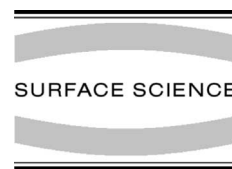




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A reflection–absorption infrared spectroscopic study of the adsorption of ethylene and ethylene oxide on oxygen-covered Ag(1 1 1)

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Abstract

The adsorption of ethylene and ethylene oxide has been studied on clean and oxygen-covered Ag(1 1 1) using temperature-programmed desorption and reflection–absorption infrared spectroscopy (RAIRS). Ethylene adsorbs weakly on Ag(1 1 1) at 80 K with the molecular plane oriented parallel to the surface. The effect of adsorbed oxygen ($\Theta(\text{O}) \sim 0.1$) is to increase the heat of adsorption slightly and to cause the ethylene to tilt. Ethylene oxide also adsorbs weakly at 80 K with the molecular plane oriented perpendicularly to the surface, where the heat of adsorption also increases due to the presence of adsorbed oxygen. The RAIR spectra of both ethylene and ethylene oxide adsorbed on oxygen-activated Ag(1 1 1) at 300 K under a pressure of 1 Torr show the formation of a number of surface species. An $\eta^2(\text{C},\text{O})$ bonded acetaldehyde species is found, where the infrared features decrease coincident with acetaldehyde/ethylene oxide desorption. A species persists on heating to 450 K which exhibits a single infrared peak at 1004 cm^{-1} . Based on the frequency shifts observed on isotopic substitution (with D and ^{18}O), it appears to contain C, O and H. This feature disappears on heating to 550 K correlating with the desorption of CO_2 in temperature-programmed desorption. Finally, a series of features is detected which may be due to an adsorbed formate or strongly distorted ethylene oxide. These results emphasize that good quality infrared spectra can be collected for adsorbed species formed at high pressures on a model, oxygen-activated Ag(1 1 1) catalyst and that the surface chemistry is completely different to that found when dosing at 80 K under ultrahigh vacuum conditions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The silver-catalyzed epoxidation of ethylene represents the largest volume of any catalytic oxida-

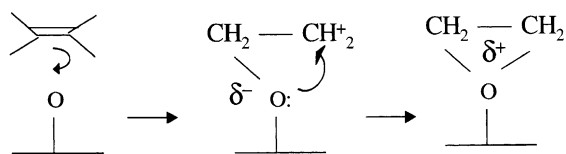
tion reaction conducted on an industrial scale and has been studied extensively [1–4]. However, there are still several questions regarding the mechanism of this reaction that remain to be answered. One of the early questions was related to the form of the active oxygen, molecular or atomic, involved in the partial oxidation of ethylene ([5] and refs. therein). This appears to be reasonably well resolved concluding that adsorbed

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atomic oxygen is responsible for both selective and total oxidation. Another, which represents the focus of this work, addresses the nature of the surface intermediates in the formation of total oxidation products, CO_2 and water, and the desired product, ethylene oxide, under catalytic conditions.

With respect to the surface intermediate to ethylene oxide, an oxametallacycle could be formed by interaction of the carbon atoms from ethylene with the surface and an oxygen atom [6,7]. An alternative intermediate has also been proposed, where both p-orbitals from ethylene interact simultaneously with an adsorbed oxygen [8]. This could be considered a cycloaddition reaction, which has previously been observed to proceed on silver [9]:



Surface oxametallacycles have been synthesized by adsorbing iodoethanol on $\text{Ag}(110)$ [6,7] and $\text{Ag}(111)$ [10]. Temperature-programmed desorption experiments showed that such species do not produce ethylene oxide but yield acetaldehyde.

Studies on $\text{Ag}(111)$ surfaces showed that ethylene oxide could be produced using high reactant pressures (Torr) [8,11]. In this way, it was possible not only to reproduce the kinetics of the reaction on supported catalysts, but also to observe ethylene oxide desorbing from the surface in temperature-programmed experiments. The ethylene-oxide-like intermediate proposed from these experiments [8] also accounts for the kinetic isotope effects found for the epoxidation reaction [12].

In the work reported in this paper, the corresponding reflection-absorption infrared spectra (RAIRS) are collected allowing the nature of the species present on the surface to be monitored. It is found that ethylene oxide adsorbs weakly on clean and oxygen-covered $\text{Ag}(111)$ at 80 K in ultrahigh vacuum, desorbing molecularly at ~ 185 K. In this case, the molecular plane of the adsorbed ethylene

oxide is oriented perpendicularly to the surface. In contrast, oxygen-activated silver pressurized with 1 Torr of ethylene oxide at 300 K results in a number of more strongly adsorbed species.

Ethylene also adsorbs weakly on clean and oxygen-covered $\text{Ag}(111)$ in ultrahigh vacuum, while more strongly adsorbed species are found after pressurizing oxygen-activated silver with ethylene. The results presented below clearly demonstrate that infrared spectra can be collected of the surface species formed during the total and partial oxidation of ethylene and emphasize that completely different species are formed in ultrahigh vacuum and at high pressures.

2. Experimental

The experiments were carried out in a stainless steel, ultrahigh vacuum chamber (base pressure, $\sim 8 \times 10^{-11}$ Torr following bakeout). This has been described in detail elsewhere [13]. Infrared data were collected from an $\text{Ag}(111)$ single crystal sample mounted in a modified $2\frac{3}{4}$ in. (7 cm) six-way cross containing infrared-transparent, KBr windows. The sample could be resistively heated to 1000 K, or cooled to 80 K by thermal contact with a liquid-nitrogen-filled reservoir. Radiation 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 2000 scans.

The infrared cell was attached to a 12 in. (30.5 cm)-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 ~ 3 K/s 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 [14,15] which consisted of bombarding with argon ions (1 keV, 2 $\mu\text{A}/\text{cm}^2$) at 300 K and the annealing to 1000 K in vacuo to remove any remaining surface species. The ethylene oxide used for the experiments (Aldrich, 99% purity) was transferred to a glass vial, attached to the gas-handling line of the vacuum system, and further purified by repeated freeze-pump-thaw cycles. Its cleanliness was monitored mass spectroscopically. Ethylene (Matheson) was transferred from the cylinder to a glass bottle and further purified by bulb-to-bulb distillations and its purity verified mass spectroscopically. Perdeuteroethylene (C_2D_4) (Cambridge Isotopes, 98% D) was used as received. Normal oxygen ($^{16}\text{O}_2$) (Gas Tech, Inc.) was also transferred to a glass bottle and further purified by several freeze-pump-thaw cycles. Isotopically labeled oxygen ($^{18}\text{O}_2$) (Cambridge Isotopes, 98% ^{18}O) was used as received.

