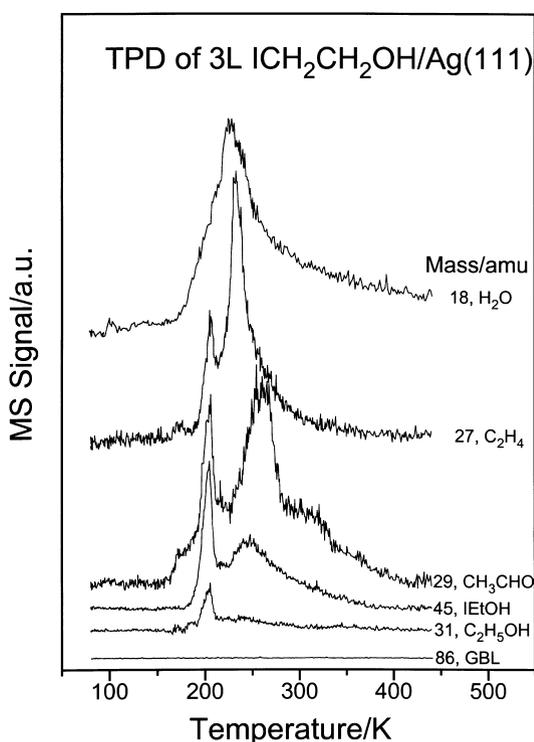


Fig. 1. Temperature-programmed desorption spectra of iodoethanol (3 L) adsorbed on Ag(111) at 80 K, monitoring 18 amu (H_2O), 27 amu (ethylene), 29 amu (acetaldehyde), 45 amu (iodoethanol), 31 amu (ethanol) and 86 amu (γ -butyrolactone). The masses and the desorbing species are marked adjacent to the corresponding spectrum.

at a slightly higher temperature (225 K) on Ag(110) [8]. In addition, the relative intensities at each mass correspond well to the mass spectrometer ionizer fragmentation pattern of iodoethanol in agreement with this conclusion. Both water and ethylene desorb simultaneously in a peak centered at ~ 230 K. This will be discussed in greater detail below. The water desorption peak is slightly broader than that for ethylene which may reflect the slower pumping speed for the former molecule. A small amount of iodoethanol (45 amu) desorbs from the adsorbed overlayer at 245 K in contrast to the behavior on Ag(110) where no molecular desorption was detected, except when multilayers had formed. Essentially no ethanol (31 amu) desorption is detected since the 205 K peak in the spectrum collected at this mass is due to iodoethanol fragmentation. Two 29 amu states are detected

at 260 and 315 K where, at this exposure, the 260 K feature is significantly more intense than that at 315 K. This contrasts the behavior on Ag(110) where the 29 amu signal was detected simultaneously with ethylene and water in two states at ~ 340 and 263 K [8]. Note that both ethylene oxide and acetaldehyde have significant mass spectrometer ionizer fragments at 29 amu. However, the 29 amu species was unequivocally identified as acetaldehyde, not ethylene oxide, by carefully measuring the mass spectrometer ionizer fragments for acetaldehyde and ethylene oxide at various masses and by comparing these with the temperature-programmed desorption spectra taken at these masses. Note that acetaldehyde desorbs from Ag(111) at substantially lower temperatures (160 K, [14]) so that the desorption states measured here represent a reaction- rather than desorption-rate-limited process. Finally, no other higher molecular weight species, in particular due to γ -butyrolactone (Fig. 1), which was found on Ag(110) [8], were detected.

Fig. 2 shows the evolution of the 29 amu desorption spectra with exposure where the exposures in Langmuirs are marked adjacent to the corresponding spectra. Note that the sharp peak at 205 K for exposures larger than 2 L are due to the desorption of iodoethanol multilayers as discussed above. At low exposures (~ 1 L), both the low- and high-temperature acetaldehyde desorption states are evident with relatively equal intensities. The high-temperature (315 K) state saturates at an exposure of ~ 1 L whereas the low-temperature (235–260 K) state continues to grow with increasing exposure. In addition, the peak temperature of the low-temperature state increases slightly with increasing exposure so that at low exposures (0.5 L) it is centered at ~ 235 K and shifts monotonically to higher values with increasing temperature to ~ 260 K for exposures of 2 L and greater. This effect may be due to the influence of some co-adsorbed iodoethanol and has been observed by others [15].

The corresponding exposure effect on the ethylene (27 amu) desorption profile is shown in Fig. 3 where again the 205 K feature that appears at larger exposures is due to multilayer iodoethanol desorption. Two peaks are seen at low exposures

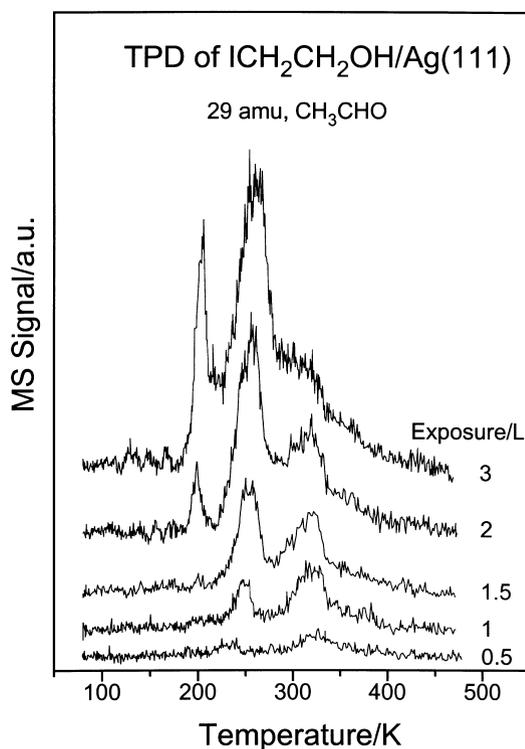


Fig. 2. 29 amu (acetaldehyde) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.

