

Differential Reactivity and Structure of Mono- and Dialkoxides: The Reactions of Ethylene Glycol on Mo(110)

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Received November 20, 1995[⊗]

Abstract: The reactions of ethylene glycol on Mo(110) were studied using temperature-programmed reaction, infrared reflection absorption, high-resolution electron energy loss, and X-ray photoelectron spectroscopies. The major reaction pathway is double C–O bond scission to evolve gas-phase ethylene at 350 and 390 K. Both X-ray photoelectron and infrared spectra demonstrate the existence of two surface intermediates, a bidentate (–OCH₂CH₂O–) and a monodentate (–OCH₂CH₂OH) species, at saturation coverage of ethylene glycol. We demonstrate that all ethylene glycol in the mixed overlayer of mono- and bidentate species reacts via a bidentate surface intermediate. Furthermore, in contrast to previous studies on other surfaces, the dialkoxide ethylene glycol intermediate is shown to be more reactive than similar monoalkoxides on Mo(110). Finally, analysis of the infrared spectra demonstrates that the bidentate species adsorbs with C₂ (or lower) symmetry at 300 K.

Introduction

The reactions of oxygen-containing compounds on metal surfaces have been extensively explored due, in part, to the prevalence of oxygenates in metal-bonding adhesives and liquid feedstocks derived from coal, shale, and tar sands. In addition, the reactions of alcohols on metal surfaces have also been widely studied because they are both primary reactants and products of catalytic partial oxidation reactions as well as reactants in deoxygenation processes. For example, the industrial conversion of methanol to formaldehyde is accomplished by catalytic partial oxidation reactions over silver surfaces.¹ The surface chemistry of diols is of particular interest because the presence of two identical alcohol groups could, in principle, permit reaction channels involving the interaction of one or both OH groups with the surface. As the simplest diol, ethylene glycol (HOCH₂CH₂OH) affords an excellent opportunity to compare the stability of alkoxide (monodentate) and dioxometallacyclic (bidentate) intermediates on extended surfaces.

On most surfaces studied to date, the C–O bond in ethylene glycol is retained. For example, ethylene glycol adsorbs reversibly on clean Ag(110) but undergoes O–H bond activation on a partially oxidized Ag(110) surface to form a cyclic ethylenedioxy (–OCH₂CH₂O–) intermediate and water (H₂O) below 300 K.² The ethylenedioxy intermediate decomposes via C–H bond activation, yielding glyoxal ((CHO)₂) at 380 K. Similarly, ethylene glycol dehydrogenation to form glyoxal also occurs on Cu(110), presumably via the same dialkoxo intermediate, although no vibrational data were reported for this surface.³ Excess atomic oxygen on Ag(110) induces C–C bond scission in the cyclic ethylenedioxy, yielding water, formaldehyde (H₂CO), and surface formate (HCO₂).⁴ On both clean Rh-

(111)⁵ and Ni(100),⁶ the C–C bond in the ethylenedioxy intermediate cleaves, liberating CO and H₂; no evidence was found for C–O bond scission on Rh(111). However, the dominant reaction channel on Ni(100) is nonselective decomposition to atomic oxygen and carbon.

The lower reactivity of the bidentate ethylenedioxy species compared to a related monodentate methoxy (CH₃O–) species on Ag(110) was attributed to the negative entropy of activation for the decomposition of the dialkoxide intermediate.² Specifically, it was proposed that during transition state formation the bidentate species loses the rotational freedom associated with chelating to a single Ag atom, while the methoxide transition state has the same entropy as the adsorbed state, presumably bound to a high coordination site. The dialkoxide intermediate is expected to be more constrained than its monoalkoxide analogue, hindering the access of the β-hydrogens to the surface and thus contributing to the decrease in the rate of β-hydrogen elimination in the dialkoxide.

The high strength of the Mo–O bond compared to other metal–oxygen bonds suggests that ethylene glycol will exhibit markedly different reactivity on Mo(110) compared to Ag(110) and, indeed, to all other surfaces investigated to date. For example, carbon–oxygen bond scission occurs in all monodentate alkoxides studied on Mo(110) at temperatures between 350 and 400 K.^{7–10}

In this study, we have used temperature-programmed reaction, X-ray photoelectron, infrared reflection absorption, and high-resolution electron energy loss spectroscopies to probe the structure, bonding, and reactivity of ethylene glycol on Mo(110). We demonstrate the existence of a direct intramolecular elimination pathway involving selective C–O bond scission, resulting in evolution of gaseous ethylene (C₂H₄) with ~85%

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[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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selectivity. For the first time, we identify both the mono- and bidentate moieties on the same surface, making use of the high resolution attainable with surface infrared spectroscopy. In contrast to findings on other transition metal surfaces, we find that the bidentate species at saturation coverage on Mo(110) is more, *not* less, reactive than both the co-existing monodentate species and similar monoalkoxide surface intermediates. Finally, by analysis of the C–H stretching region of the infrared spectrum, we deduce that the bidentate moiety adsorbs with C_2 symmetry or less, i.e. the ethylene dialkoxy intermediate has no mirror plane of symmetry on Mo(110).