3. Results

Fig. 1 displays a series of temperature programmed-desorption spectra for ethylene (3 L; 1 L = 1×10^{-6} Torr) and ethylene oxide (3 L) adsorbed on Ag(111) and oxygen-covered Ag(111), where the oxygen coverage was ~ 0.1 monolayers [16]. Ethylene desorbs from clean Ag(111) at ~ 138 K, a temperature very close to that found on Ag(110) [17]. A Redhead analysis [18], assuming first-order desorption kinetics and a pre-exponential factor of $1 \times 10^{13} \text{ s}^{-1}$, yields a desorption activation energy of ~ 39 kJ/mol. The effect of adsorbed oxygen is to increase the desorption activation energy so that the peak desorption temperature increases to ~ 161 K which, from an identical Redhead analysis, corresponds to a desorption activation energy of ~ 46 kJ/mol. A similar effect is noted for ethylene oxide which desorbs at 158 K ($E_{\text{act}} = 45$ kJ/mol) from clean Ag(111) and at 180 K ($E_{\text{act}} = 51$ kJ/mol) from the oxygen-covered surface. The desorption tempera-

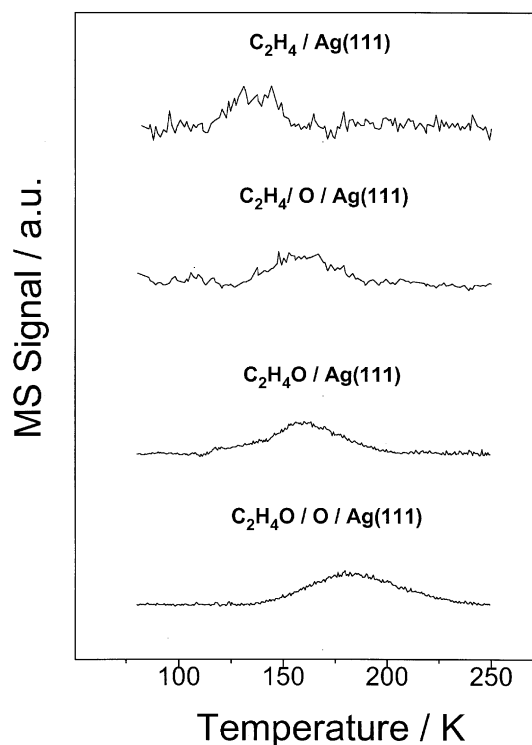


Fig. 1. Temperature-programmed desorption spectra for ethylene and ethylene oxide (3 L) adsorbed on clean and oxygen-covered Ag(111) ($\theta(\text{O}) \sim 0.1$) at 80 K.

ture of ethylene oxide from Ag(111) is also very close to that found on Ag(110) [19].

The infrared spectra for ethylene on clean and oxygen-covered Ag(111) are displayed in Fig. 2. These exhibit a sharp single feature at 949 cm^{-1} on clean Ag(111) following adsorption at 80 K and no other modes are detected in this spectral region. This value is very close to the vibrational frequency for ethylene adsorbed on clean Ag(110) of 955 cm^{-1} from RAIRS [20] and 967 cm^{-1} from HREELS [21] and is assigned to the $\omega(\text{CH}_2)$ mode ($\text{b}_{1\text{u}}$). Addition of oxygen to the surface causes the appearance of additional features at 968 and 3076 cm^{-1} . Such a shift in the 968-cm^{-1} , $\omega(\text{CH}_2)$ mode on the addition of oxygen has been noted previously on Ag(110) [20], and the appearance of a 3076-cm^{-1} mode observed under a high pressure of ethylene on Ag(100) [19] has been interpreted as due to tilted ethylene. Heating to ~ 160 K causes the 949 and 3076-cm^{-1} features to disappear and the 968-cm^{-1}

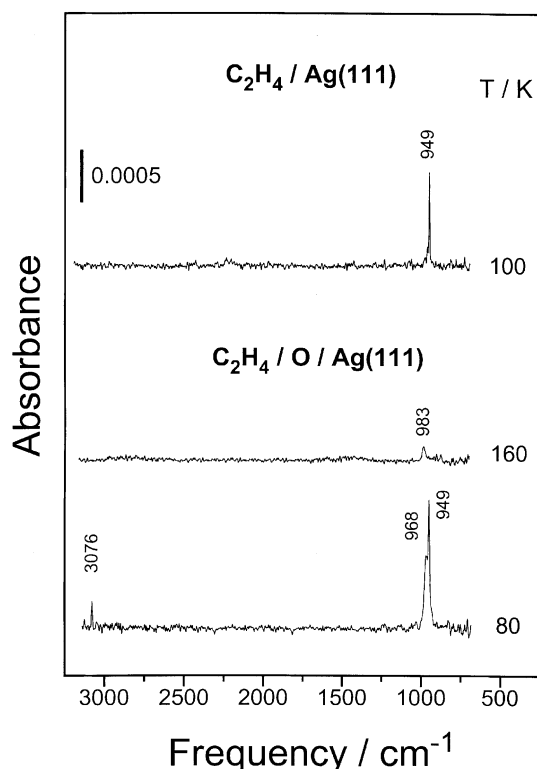


Fig. 2. RAIR spectra of ethylene (3 L) adsorbed on clean and oxygen-covered Ag(111) ($\theta(O) \sim 0.1$) at 80 K and heated to 100 K in the case of adsorption on Ag(111) and 160 K on oxygen-covered Ag(111).

mode to attenuate and shift to 983 cm^{-1} corresponding to the desorption of ethylene (Fig. 1).

The corresponding infrared spectra of ethylene oxide (5 L) adsorbed on Ag(111) are displayed in Fig. 3. Major features are observed at 869 and 1267 cm^{-1} with smaller peaks at 3070, 3000, 2918, 1148 and 796 cm^{-1} following adsorption on Ag(111) at 80 K. Heating to 140 K causes multilayer desorption resulting in the smaller features disappearing completely leaving a spectrum with sharp peaks at 1263 and 860 cm^{-1} . These frequencies are close to those found for ethylene oxide adsorbed on Ag(110) [22]. Similarly, adsorption of ethylene oxide on oxygen-covered Ag(111) at 80 K yields intense peaks at 1265 and 866 cm^{-1} with weaker features at 3066, 3001, 2920, 1149 and 795 cm^{-1} . The weaker features disappear on heating to 160 K leaving two peaks centered at 1263 and 852 cm^{-1} .

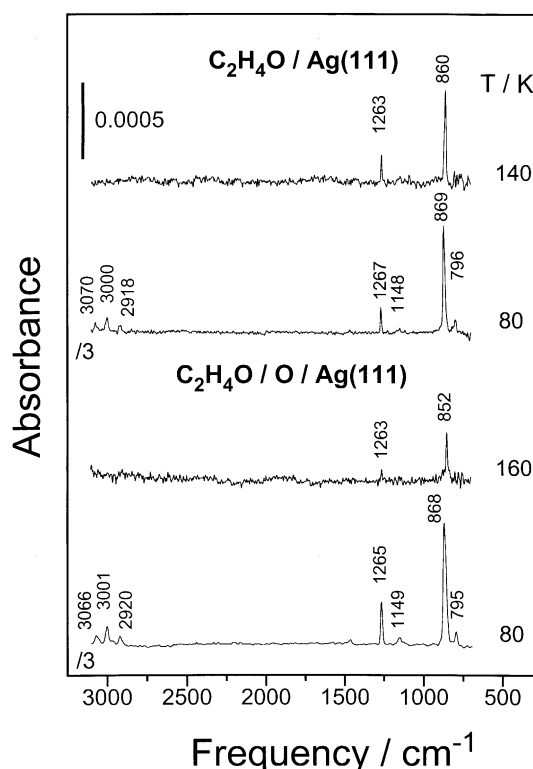


Fig. 3. RAIR spectra of ethylene oxide (5 L) adsorbed on clean and oxygen-covered Ag(111) ($\theta(O) \sim 0.1$) at 80 K and heated to 140 K in the case of adsorption on Ag(111) and 160 K on oxygen-covered Ag(111).