(0.5 L) at 205 and 225 K. The high-temperature peak of a similar two-peaked spectrum on Ag(110) was ascribed to the effect of surface defects [8]. The ethylene desorption yield and peak temperature increase with increasing exposure with the peak temperature varying from 205 K at low exposures (0.5 L) to 230 K at high (3 L).

The desorption spectra for iodoethanol (45 amu) are displayed as a function of exposure in Fig. 4 where the growth of the multilayer (205 K) feature is clearly evident. A peak also appears at 245 K due to the desorption of iodoethanol adsorbed on the (111) surface. A Redhead analysis of the desorption state [16], assuming a pre-exponential factor of $1 \times 10^{13} \text{ s}^{-1}$, yields a desorption activation energy for this state of $\sim 63 \text{ kJ mol}^{-1}$.

The relative molar desorption yields for ethylene, water and acetaldehyde are plotted as a

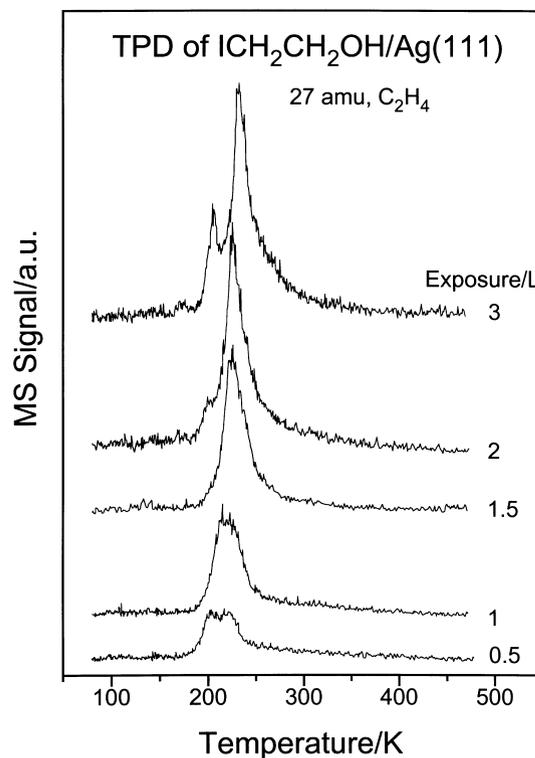


Fig. 3. 27 amu (ethylene) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.

function of iodoethanol exposure in Fig. 5. In this case, desorption yields are calculated from the integrated intensity under the desorption profile. This yield is converted to relative molar quantities by measuring the intensity at each of the masses detected in the desorption spectra (29 amu for acetaldehyde, 27 amu for ethylene and 18 amu for water) for known pressures of each of these gases. These pressures were corrected for ionization gauge sensitivities. It is clear from these data that essentially equimolar amounts of ethylene, water and acetaldehyde are evolved for all iodoethanol exposures. Similar results were obtained for iodoethanol adsorbed on Ag(110) where equimolar amounts of water and ethylene desorbed in both the 263 and the 340 K desorption states [8]. However, in contrast to the results obtained here on Ag(111), approximately 2 mol of acetaldehyde

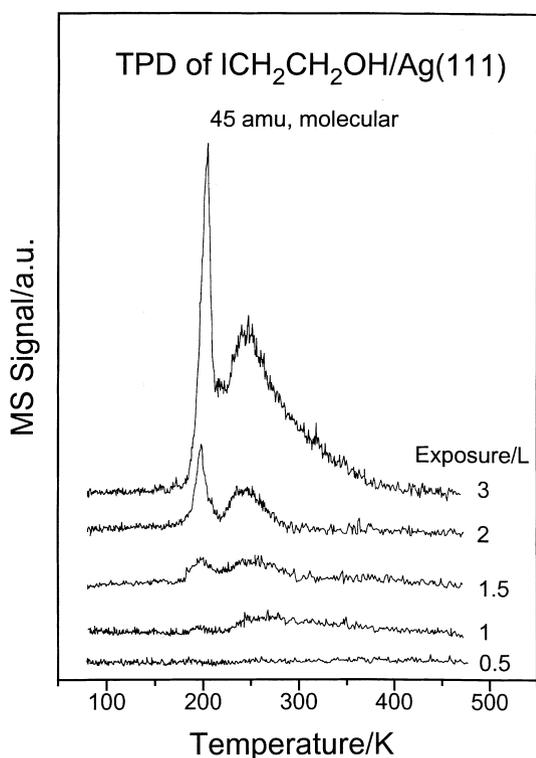


Fig. 4. 45 amu (iodoethanol) temperature-programmed desorption spectra collected as a function of iodoethanol exposure at 80 K. The exposures (in Langmuirs) are marked adjacent to the corresponding spectra.

were formed for each mole of water or ethylene on Ag(110).

Temperature-desorption spectra were also collected as a function of dosing temperature. In this experiment, the sample was held at various temperatures (80, 185 and 215 K) and dosed with 1.5 L of iodoethanol. The sample was allowed to cool to 80 K following which the temperature-programmed desorption spectrum was collected. This procedure was adopted to ensure that each of the desorption spectra were collected under identical conditions. The results for acetaldehyde (29 amu) desorption are displayed in Fig. 6. The desorption yield from the high-temperature state is only marginally affected by varying the dosing temperature, the most marked effect being a broadening and shift to high temperature when iodoethanol is dosed at 215 K. Similarly, the low-temperature (250 K) state changes slightly when iodoethanol

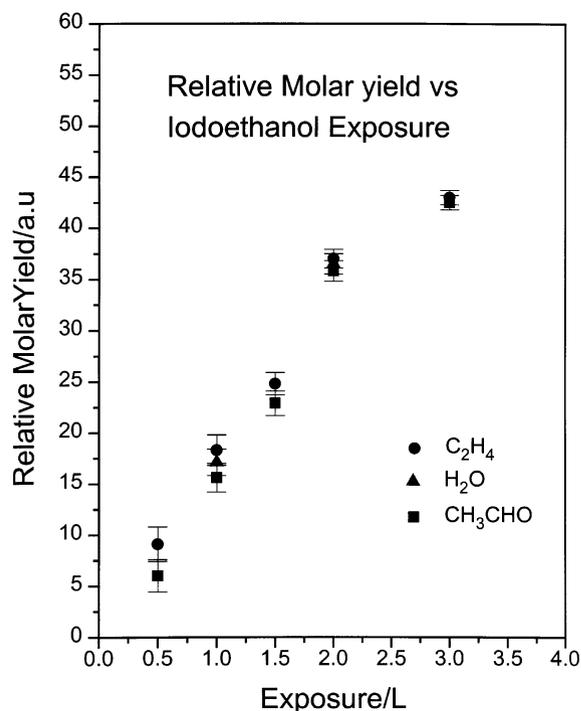


Fig. 5. Plot of the relative molar desorption yield of water, ethylene and acetaldehyde in temperature-programmed desorption as a function of iodoethanol exposure.

is dosed at 185 K but the yield increase substantially when the sample is dosed at 215 K. Note that multilayer desorption is completely suppressed by dosing the sample at 185 K even at higher iodoethanol exposures.

The RAIRS spectra associated with these desorption data are displayed in Figs. 7–9 which display the spectral region between 700 and 2000 cm^{-1} . The low sensitivity of the mercury cadmium telluride detector precluded collecting meaningful data at higher frequencies. These data were collected by dosing iodoethanol (3 L) at various temperatures (80 K, Fig. 7; 185 K, Fig. 8; 215 K, Fig. 9). The temperature evolution was followed by annealing to the temperature indicated adjacent to each spectrum. The sample was then allowed to cool to the dosing temperature and the spectrum collected. The spectra obtained by dosing at 80 K are shown in Fig. 7. Clearly evident after dosing at 80 K and also after annealing to 185 K are a relatively large number of peaks, the majority

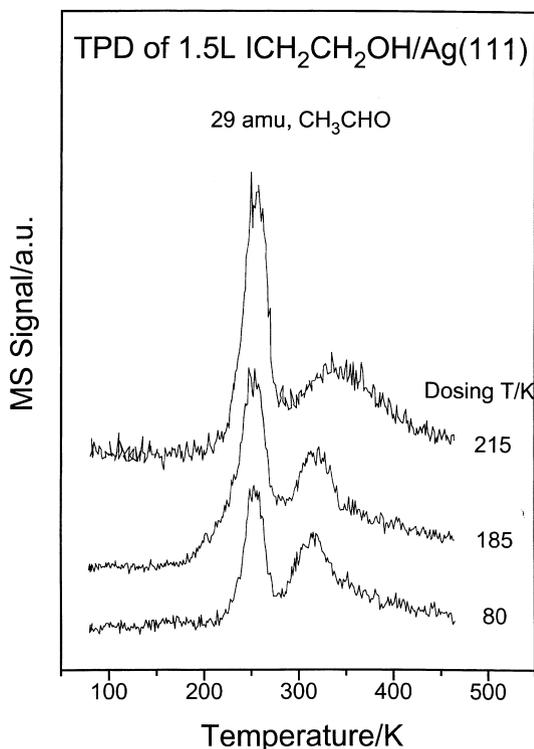


Fig. 6. 29 amu (acetaldehyde) temperature-programmed desorption spectra collected following a 1.5 L exposure of iodoethanol on Ag(111) as a function of dosing temperature. The dosing temperatures are marked adjacent to the corresponding spectrum.

of which disappear on annealing to 215 K. This temperature corresponds to multilayer iodoethanol desorption (Figs. 1–4) suggesting that these features are predominantly due to condensed iodoethanol. This conclusion is confirmed by the data in Table 1 which compares the observed frequencies with those for liquid [18] and matrix-isolated [17] iodoethanol. The frequencies are also compared with those for multilayers of iodoethanol condensed on Ag(110) [9] collected using electron energy loss spectroscopy, where the agreement between the two sets of data is good.