The second series of experiments consisted of pressurizing an oxygen-activated surface with various gases. The oxygen activation process follows a recipe reported in the literature [8,11] to form both adsorbed and sub-surface oxygen. The presence of both adsorbed, atomic and sub-surface oxygen was confirmed using temperature-programmed desorption. In order to establish whether surface infrared features were caused by species being displaced from the walls of the vacuum chamber by the high gas pressures, test experiments were carried out in which an infrared spectrum of the silver surface was collected after pressurizing the cell with 100 Torr of nitrogen. No surface infrared features were detected.

Exposure of the oxygen-activated surface to ethylene (for exposures $> 10^6$ L) forms CO_2 in two states (an α state at ~ 380 K and a β state at ~ 450

K) in temperature-programmed desorption with ethylene oxide and acetaldehyde desorbing at ~ 360 K. A careful analysis of this feature shows that $35 \pm 15\%$ of the intensity is due to ethylene oxide, the remainder being acetaldehyde [8]. The yield from this state is substantially lower than from the CO_2 states. These results emphasize that epoxidation, isomerization and total oxidation reactions all proceed simultaneously on the surface. In order to establish which features detected on the surface are associated with each other, RAIR spectra were collected for a surface pressurized with ethylene at 300 K, after evacuation, and after annealing to various temperatures (Fig. 4). In addition, spectra were also collected using isotopically labeled ethylene (C_2D_4) (Fig. 6), following C_2H_4 adsorption on a surface oxidized using ^{18}O (Fig. 5), as well as after reacting with ethylene oxide (Fig. 7).

The spectrum collected at 300 K in the presence of 1 Torr of ethylene is displayed in Fig. 4(a). Very intense gas-phase features are detected at ~ 2000 , ~ 1400 and ~ 1000 cm^{-1} which are indicated by horizontal lines at the bottom of the spectrum [23]. All of these gas-phase features are due to ethylene. No other features were detected confirming the purity of the ethylene. Additional peaks are detected at 752, 1327, 2808 and 2885 cm^{-1} that are not assignable to gas-phase features and which saturate with increasing ethylene pressure. These are assigned to species adsorbed onto the surface. They persist when the ethylene is evacuated with the sample held at 300 K (Fig. 4(b)), but with intensities that are attenuated by about 40%, indicating that a portion of the species present under a pressure of ~ 1 Torr of ethylene either desorbs at 300 K or converts into other species. Note that spectrum 4(b) was collected after spectrum 4(a) so that the ethylene exposures are $\sim 300 \times 10^6$ L. This corresponds to saturation of the CO_2 desorption yield and results in the consumption of all surface oxygen [8]. Under these conditions, the α and β CO_2 states, which are well separated at lower ethylene exposures, coalesce into a single broad state [8]. Once the ethylene is removed, additional vibrational features become evident so that the spectrum collected at 300 K in ultrahigh vacuum exhibits peaks at 752, 1004, 1327, 1389, 1689, 2808

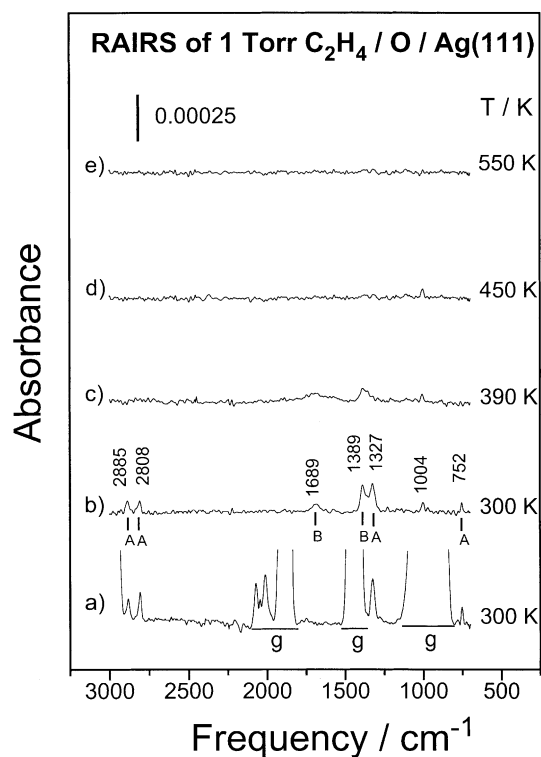


Fig. 4. RAIR spectra of an oxygen-activated Ag(111) surface also containing sub-surface oxygen pressurized with 1 Torr of ethylene at 300 K. The infrared cell was then evacuated and the spectrum collected at 300 K. The sample was then annealed to various temperatures in ultrahigh vacuum and allowed to cool to 300 K and the infrared spectrum recorded. The annealing temperatures are marked adjacent to the corresponding spectra.

and 2885 cm^{-1} . In addition, a closer examination of the doublet at 1389 and 1327 cm^{-1} suggests the presence of an additional feature between these peaks at ~ 1358 cm^{-1} .

It is clear that reaction of ethylene with an oxygen-activated silver surface results in the formation of a number of surface species that are stable at 300 K. None of the peaks evident in this spectrum can be assigned to adsorbed ethylene on Ag(111) (Fig. 1). This is entirely in accord with the work of Grant and Lambert who showed that large ethylene exposures were required to induce a surface chemical reaction. It is also interesting to note that ethylene adsorbed at high pressures (several hundred Torr) on clean Ag(111) at 300 K, desorbs completely reversibly [24].

The majority of the infrared features diminish substantially in intensity as the sample is heated to ~ 390 K (Fig. 4(c)). Weak features persist at 1689, 1004 and 1389 cm^{-1} with small peaks evident at 1358 and 1327 cm^{-1} . The persistence of the small feature at 1358 cm^{-1} after heating to 390 K confirms its presence in the 300-K spectrum (Fig. 4(b)). All features, except that at 1004 cm^{-1} , are completely removed by annealing to 450 K. This suggests that the 1004-cm^{-1} peak is due to a surface species that thermally decomposes to yield the $\beta\text{-CO}_2$ state. It should be noted that temperature-programmed desorption data were collected as part of this work (not shown) and agreed well with the results of Grant and Lambert [8], although the desorption temperatures measured in our work were ~ 20 K higher.

In order to establish which of these surface modes involve oxygen, spectra were collected after pressurizing an ^{18}O -activated Ag(111) surface (prepared in exactly the same way as for the data displayed in Fig. 4) with ethylene. The resulting spectra are shown in Fig. 5. Fig. 5(a) displays the spectrum of the surface in the presence of 1 Torr of ethylene (C_2H_4), and Fig. 5(b) the infrared spectrum after ethylene evacuation, where the total ethylene exposure is $\sim 300 \times 10^6$ L. The positions of the gas-phase features are indicated by horizontal lines at the bottom of the figure [23]. Features are present at 2878, 2810, 1356, 1330 and 717 cm^{-1} in the presence of gas-phase ethylene. The spectrum in Fig. 5(b) collected after evacuating the ethylene displays features at 717, 972, 1303, 1330, 1356, 1384, 1589, 2810 and 2878 cm^{-1} . Thus, the peaks formed by ethylene adsorption on ^{16}O -covered Ag(111) between 1389 and 1327 cm^{-1} (Fig. 4) split into a manifold of four peaks at 1384, 1356, 1330 and 1303 cm^{-1} on isotopic substitution with ^{18}O . On annealing to 390 K, the peaks at 1589 and 1384 cm^{-1} are attenuated by about 50%. This decrease is approximately the same as found for the 1689- and 1389-cm^{-1} features in Fig. 4. The peaks at 1356, 1330 and 1303 cm^{-1} decrease in intensity significantly more than this. Finally, the 972-cm^{-1} peak is still evident at 450 K indicating that it is associated with the 1004-cm^{-1} mode for a $^{16}\text{O}/\text{Ag}(111)$ surface (Fig. 4). These frequencies are compared with the corresponding modes found for