Heating to 215 K, as noted above, removes the iodoethanol multilayer, and leads to a rather weak spectrum consisting of a peak at 1070 cm^{-1} and broad, rather low-intensity features centered at ~ 975 and 1175 cm^{-1} (Fig. 7). Simultaneously at this temperature, ethylene and water start to

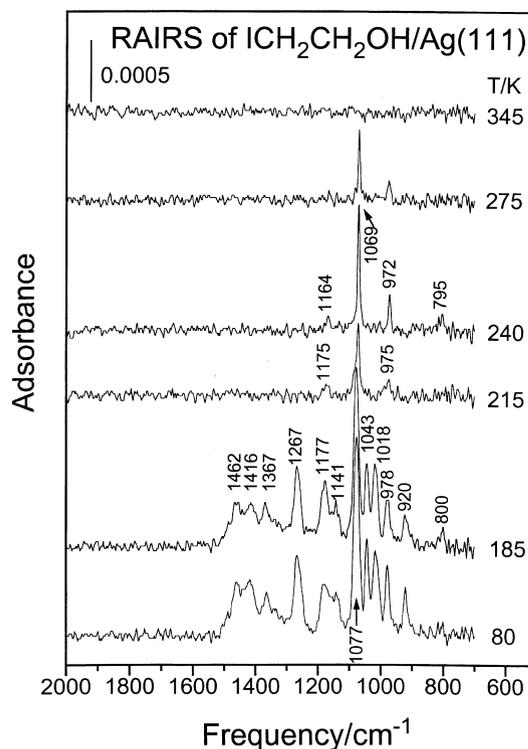


Fig. 7. RAIRS spectra of iodoethanol (3 L) adsorbed on Ag(111) at 80 K between 700 and 2000 cm^{-1} as a function of annealing temperature. Annealing temperatures are marked adjacent to the corresponding spectra.

desorb (Fig. 1). Heating to 240 K essentially completes ethylene and water desorption (Fig. 1) and the infrared spectrum consists of two rather intense features at 1069 and 972 cm^{-1} with weaker peaks at ~ 1164 and 795 cm^{-1} . Further heating to 275 K causes both the 1069 and 972 cm^{-1} modes to decrease substantially in intensity while acetaldehyde desorbs from the surface (Figs. 1 and 2). The relationship between these infrared features and the desorption of acetaldehyde is further confirmed by heating to 345 K since all infrared spectral features are absent (Fig. 7) and acetaldehyde desorption is complete (Figs. 1 and 2). The detection of decomposition products (ethylene and water) at 215 K (Fig. 1) suggests that a portion of the adsorbed iodoethanol has reacted on the surface by this temperature. This reaction is clearly not complete since some iodoethanol still desorbs above this temperature (Fig. 1). It is suggested

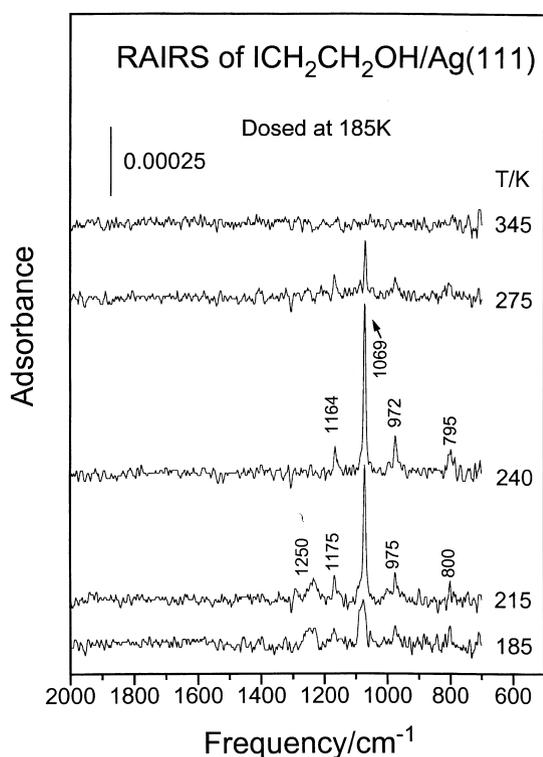


Fig. 8. RAIRS spectra of iodoethanol (3 L) adsorbed on Ag(111) at 185 K between 700 and 2000 cm^{-1} as a function of annealing temperature. Annealing temperatures are marked adjacent to the corresponding spectra.

that this intermediate species yields the relatively weak infrared spectrum found after annealing to 215 K shown in Fig. 7 consisting of features at ~ 975 , 1070 and 1175 cm^{-1} .

The yield of acetaldehyde changes with dosing temperature (Fig. 6) and the corresponding infrared spectra are displayed in Figs. 8 and 9 for samples dosed at 185 and 215 K respectively. The RAIRS spectrum formed by dosing at 185 K (Fig. 8) shows a broad feature at $\sim 1250 \text{ cm}^{-1}$, a small peak at $\sim 1175 \text{ cm}^{-1}$, a broad, more intense peak at $\sim 1075 \text{ cm}^{-1}$, a small feature at $\sim 975 \text{ cm}^{-1}$ and a weak, rather sharp peak at $\sim 800 \text{ cm}^{-1}$. These resemble the peaks found after dosing at 80 K and annealing to 215 K (Fig. 7) but are more clearly seen in Fig. 8. Heating the sample dosed at 185 K to 240 K (Fig. 8) produces the features at 1164, 1069 and 972 cm^{-1} seen in the spectrum for the sample dosed at 80 K and

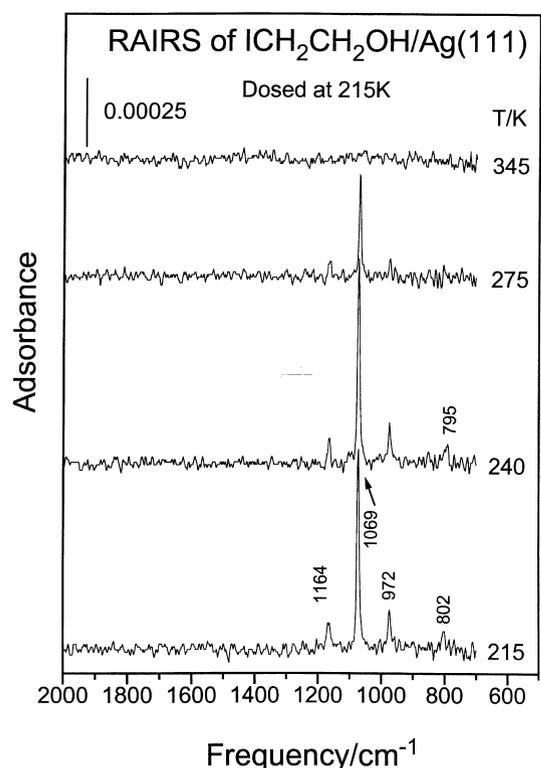


Fig. 9. RAIRS spectra of iodoethanol (3 L) adsorbed on Ag(111) at 215 K between 700 and 2000 cm^{-1} as a function of annealing temperature. Annealing temperatures are marked adjacent to the corresponding spectra.

heated to the same temperature (Fig. 7) with a peak evident at 795 cm^{-1} which is detected as a weak feature in the spectra of Fig. 7 collected after annealing to 240 K. These spectral changes further suggest that different surface species are formed at 215 and 240 K. These are again completely removed by heating to 340 K confirming that the surface species that give rise to these modes thermally decompose to form acetaldehyde (Figs. 1 and 2).

Features are detected at 1164, 1069, 972 and 802 cm^{-1} for a sample dosed at 215 K (Fig. 9) and their evolution with heating agrees well with that seen for the sample dosed at 185 K (Fig. 9) and which disappear as acetaldehyde desorbs (Figs. 1 and 2)

As noted above, the acetaldehyde desorption yield varies with iodoethanol adsorption temper-

Table 1

Assignments of the vibrational spectrum in the region 600–2000 cm^{-1} of iodoethanol adsorbed on Ag(111) by comparison with liquid and matrix-isolated iodoethanol. Shown also for comparison are the frequencies for iodoethanol adsorbed on Ag(110) using electron energy loss spectroscopy^a

Mode	Frequency (cm^{-1})			
	Multilayer on Ag(111)	Gas matrix [17]	Liquid [18]	Multilayer on Ag(110) [9]
$\rho(\text{CH}_2)$	920 978	751–911	795–905	720–868
$\nu(\text{C}-\text{C})$	1018 1043	1018	977	1020
$\nu(\text{C}-\text{O})$	1077	1073	1068	1058
$\delta(\text{C}-\text{OH})$	1141	1111–1153	1147–1174	1132–1181
$\delta(\text{C}-\text{OH})$	1177	1111–1153	1147–1174	1132–1181
$w(\text{CH}_2)$	1267 1367	1236/1262	1265	1268
$w,b(\text{CH}_2)$	1416	1385–1469	1414–1455	1400–1450
$w,b(\text{CH}_2)$	1462	1385–1469	1414–1455	1400–1450

^a b = bend; ν = stretch; ρ = rock; δ = deformation; w = wag.

ature (Fig. 6). This effect is mirrored in the intensity of the 1069 cm^{-1} RAIRS feature as a function of dosing temperature. The peak absorbance of this feature, when dosing at 80 K, is 5×10^{-4} after annealing the sample to 240 K (Fig. 7). When the sample is dosed at 185 K and annealed to 240 K, this increases to 6×10^{-4} (Fig. 8), and at a dosing temperature of 215 K, after annealing to 240 K, it has grown further to 7.5×10^{-4} (Fig. 9).