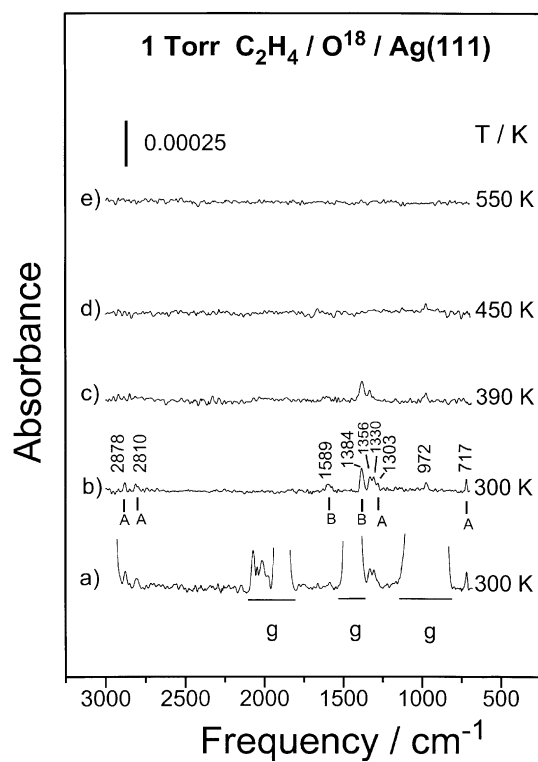


Fig. 5. RAIR spectra of an ^{18}O -activated Ag(111) surface also containing sub-surface ^{18}O pressurized with 1 Torr of ethylene at 300 K. Spectrum (a) shows both the surface and gas-phase species and thus reflects the nature of the surface under a pressure of ethylene. The infrared cell was then evacuated and the spectrum collected at 300 K (b). The sample was then annealed to various temperatures in ultrahigh vacuum and allowed to cool to 300 K and the infrared spectrum recorded. The annealing temperatures are marked adjacent to the corresponding spectra.

an ^{16}O -covered surface, in Table 1. The ratio of these vibrational frequencies, designated $\nu(^{16}\text{O})/\nu(^{18}\text{O})$, is also displayed. These data indicate that the 753, 1004, 1689-cm^{-1} features involve oxygen. The largest shift is for the 1689-cm^{-1} mode and is close to $\sqrt{(18/16)}$ (which is 1.061) suggesting that the normal mode involves primarily oxygen.

Similar experiments were carried out by pressurizing an ^{16}O -activated surface with 1 Torr of perdeuterioethylene (C_2D_4). Strong deuterium isotope effects are seen both in high-pressure reactions [12] and in temperature-programmed desorption experiments [8]. In particular, the yields of ethylene oxide and acetic acid, proposed to be a

Table 1

Infrared frequencies of the surface species formed by pressurizing an oxygen-activated Ag(111) surface with ethylene (1 Torr) and evacuating

Frequency/cm ⁻¹ , C ₂ H ₄ / ¹⁶ O/Ag(111)	Frequency/cm ⁻¹ , C ₂ H ₄ / ¹⁸ O/Ag(111)	$\nu(^{16}\text{O})/\nu(^{18}\text{O})$
752	717	1.049
1004	972	1.033
1327	1330	0.998
1356	1358	0.999
1389	1384	1.004
1689	1589	1.063
2808	2810	1.00
2885	2878	1.002

precursor to the β -CO₂ state, are significantly enhanced when using C₂D₄. The resulting infrared spectra are shown in Fig. 6. Again, the gas-phase features are indicated by a horizontal line [23]. The spectrum collected in the presence of 1 Torr of C₂D₄ is shown in Fig. 6(a) and that following evacuation of the ethylene in Fig. 6(b). These spectra are much simpler than those found when pressurizing with C₂H₄ reflecting the isotope effects discussed above [8,12]. The spectrum measured in the presence of d₄-ethylene (Fig. 6(a)) displays a single intense feature at 2021 cm⁻¹. That found after ethylene evacuation (Fig. 6(b)) displays features at 2021 cm⁻¹ with a shoulder apparent at ~1997 cm⁻¹, and a peak at 999 cm⁻¹. The 1997- and 2021-cm⁻¹ peaks disappear completely on heating to 390 K while the 999-cm⁻¹ mode is attenuated by ~50% in intensity, and only disappears completely after heating to 550 K. This implies that this peak corresponds to the 1004-cm⁻¹ (Fig. 4) and 972-cm⁻¹ (Fig. 5) features. It should be noted, however, that this feature decreases in intensity by 50% after heating to 390 K when formed from d₄-ethylene (Fig. 6), while its intensity remains constant when formed from C₂H₄ (Figs. 4 and 5).

In order to provide additional clues to the nature of the surface species, an ¹⁶O-activated surface was pressurized with ethylene oxide. It was found by Grant and Lambert that the β -CO₂ state arose from subsequent ethylene oxide oxidation [8]. It was also suggested that adsorbing ethylene oxide on oxygen-activated silver leads exclusively

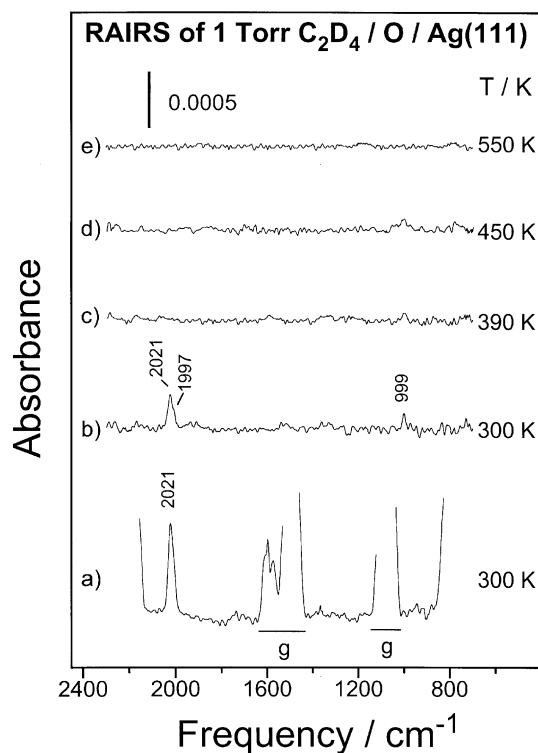


Fig. 6. RAIR spectra of an oxygen-activated Ag(111) surface also containing sub-surface oxygen pressurized with 1 Torr of d₄-ethylene at 300 K. Spectrum (a) shows both the surface and gas-phase species and thus reflects the nature of the surface under a pressure of ethylene. The infrared cell was then evacuated and the spectrum collected at 300 K (b). The sample was then annealed at various temperatures in ultrahigh vacuum and allowed to cool to 300 K and the infrared spectrum recorded. The annealing temperatures are marked adjacent to the corresponding spectra.

to the formation of ethylene oxide in temperature-programmed desorption [25]. However, silver-catalyzed isomerization of ethylene oxide to acetaldehyde has been investigated and the activation energy for this reaction on the surface was found to be ~30 kJ/mol [25].