The intensity of the 972 cm^{-1} peak compared with that at 1069 cm^{-1} also varies with dosing temperature so that after dosing at 80 K and annealing to 240 K, the ratio $I(1069)/I(972)$, where I refers to the peak height of the respective features, is 3.2 (Fig. 7), when dosing at 185 K it is 5.9 (Fig. 8), and increases further to 7.1 when the sample is dosed at 215 K (Fig. 9). This implies either that the geometry of the species changes with dosing temperature or that the features at 1069 and 972 cm^{-1} correspond to two different surface species. The appearance of two different acetaldehyde desorption states (Figs. 1 and 2) is in accord with the presence of two distinct surface species. Note finally, that the 1164 cm^{-1} feature persists relatively unattenuated up to an annealing temperature of 275 K (Fig. 8) suggesting that it is associated with the high-temperature (315 K) acetaldehyde desorption state.

4. Discussion

Iodoethanol adsorbs at 80 K on Ag(111) to form a condensed layer that desorbs at ~ 205 K (Fig. 1 and Table 1). Dosing at 185 K completely suppresses multilayer condensation and yields infrared features at ~ 800 , 975, 1075, 1175 and 1250 cm^{-1} (seen most clearly in Fig. 8). These features can be assigned to the presence of either molecular iodoethanol or an adsorbed hydroxy ethyl species and the peak positions and assignments are summarized in Table 2. The frequencies agree slightly better with those for 2-hydroxyethyl than for iodoethanol, but both sets of frequencies are sufficiently close that they could equally well be assigned to either. Certainly, in view of the fact that iodoethanol desorbs from the surface (Figs. 1 and 4), the presence of adsorbed iodoethanol cannot be ruled out. In general, alkyl iodides adsorbed on silver react rapidly to form adsorbed alkyl species and iodine where, for example, this reaction occurs at ~ 120 K for methyl iodide on Ag(111) [19]. Clearly, however, this reaction is likely to be inhibited by the presence of a hydroxyl group. However, the surface species *initially* reacts to desorb equimolar amounts of water and ethylene (Fig. 5) at ~ 180 K with a maximum rate at ~ 230 K (Fig. 1). Adsorbed hydroxyl species react

Table 2

Comparison of the infrared modes for iodoethanol adsorbed on Ag(111) at 185 K (Fig. 8) with the frequencies of iodoethanol and an adsorbed hydroxyethyl species on Ag(110) [9]^a

Mode	Frequency (cm ⁻¹)		
	Iodoethanol on Ag(111) at 185 K (Fig. 8)	2-hydroxyethyl on Ag(110) [9]	Liquid iodoethanol
$\rho(\text{CH}_2)$	800	793	796–905
$\nu(\text{C}-\text{C})$	975	972	977
$\nu(\text{C}-\text{O})$	1070	1076	1068
$\delta(\text{C}-\text{OH})$	1175	1150/1175	1147–1174
$w(\text{CH}_2)\text{Q}$	1250	1290	1265

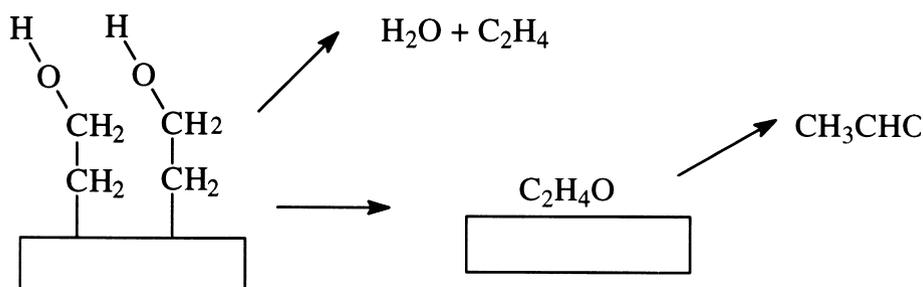
^a b = bend; ν = stretch; ρ = rock; δ = deformation; w = wag.

to form water on Ag(111) at 300 K [20,21], substantially higher than the water desorption temperature found following iodoethanol adsorption (Fig. 1). Furthermore, adsorbed ethylene desorbs from Ag(111) at ~ 145 K [22] so that ethylene desorption at 230 K is clearly limited by the rate that it is formed during reaction. This suggests that water formation is not mediated by the surface but that two alcohol groups react directly to evolve water and ethylene. Elimination of water from alcohols is well known in organic chemistry to form ethers [23]. An analogous dehydration reaction for adsorbed molecular iodoethanol would yield (*bis*)-(2-iodoethyl) ether ($\text{ICH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{I}$) and water but no ethylene. Neither was (*bis*)-(2-iodoethyl)ether detected in temperature-programmed desorption. In the case of adsorbed 2-hydroxyethyl species, an analogous elimination of water would yield equimolar amounts of ethylene and a species of stoichiometry $\text{C}_2\text{H}_4\text{O}$. The formation of equimolar amounts of water and ethylene evolved in temperature-programmed desorption (Fig. 5) is certainly in accord

with this suggestion. A final possibility, that cannot be ruled out, is a reaction between an adsorbed iodoethanol and a hydroxyethyl species which would yield either ethylene and iodoethoxy or a species with stoichiometry $\text{C}_2\text{H}_4\text{O}$ and an adsorbed iodoethyl species. The equimolar amounts of ethylene and water formed in temperature-programmed desorption (Fig. 5) argues against this reaction. The resulting species with stoichiometry $\text{C}_2\text{H}_4\text{O}$ desorb as acetaldehyde in two states at 260 and 315 K (Fig. 1). Again, the amount of acetaldehyde formed compared to ethylene and water (Fig. 5) is in accord with this suggestion.