The infrared spectrum obtained after exposing an ¹⁶O-activated Ag(111) surface to 1 Torr of ethylene oxide (~300 × 10⁶ L) at 300 K and evacuating is shown in Fig. 7(a). The gas-phase spectrum is not shown, in this case, since the gas-phase ethylene oxide spectrum completely obscures any surface species. The spectrum yields features at 756, 1003, 1330, 1389, 1681, 2808 and

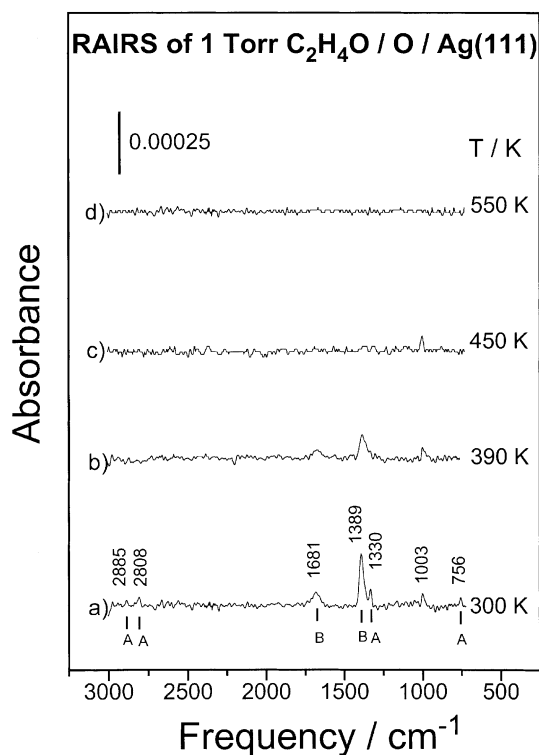


Fig. 7. RAIR spectra of an oxygen-activated Ag(111) surface also containing subsurface oxygen pressurized with 1 Torr of ethylene oxide at 300 K. The sample was then annealed to various temperatures in ultrahigh vacuum and allowed to cool to 300 K and the infrared spectrum recorded. The annealing temperatures are marked adjacent to the corresponding spectra.

2885 cm^{-1} . These peak positions are in good agreement with those found by adsorbing ethylene on an ^{16}O -activated surface (Fig. 4). However, the relative intensities of the features found by dosing ethylene oxide (Fig. 7) are substantially different to those observed after dosing ethylene (Fig. 4). Heating to 390 K causes the 1681 and 1389- cm^{-1} features to decrease in intensity by $\sim 50\%$, in accord with the corresponding decrease found for these features formed from ethylene (Fig. 4). The 2885, 2808 and 756- cm^{-1} modes disappear completely after annealing to 390 K, while the 1003- cm^{-1} mode persists to 450 K (compare with Fig. 4). It is also somewhat more intense (by $\sim 30\%$) when formed from ethylene oxide (Fig. 6) than ethylene (Fig. 4).

4. Discussion

Ethylene adsorbs weakly on clean Ag(111), desorbing with an activation energy of ~ 39 kJ/mol (Fig. 1). The presence of a single infrared feature at 949 cm^{-1} (Fig. 2), assigned to the $\omega(\text{CH}_2)$ mode (b_{1u}) of ethylene, confirms that ethylene adsorbs with the molecular plane of ethylene parallel to the surface in a π -bonded configuration. Similar conclusions have been arrived at from photoelectron spectroscopic [17] and vibrational experiments [20,21] on Ag(110). Ethylene oxide also adsorbs relatively weakly on Ag(111) desorbing with an activation energy of 45 kJ/mol (Fig. 1). Adsorption at 80 K gives rise to a number of infrared peaks, the majority of which disappear on heating to 140 K (Fig. 3). These peaks are compared with gas-phase ethylene oxide in Table 2 and the adsorbate-induced frequencies agree well with those in the gas phase suggesting that they are due to the presence of a randomly adsorbed multilayer of ethylene oxide. Following desorption of the multilayer, features remain at 1263 and 860 cm^{-1} on clean Ag(111) and at 1263 and 852 cm^{-1} on oxygen-covered Ag(111) (Fig. 3). These are assigned to epoxide ring stretching and deformation modes respectively and both are of a_1 symmetry (Table 2). According to the surface selection rules for RAIRS [26], if ethylene oxide, with C_{2v} symmetry, adsorbs with its principal C_2 symmetry axis oriented perpendicularly to the surface, only modes of a_1 symmetry are allowed. The appearance of modes with only a_1 symmetry indicates that the molecular symmetry axis of ethylene oxide is oriented perpendicularly to the surface following adsorption in ultrahigh vacuum. A similar orientation has been suggested for ethylene oxide adsorbed on Ag(110) [21] where the ethylene oxide was proposed to bond via lone pairs on the oxygen atoms.

The behavior of ethylene and ethylene oxide on oxygen-activated Ag(111), when pressurized at 1 Torr with a sample held at 300 K, is substantially different. It is clear also that there are a number of species present on the surface. However, combining results from various experiments allows features to be grouped depending on their behavior as a function of temperature and pressure, and by using isotopically labeled compounds. The work of

Table 2

Assignments of the modes assigned to ethylene oxide found following adsorption of ethylene oxide on clean and oxygen-covered Ag(1 1 1) (5 L)

Mode	Symmetry	Frequency/cm ⁻¹				
		C ₂ H ₄ O _(g) [40]	C ₂ H ₄ O/Ag 80 K	C ₂ H ₄ O/Ag 140 K	C ₂ H ₄ O/O/Ag 80 K	C ₂ H ₄ O/O/Ag 140 K
$\nu_a(\text{CH}_2)$	b ₂	3065	3070	–	3066	–
$\nu_s(\text{CH}_2)$	a ₁ , b ₂	3006	3000, 2918	–	3001, 2920	–
Ring str.	a ₁	1271	1267	1263	1265	1263
tw(CH ₂)	b ₂	1142	–	–	1149	–
Ring def.	b ₁	892	869	–	868	–
Ring def.	a ₁	877	869	860	868	852
$\rho(\text{CH}_2)$	b ₂	822	796	–	795	–

ν = stretch, ρ = rock, tw = twist.

Grant and Lambert on the chemistry of ethylene on oxygen-activated Ag(1 1 1) [8] suggests that the presence of both adsorbed and subsurface oxygen is required for the formation of ethylene oxide from ethylene. Adsorbed *atomic* oxygen is responsible for both total oxidation to form CO₂ and water as well as partial oxidation to ethylene oxide. Two total oxidation pathways were identified. The first was a direct combustion of adsorbed ethylene which does not require the presence of sub-surface oxygen and produces an α -CO₂ desorption state at \sim 360 K. The second pathway involves the further oxidation of ethylene oxide and requires the presence of sub-surface oxygen which was proposed to proceed via CH₃CHO, CH₃COOH and (COOH)₂ to produce a β -CO₂ desorption state at \sim 450 K. The infrared measurements (Figs. 4–7) are in broad agreement with these observations, since the majority of the infrared features disappear at \sim 390 K, corresponding to ethylene oxide/acetaldehyde desorption, and the α -CO₂ state. A feature persists at this temperature but disappears on heating to above 450 K corresponding to the β -CO₂ desorption state.

The frequencies of ethylene on clean and oxygen-covered Ag(1 1 1) adsorbed in ultrahigh vacuum (Fig. 2) are completely different to those found after pressurizing the surface (Fig. 4) indicating that no π -bonded ethylene appears to adsorb on the silver surface under these circumstances, but that all products are formed by reaction with adsorbed atomic oxygen. This reaction also appears to be activated since it is induced by high exposures and temperatures.

It is evident that, while similar species are formed from ethylene (Fig. 4) and ethylene oxide (Fig. 7) on oxygen-activated Ag(1 1 1) at 300 K following evacuation, the intensities of the features are different. The ratios of the intensities, measured from the heights of the peaks of the most prominent features, are displayed in Table 3. The peak at 1004 cm⁻¹ is excluded from this list since it is clearly due to a different species since it persists as the sample is heated to 450 K (Figs. 4–7). The data in Table 3 indicate that these features can be classified into two groups. In the first group, the features are less intense when formed from ethylene oxide and characterized by frequencies at 752, 1327, 2808 and 2885 cm⁻¹ (designated species A in Figs. 4, 5 and 7). Note that this does not necessarily imply that they are all due to a single species, merely that they behave similarly when formed from ethylene or ethylene oxide. In the second group, the peaks are more intense when formed from ethylene oxide and have characteristic fre-

Table 3

Ratio of the infrared intensities of modes formed by the adsorption of ethylene oxide and of ethylene on oxygen-activated Ag(1 1 1)

Frequency/cm ⁻¹	$I(\text{ethylene oxide})/I(\text{ethylene})$
752 (756)	0.30 \pm 0.05
1327 (1330)	0.45 \pm 0.05
1389 (1389)	1.6 \pm 0.1
1689 (1681)	1.5 \pm 0.1
2808 (2808)	0.40 \pm 0.05
2885 (2885)	0.45 \pm 0.05

Frequencies in parentheses are those measured for ethylene oxide adsorption on oxygen-activated Ag(1 1 1).

quencies at 1389 and 1681 cm^{-1} (designated species B in Figs. 4, 5 and 7).

We turn our attention first to exploring the nature of species B, characterized by peaks at 1689 and 1389 cm^{-1} . The data in Table 1 indicate that the 1689- cm^{-1} peak involves oxygen while that at 1389 cm^{-1} does not. The intensity of the 1689- and 1389- cm^{-1} features decreases substantially as the sample is heated to 390 K and they are completely absent at 450 K. The intensities of the features at 390 K are approximately 50% of those at 300 K implying that gas-phase products would be formed in a desorption peak centered at ~ 390 K. Both the α - CO_2 and the ethylene oxide/acetaldehyde desorption peaks have approximately this desorption temperature [8]. Since these RAIRS features are more intense when formed from ethylene oxide (Table 3) while the α - CO_2 state found in temperature-programmed desorption [8] is much less intense than when formed from ethylene, this implies that this surface species desorbs to yield ethylene oxide and/or acetaldehyde. Furthermore, the relative intensities of the 1689 and 1389 cm^{-1} modes remain constant irrespective of how the sample was prepared (Figs. 4, 5 and 7) indicating that they are due to a single species. Also, the frequencies due to adsorbed ethylene oxide on silver (Table 2) are substantially different to those of species B. In addition, the most intense features for ethylene oxide are ring modes and would therefore both be expected to shift on isotopic substitution. Adsorption of acetaldehyde on Ag(1 1 1) at 80 K in ultrahigh vacuum yields the most intense peaks at 1702 and 1348 cm^{-1} assigned to $\nu(\text{C}=\text{O})$ and $\delta_s(\text{CH}_3)$ vibrations respectively [27]. These frequencies are close to, but somewhat higher than those for species B. However, the isotopic shift found for the 1689- cm^{-1} peak (Table 1), as well as its frequency, are consistent with a $\text{C}=\text{O}$ stretching mode. A monolayer of acetaldehyde desorbs from clean Ag(1 1 1) at between 100 and 200 K assigned to the presence of an $\eta^1(\text{O})$ species. It has been shown that the $\text{C}=\text{O}$ stretching frequency decreases when acetaldehyde adsorbs in a $\eta^2(\text{C},\text{O})$ configuration and the frequency found here is close to those measured for acetaldehyde adsorbed on Pd(1 1 1) [28], Ru(0 0 1) [29] and Cu(1 1 1) [30] in ultrahigh vacuum. The 1689- cm^{-1} peak is there-

fore assigned to a $\text{C}=\text{O}$ stretching mode and the 1384- cm^{-1} feature to a symmetric methyl bending mode; the shifts on ^{18}O substitution are consistent with these assignments. It is also found that acetaldehyde desorbs from an oxygen-activated surface following a large exposure (9×10^6 L, 300 K) at ~ 400 K, significantly higher than when chemisorbed in ultrahigh vacuum [25], but consistent with the formation of a more stable $\eta^2(\text{C},\text{O})$ configuration. The relative intensities of the 1689- and 1384- cm^{-1} features are also consistent with an $\eta^2(\text{C},\text{O})$ configuration. In both the gas phase and monolayer, the $\nu(\text{C}=\text{O})$ mode is more intense than that due to $\delta_s(\text{CH}_3)$. In the case of the species formed from ethylene (Figs. 4 and 5) or ethylene oxide (Fig. 6), the reverse is true. This suggests that the $\text{C}=\text{O}$ bond is oriented so that it is close to parallel to the surface as expected for the $\eta^2(\text{C},\text{O})$ configuration. The assignments are summarized in Table 4.

There is no evidence for the presence of adsorbed acetaldehyde when an oxygen-activated surface is pressurized with d_4 -ethylene (Fig. 6) consistent with the isotope effects referred to above. The features due to $\eta^2(\text{C},\text{O})$ -acetaldehyde are significantly more intense for a surface pressurized with ethylene oxide (Fig. 7) than ethylene (Figs. 4 and 5, Table 3). This appears to contradict temperature-programmed desorption results for ethylene oxide and acetaldehyde adsorbed on oxygen-activated silver where each of these species was found to desorb molecularly and the activation energy for interconversion was found to be ~ 30 kJ/mol [25]. Infrared results, on the contrary, indicate that acetaldehyde is formed at 300 K both from ethylene (Figs. 4 and 5) and ethylene oxide (Fig. 6). The origin of this discrepancy is not clear although it may arise from differences in exposures; exposures in the infrared experiments were large to allow spectra to be collected in the presence of the gas phase.

It has been proposed that the isomerization of ethylene oxide to acetaldehyde proceeds via an oxametallacyclic intermediate. Oxametallacycles have been formed on clean Ag(1 1 1) and found to decompose to form acetaldehyde, consistent with this proposal [10]. Acetaldehyde desorbs at ~ 250 and ~ 350 K from clean Ag(1 1 1) [27] although it is

Table 4

Assignments of the modes assigned to acetaldehyde found following adsorption of ethylene oxide and ethylene on oxygen-activated Ag(111) (1 Torr at 300 K)

Mode	Symmetry	Frequency/cm ⁻¹			
		Crystalline CH ₃ CHO	CH ₃ CHO/Ag(111), UHV [27]	C ₂ H ₄ / ¹⁶ O/Ag C ₂ H ₄ / ¹⁶ O/Ag 1 Torr	C ₂ H ₄ / ¹⁸ O/Ag 1 Torr
$\nu(\text{C}=\text{O})$	a'	1722	1702	1689, 1681 ^a	1589
$\delta_{\text{a}}(\text{CH}_3)$	a'	1431, 1422	–	–	–
$\pi(\text{CH})$	a'	1389	–	–	–
$\delta_{\text{s}}(\text{CH}_3)$	a'	1347	1348	1389, 1389 ^a	1384
$\nu_{\text{a}}(\text{OCO})$	a'	–	–	–	–
$\nu_{\text{s}}(\text{OCO})$	a'	–	–	–	–
$\nu(\text{C}-\text{C})$	a'	1118	1121	–	–

ν = stretch, δ = deformation, π = bend.