This proposed reaction pathway is summarized in Scheme 1.

Alternative dehydrogenation pathways of a precursor with stoichiometry $\text{C}_2\text{H}_5\text{O}$ (formed by removing iodine from iodoethanol) would involve cleavage of a C–H or O–H bond. Adsorbed alkyl species do not tend to dehydrogenate on silver and rather dimerize to yield an alkane [15]. In addition, O–H bond cleavage is only induced on silver by the presence of adsorbed oxygen



Scheme 1.

whereas reaction, in this case takes, place on clean Ag(111) [10]. In addition, such direct abstraction pathways would be accompanied by hydrogen desorption. Small 2 amu (H_2) signals are detected in temperature-programmed desorption (not shown) but these can be entirely ascribed to the fragmentation of desorbing water, ethylene and acetaldehyde. Broadly similar reaction products are found on Ag(110) except that ethylene, water and acetaldehyde all desorb simultaneously [8] so that subsequent reaction of the species of stoichiometry C_2H_4O appears to be rather rapid on Ag(110). Almost equimolar amounts of water and ethylene desorb from Ag(110). However, the amount of acetaldehyde from Ag(110) is approximately twice that predicted by Scheme 1. This implies that there may be an additional dehydrogenation pathway available on Ag(110) not seen on Ag(111).

We turn our attention now to the nature of the species of stoichiometry C_2H_4O formed on the surface as a result of the reaction depicted in Scheme 1. Temperature-programmed desorption data suggest that there are two distinct species formed on the surface that react to form acetaldehyde at 260 and 315 K (Figs. 1–3). Note that acetaldehyde adsorbed on Ag(111) desorbs at 160 K indicating that these desorption states are indeed surface-reaction-rate limited [14]. The relative proportion of these two states and the total yield depend on the temperature at which iodoethanol adsorbs (Fig. 6). The intensity of the 1069 cm^{-1} vibrational mode also increases as a function of dosing temperature (Figs. 7–9) corresponding to the increase in acetaldehyde desorption yield. When the sample is dosed at 80 K, the RAIRS spectrum found on heating to $\sim 240\text{ K}$ exhibits sharp features at 972, 1069 and 1164 cm^{-1} (Fig. 7). Dosing the sample at 185 K and annealing to $\sim 240\text{ K}$ increases the intensity of the 1069 cm^{-1} peak, decreases the relative intensity of the 972 cm^{-1} feature, and an additional peak becomes evident at 795 cm^{-1} (Fig. 8) which is weakly visible in the data of Fig. 7. Adsorbing at 214 K and annealing to $\sim 240\text{ K}$ causes the intensity of the 1069 cm^{-1} peak to increase further, the relative intensity of the 972 cm^{-1} feature to diminish somewhat and the 1164 and $\sim 795\text{ cm}^{-1}$

Table 3

Relative intensities of the infrared modes measured from the peak heights (I) taken from the infrared spectra displayed in Fig. 8 for iodoethanol adsorbed on Ag(111) at 185 K

	Frequency (cm^{-1})			
	795	972	1069	1164
$I(275)/I(240)$	0.3 ± 0.3	0.5 ± 0.1	0.3 ± 0.1	1.0 ± 0.2
$I(345)/I(240)$	0	0	0	0

features to become more clearly evident (Fig. 9). The relative intensity changes of these features indeed suggest that more than one type of surface species is present. This is illustrated in Table 3 taken from the data shown in Fig. 8 which displays the intensities of these features at various annealing temperatures relative to the intensity measured at 240 K. These data were measured by integrating the area under each peak for several spectra. All of the infrared features decrease to zero intensity on heating to 340 K corresponding to the desorption of all acetaldehyde from the surface (Figs. 1 and 2). The 1164 cm^{-1} peak maintains its intensity on heating to 275 K suggesting that it is associated with the high-temperature (315 K) acetaldehyde desorption state. Both the 1069 and 795 cm^{-1} states decrease to $\sim 30\%$ of the intensity found at $\sim 240\text{ K}$ implying that they are associated with the same surface species and the decrease in intensity of the 972 cm^{-1} mode is intermediate between these two values and suggests that it is coincidentally common to both species. This conclusion is in accord with the variable relative intensity of this feature compared with the 1069 cm^{-1} peak as a function of dosing temperature (Figs. 7–9). These results imply the presence of one surface species having infrared frequencies of 1069, 972 and 795 cm^{-1} which is associated with the low-temperature (260 K) desorption state (Fig. 2). The other species is characterized by frequencies of 972 and 1164 cm^{-1} and decomposes at 315 K to yield acetaldehyde.

We turn our attention initially to the majority species exhibiting infrared frequencies at 795, 972 and 1069 cm^{-1} which desorbs as acetaldehyde at 260 K. Frequencies close to these for iodoethanol and hydroxyethyl on Ag(110) [9] are assigned to

Table 4

Comparison of the frequencies assigned to a metallacycle on Ag(110) measured using high-resolution electron energy loss with those formed by adsorbing iodoethane on Ag(111) and heating to 240 K measured using infrared spectroscopy^a

Assignment	Frequency (cm ⁻¹)	
	Oxametallacycle/ Ag(110) [9]	Species formed from iodoethanol on Ag(111) (this work)
v _s (OCC)	793	795
v _a (OCC)	996	972
v _a (OCC)	1052	1069
tw(CH ₂)	1218	–
w(CH ₂)	1273	–
CH ₂ sciss	1446	–

^a sciss = scissor; v = stretch; tw = twist; δ = deformation; w = wag.

CH₂ rocking modes, and C–C and C–O stretching modes respectively (Table 2) although the surface species on Ag(111) apparently contains no OH groups. The most likely candidate is a surface oxametallacycle and the experimental frequencies are compared with those assigned to an oxametallacycle on Ag(110) [9] in Table 4, where the higher frequency CH₂ modes are not detected since they are relatively weak. The agreement between the two sets of data is reasonably good. The major discrepancy is that the 996 cm⁻¹ peak is the most intense in the electron energy loss data for Ag(110) [9] while the 1069 cm⁻¹ peak is the most intense in the infrared spectra for Ag(111). There may be two possible causes for these intensity differences. First, the HREELS data may also contain contributions from impact scattering and second, the oxametallacycle structure on Ag(111) may be different to that on Ag(110).

There are two possible explanations for the second, minority species. The first is that this is also due to the presence of an oxametallacycle which adopts a different orientation as a function of temperature and coverage. However, the presence of a mode at 1164 cm⁻¹ for the second species implies that this has a COH functionality since this frequency is characteristic of a C–OH deformation mode (see Tables 1 and 2). Since there is no evidence of any C–C bond cleavage in any of

the temperature-programmed desorption experiments, an alternative possibility is that it is due to a different species of formula CH_xCH_yOH(ads), where $x + y = 3$. A similar intermediate has been proposed on Ag(110) as an enol (with $x = 2$ and $y = 1$) [9]. This would presumably be produced from the CH₂CH₂O species formed in Scheme 1 by a hydrogen transfer to the oxygen from the CH₂ adjacent to the oxygen. This would form an OH species but leave a carbon–carbon double bond. This is likely to be only weakly adsorbed on silver. In addition, the presence of a mode for this species at 972 cm⁻¹ suggest that it contains a carbon–carbon single bond. Another possibility is that hydrogen is transferred from the CH₂ species more remote from the oxygen to yield adsorbed 2-hydroxyethylidene (HO–CH₂–CH=(ads)). Alkylidenes dimerize on Ag(111) to form alkenes although no 1,4-dihydroxybutene (HOCH₂–CHCHCH₂OH) is detected in temperature-programmed desorption. However, such dimerization reactions are more rapid for alkyl species but no analogous dimerization reactions are found for adsorbed hydroxyethyl species so that the presence of a hydroxyl group apparently inhibits this reaction pathway. Since the 1164 cm⁻¹ mode persists on annealing to 275 K (Table 3), this species is proposed to react forming acetaldehyde at 315 K in temperature-programmed desorption. The relatively low desorption yield from this state (Figs. 1 and 2) implies that it is present on the surface as a minority species.

There are, in principle, a number of possible decomposition pathways for an oxametallacycle. It can undergo a reductive elimination reaction to yield ethylene oxide, undergo hydrogen transfer to yield acetaldehyde, or can decompose to form ethylene and adsorbed oxygen or formaldehyde and adsorbed methylene species [24]. The temperature-programmed desorption data indicate that the hydrogen transfer reaction to form acetaldehyde is the favored decomposition pathway. However, ethylene oxidation takes place on a silver surface that includes both adsorbed and subsurface oxygen so that this may affect the reactivity of the oxametallacycle. Note, however, that acetaldehyde is significantly more thermodynamically stable than ethylene oxide ($\Delta H_f^0(\text{ethylene oxide(g)}) =$

$-52.6 \text{ kJ mol}^{-1}$; $\Delta H_f^0(\text{acetaldehyde(g)}) = -170.7 \text{ kJ mol}^{-1}$ [25,26]) indicating that the thermal decomposition of a surface species of stoichiometry $\text{C}_2\text{H}_4\text{O}$ is likely thermodynamically to favor the formation of acetaldehyde.

5. Conclusions

2-Iodoethanol adsorbs on Ag(111) at 80 K and is proposed to react at relatively low temperatures to form 2-hydroxyethyl species and to deposit iodine onto the surface. These react to eliminate water and simultaneously desorb ethylene to leave a surface fragment of stoichiometry $\text{C}_2\text{H}_4\text{O}$. Surface infrared data suggest that two surface species are formed, the majority species being an oxametallacycle which thermally decomposes at $\sim 260 \text{ K}$ to desorb acetaldehyde. The other may be an oxametallacycle adopting a different orientation or a 2-hydroxyethylidene species which also reacts to desorb acetaldehyde at $\sim 315 \text{ K}$.

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