^a Frequencies for ethylene oxide adsorption on oxygen-activated Ag(111).

evident from the above discussion that acetaldehyde is stabilized on an oxygen-activated surface by bonding in an $\eta^2(\text{C},\text{O})$ configuration. The correspondence between the ethylene oxide/acetaldehyde peak positions when formed from ethylene [8] and when the surface is dosed directly with either acetaldehyde or ethylene oxide indicates that product formation is desorption-rate-limited in the epoxidation reaction.

We turn our attention now to the feature that is stable up to 450 K at 1004 cm⁻¹ (Figs. 4 and 7), 972 cm⁻¹ (Fig. 5) and 999 cm⁻¹ (Fig. 6). Based on its stability with temperature, this feature appears to decompose to produce the β -CO₂ desorption state (at \sim 450 K [8]). This state has been suggested to arise from further oxidation of adsorbed aldehyde via the sequence CH₃CHO \rightarrow CH₃COOH \rightarrow (COOH)₂ to finally produce the β -CO₂ state. The spectroscopic data do not support this proposal. Any effect due to the further oxidation of acetaldehyde should be particularly evident in the case in which the most acetaldehyde was made on the surface, that is, from the adsorption of ethylene oxide (Fig. 7). The oxidation of acetaldehyde would be manifest by the growth of additional features due to oxidation products which should be detectable on the surface since these do not finally decompose to form CO₂ until \sim 450 K [8]. In particular, the 1003-cm⁻¹ feature, which disappears coincident with the β -CO₂ desorption state, does not grow. Indeed, it is evident on the surface immediately following adsorption at 300 K (Figs. 4–7) implying that the precursor to the β -CO₂ state

is formed at 300 K and persists up to 450 K when it thermally decomposes to yield CO₂. The C=O stretching mode is the most intense band for acetic acid (1732 cm⁻¹ for CH₃COOH, and 1721 cm⁻¹ for CD₃COOD on Ru(0001) [31]). However, the proton is rapidly extracted, for example, on oxygen-covered Ag(111), to yield an acetate species [15]. CH₃COO_(ads) exhibits a sharp feature at 1396 cm⁻¹ and CD₃COO_(ads) a feature at 1388 cm⁻¹ [15]. Acetate intermediates have been shown to dehydrogenate to yield H₂ and CO₂ and, in some cases, CO and adsorbed C, on nickel [32], platinum [33], palladium [34] and rhodium [35]. However, the only feature close to this is the peak at \sim 1389 cm⁻¹ assigned to methyl mode of adsorbed acetaldehyde. The 1396-cm⁻¹ mode of the acetate species is due to a $\nu_{\text{s}}(\text{OCO})$ mode and would therefore be expected to shift on substitution of ¹⁸O for ¹⁶O, whereas the 1389-cm⁻¹ feature does not. The frequency shift of the 1003-cm⁻¹ mode to 972 cm⁻¹ when formed on an ¹⁸O-activated surface (Fig. 5, Table 1) suggests that it is due to a C–O vibration since the ratio of these frequencies (1.033, Table 1) is in good agreement with the reduced mass change in substituting ¹⁸O for ¹⁶O in a CO bond (1.025). In addition, a peak appears in this region (at 999 cm⁻¹) for a surface dosed with C₂D₄. This peak decreases in intensity on heating to 390 K, but is still present on the surface on annealing at 450 K implying that it corresponds to the 1004-cm⁻¹ peak formed from C₂H₄ (Fig. 4) and ethylene oxide (1004-cm⁻¹, Fig. 7). The decrease in intensity on heating from 300 to 390 K suggests that it is

due to the presence of two species. This will be discussed in greater detail below. This peak, therefore, apparently also shifts slightly on deuteration indicating that the mode also involves hydrogen. A C–O–H surface species is consistent with these observations. However, no corresponding C=O modes are detected (at $\sim 1700\text{ cm}^{-1}$). A possible explanation for this could be that these are oriented parallel to the surface and become infrared invisible. Further infrared experiments with model compounds are required to clarify this issue.

We next focus on the features formed from C_2D_4 on oxygen-activated Ag(111) (Fig. 6). It is clear that the spectrum formed at 300 K after ethylene evacuation is significantly simpler than the corresponding spectra formed from C_2H_4 (Fig. 4) or ethylene oxide (Fig. 7) under similar conditions. The peak at 2021 cm^{-1} is clearly due to a C–D stretching mode. Deuterium isotope shifts, $\nu_{\text{H}}/\nu_{\text{D}}$, for stretching modes vary between 1.32 and 1.39 indicating that the corresponding C–H mode should lie between 2668 and 2809 cm^{-1} . This suggests that this peak is associated with the 2808 cm^{-1} feature found when ethylene (Fig. 4) and ethylene oxide (Fig. 7) are allowed to react with the surface. It appears also that the 999 cm^{-1} feature is also due to the species that gives rise to the 2021 cm^{-1} mode. As noted above, this is accidentally degenerate with the mode assigned to a COH vibration above. If it is a CH (CD) mode, it is also likely to be shifted from one of the manifold of features between 1300 and 1400 cm^{-1} evident in Figs. 5–7 and would therefore be due to a CH_2 scissor mode. Both the CH_2 symmetric stretch (at 2989 cm^{-1} for ethylene and 2220 cm^{-1} for d_4 -ethylene) and the scissor mode (at 1444 cm^{-1} for ethylene and 1078 cm^{-1} for d_4 -ethylene) transform as a vector oriented along the carbon–carbon double bond. According to the surface selection rules, where only vibrational modes perpendicular to the metal surface are detected, this implies a C=C bond oriented normal to the surface. Such an ethylene orientation has been detected previously [36,37] but the desorption temperature is, in that case, significantly lower than found here.

We now address the nature of the species designated A with modes at 752, 1327, 2808 and 2885 cm^{-1}

(see Table 1). The peak at 2808 cm^{-1} was assigned to the “ethylene-like” species discussed above. The 1327 cm^{-1} mode also appears to include a feature at $\sim 1358\text{ cm}^{-1}$ where this is more clearly evident when ethylene is allowed to react with ^{18}O -activated silver (Fig. 5) where three peaks at 1356, 1330 and 1303 cm^{-1} can be resolved. The 752 cm^{-1} mode involves the participation of oxygen (Table 1) while the 2885 cm^{-1} modes are due to C–H stretches. The 2885, 1330 and 756 cm^{-1} modes are all proportionately weaker when formed from ethylene oxide.

There are several possibilities for this species. These frequencies are strikingly similar to those found for a formate species on Ag(110) [38]. The relative peak intensities measured by HREELS vary with annealing temperature but at $\sim 325\text{ K}$ the spectrum displays strong features at 770, 1340 and 2900 cm^{-1} , in good agreement with the values found here. Other much less intense peaks were noted at ~ 1050 and 1640 cm^{-1} not detectable in the spectra presented in this work. The formate thermally decomposes to yield CO_2 at 400 K coincident with the temperature at which these features decrease in intensity on annealing. The 2900 cm^{-1} feature is a CH stretching mode, that at 1340 cm^{-1} due to a symmetric COO stretch, and the 770 cm^{-1} peak due to a OCO in-plane bend. No ^{18}O spectra are available for the formate species on Ag(110). Nevertheless, the shift of the 756 cm^{-1} mode is consistent with this assignment where the ratio of the frequencies for ^{16}O -activated to ^{18}O -activated surfaces is 1.033. However, a similar shift for the COO stretch would produce a peak at $\sim 1288\text{ cm}^{-1}$, whereas no features are detected at this frequency (Fig. 5), arguing against this assignment. The thermal decomposition of this species to form CO_2 is consistent with the appearance of the α desorption state. Note, however, that temperature-programmed desorption data indicate that this state is completely suppressed for an oxygen-activated Ag(111) surface pressurized with ethylene oxide [25], whereas the 756, 1330 and 2885 cm^{-1} features are present on the surface prepared from ethylene oxide (Fig. 7), albeit with lower intensity. Based on the TPD results, these features should be completely absent.

It should be mentioned that the methyl analog of this species (an acetate) has been formed on Ag(1 1 1) [15] and yields an intense feature at 1396 cm^{-1} . No features are detected at this frequency so that this possibility may be excluded.

It was found above that pressurizing an oxygen-activated surface with ethylene or ethylene oxide formed a more stable $\eta^2(\text{C},\text{O})$ acetaldehyde species than found in ultrahigh vacuum. This raises the possibility that the 756, 1330 and 2885- cm^{-1} features are due to ethylene oxide as suggested previously [39], in particular in view of the fact that these are detected on a surface dosed with ethylene oxide (Fig. 7). In this case, the 752- cm^{-1} peak would be assigned to a ring deformation mode (a_1 symmetry) and be shifted by $\sim 125 \text{ cm}^{-1}$ from the corresponding gas-phase value [40] and the surface species formed by adsorption in ultrahigh vacuum (Fig. 3). This shift is larger than that for ethylene oxide chemisorbed on oxygen-covered Ag(1 1 1) at 160 K where the shift is $\sim 17 \text{ cm}^{-1}$ (Table 2). It is also substantially larger than for ethylene oxide adsorbed on other transition-metal surfaces [41]. This would imply that the epoxide ring is substantially distorted when formed at 300 K at high pressures. The peak at 1327 cm^{-1} would be assigned to a ring stretching mode (a_1 symmetry) which appears at 1271 cm^{-1} in the gas phase and is thus shifted by $\sim 55 \text{ cm}^{-1}$. The peak at 2885 cm^{-1} would be assigned to a C–H stretching mode. The disappearance of these features does coincide with ethylene oxide desorption in temperature-programmed desorption [8].

If these features are due to adsorbed ethylene oxide, this species is radically different to that formed by ethylene oxide adsorption in ultrahigh vacuum (Fig. 3). The bonding of ethylene oxide oxygen lone pairs to silver is likely to be substantially different to other transition metals. In the main group metals, the $6a_1$ (oxygen lone pair) and $2b_1$ (σ_{CO} , σ_{CC} with some lone pair character) levels lie below the substrate b-bands and donate electron density to the vacant d-levels [42]. Stabilization of these levels has been observed on Cu(1 1 0) [43], Fe(1 0 0) and Ni(1 1 1) [42], confirming this picture. In contrast, on silver, these energy levels are coincident with the d-band of silver [17] leading to the weak bonding found on clean and oxygen-covered Ag(1 1 1) (Fig. 1).

If the features at 2885, 1330 and 756 cm^{-1} are due to adsorbed ethylene oxide, worthy of further comment in the spectra of the strongly adsorbed ethylene oxide species is the relatively strong perturbation of the epoxide ring modes, and the softening of the C–H stretching modes. A recent density functional study of olefin epoxidation by transition-metal peroxo complexes proposes an ethylene-oxide-like intermediate with a carbon–carbon bond length of $\sim 1.35 \text{ \AA}$; much closer to the carbon–carbon bond length in ethylene (1.33 \AA) than ethylene oxide ($\sim 1.47 \text{ \AA}$) [44]. These calculations also suggested a C–O bond length of $\sim 2.1 \text{ \AA}$, much longer than in gas-phase ethylene oxide ($\sim 1.44 \text{ \AA}$). The ring mode at 877 cm^{-1} for gas-phase ethylene oxide (756 cm^{-1} for the proposed surface species) is primarily a COC bending mode involving some C–O bond stretching, but primarily C–C stretches. A shortening of the C–C bond would be expected to substantially increase this frequency in contrast to what is observed experimentally. The ring stretching mode at 1271 cm^{-1} in the gas phase (at 1327 cm^{-1} for the surface species) is a symmetric C–O stretching mode in which the C–O and C–C bonds expand simultaneously, but involves primarily C–O stretches. This would be expected, based on the organometallic model [44], to decrease in frequency, whereas a frequency increase is found. Thus, the experimentally measured frequencies imply a shorter C–O bond and a longer C–C bond than in gas-phase ethylene oxide.

A longer C–C bond would lead to a lowering in the CH stretching modes. Ethylene glycol, with a C–C bond length of $\sim 1.5 \text{ \AA}$ (compared to 1.47 \AA for ethylene oxide) has CH stretching frequencies at ~ 2944 and 2885 cm^{-1} , substantially lower than 3065 and 3006 cm^{-1} for ethylene oxide, and is in accord with the longer C–C bond as suggested from the ring deformation modes. In summary, both the ring and C–H vibrational modes suggest that the epoxide surface species, if formed from ethylene or ethylene oxide on oxygen-activated Ag(1 1 1) at ~ 1 Torr, has an elongated C–C bond and a somewhat shortened C–O bond. It should finally be mentioned that the species is not due to a surface glycolate since this has been studied on silver [38] and yields completely different surface modes.

5. Conclusions

Ethylene adsorbs weakly on clean Ag(111) in ultrahigh vacuum with the molecular plane parallel to the surface with a heat of adsorption that increases when the surface is covered by oxygen. Similar effects are seen with ethylene oxide which adsorbs with the molecular plane perpendicular to the surface where the heat of adsorption also increases in the presence of adsorbed oxygen.

Infrared spectra were also collected of an oxygen-activated surface pressurized with both ethylene and ethylene oxide. A strongly bound $\eta^2(\text{C},\text{O})$ acetaldehyde species was found following the adsorption of both ethylene and ethylene oxide which disappeared coincident with the detection of acetaldehyde in temperature-programmed desorption. Substantial acetaldehyde was formed from ethylene oxide at 300 K suggesting that the isomerization of ethylene oxide to acetaldehyde is relatively facile. Other surface species were tentatively identified, namely a species containing a COH group that thermally decomposed at above 450 K to yield the $\beta\text{-CO}_2$ desorption state in temperature-programmed desorption. An ethylene-like state was detected after pressurizing the surface with d_4 -ethylene and finally a species that may correspond to the formation of a formate or distorted ethylene oxide species. It is clear that further work needs to be done to further clarify the nature of these surface species, although the results clearly show that good quality infrared spectra can be collected for model catalysts under realistic conditions. In order to maximize the spectral intensity, spectra were collected using high ethylene and ethylene oxide exposures. It is likely that these assignments will be further clarified by collecting spectra as a function of exposure and also by examining the surface under reaction conditions using polarization modulation techniques.

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