Experimental Section

Temperature-programmed reaction experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure of 5×10^{-11} Torr at Wellesley College. The UTI Model 100C quadrupole mass spectrometer used in these experiments was enclosed by a shield possessing a small (0.125-in. diameter) aperture in line-of-sight with the crystal surface, in order to optimize the detection of molecules desorbing from the center of the Mo(110) crystal. The crystal could be cooled to 85 K with liquid nitrogen and heated to 800 K radiatively or to 2200 K by electron bombardment. The temperature was measured by a W-5% Re-vs-W-26% Re thermocouple spot-welded to the edge of the crystal. As the surface was radiatively heated from 85 to 650 K at a rate of $\sim 5 \text{ K s}^{-1}$ several masses were sampled as a function of temperature during a single temperature-programmed experiment under a multiplexing arrangement.¹¹ Since the crystal is close to the mass spectrometer filament during these experiments, the crystal was negatively biased (-100 V) prior to each experiment to prevent electron-induced reactions. The temperature-programmed reaction experiments were repeated in conjunction with all spectroscopic measurements to confirm that the spectra probed intermediates important in the chemical processes.

X-ray photoelectron experiments were performed in an ultrahigh vacuum chamber, described elsewhere,^{12,13} which is equipped with a Physical Electronics ESCA 5300 X-ray photoelectron spectroscopy system. The spectra were collected using a Mg K α (1253.6 eV) anode and a bandpass energy of 17.9 eV. All binding energies are referenced to the Mo(3d_{5/2}) peak at 228.3 eV. Spectra were recorded at 100 K after annealing the ethylene glycol overlayer to the indicated temperature, using the same heating rate as for the temperature-programmed reaction experiments. The O(1s), Mo(3d), and C(1s) regions were collected in a single experiment consisting of 75, 5, and 100 scans, respectively, resulting in a total collection time of 15 min. The spectra did not change as a function of time, indicating that there was no significant X-ray induced decomposition of the adsorbate during data acquisition. This conclusion was further verified by the correspondence of temperature-programmed reaction data obtained prior to and after a 15-min exposure of the adsorbate layer to the X-ray source.

Surface infrared experiments were performed in a third ultrahigh vacuum chamber, also described in detail elsewhere.^{10,14} All infrared reflection absorption spectra were collected at a surface temperature of 100 K using a single-beam, clean-air-purged Fourier transform infrared spectrometer (Nicolet, Series 800) and averaged over 1000 scans using an MCT-A detector at 2-cm^{-1} resolution, resulting in a scan time of approximately 15 min. Sample spectra were ratioed against a background taken immediately after the sample scan by flashing the crystal to 700 K. The background scan was initiated after the crystal temperature had returned to 100 K. Temperature-programmed reaction investigations of isotopically mixed ethylene glycol overlayers were also performed in this chamber, using the same type of mass spectrometer and experimental setup as in the chamber at Wellesley College. The high-resolution electron energy loss spectrum of ethylene glycol was recorded in a separate ultrahigh vacuum chamber equipped with an LK2000-14-R spectrometer operated at a primary beam energy of 3 eV. Both the chamber and the experimental procedure are described in detail elsewhere.^{15,16}

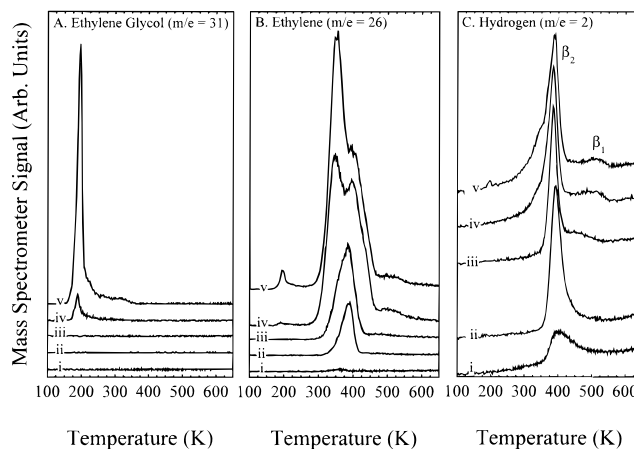


Figure 1. Temperature-programmed reaction spectra of ethylene glycol on Mo(110) for (A) ethylene glycol (m/e 31), (B) ethylene (C_2H_4 , m/e 26), and (C) dihydrogen (H_2 , m/e 2) as a function of ethylene glycol exposure. The relative exposures are (i) 0.11, (ii) 0.15, (iii) 0.38, (iv) 0.81, and (v) 1 (saturation) = 0.14 ML.¹⁸ The spectra are uncorrected for fragmentation, and the m/e 26 trace contains a contribution from the parent molecule. All masses shown are the most intense for that species, except for ethylene, where m/e 26 was chosen over the most intense fragment, m/e 28, to avoid contributions from background CO. A nearly constant heating rate of $\sim 5 \text{ K s}^{-1}$ was used.

The long-range order and surface cleanliness of the Mo(110) crystals were verified with low-energy electron diffraction and Auger electron spectroscopy, respectively, in ultrahigh vacuum chambers at Harvard University. One Mo(110) crystal was transferred to the chamber at Wellesley and subsequently cleaned *in situ* by oxidation in oxygen (2×10^{-9} Torr at a surface temperature of 1200 K for 5 min) followed by heating briefly to 2200 K. The carbon coverage on the surface after the cleaning procedure described above was estimated to be 0.002 ML (1 monolayer (ML) = 1.4×10^{15} atoms/cm²), using temperature-programmed reaction spectroscopy to quantify the evolution of CO at high temperature from the reaction of C_(a) and O_(a) following oxygen adsorption at 85 K.

Both ethylene glycol samples, HOCH₂CH₂OH (Aldrich, 99.8%) and HOCD₂CD₂OH (Cambridge Isotope, 98% D enrichment), were stored over baked molecular sieves, distilled under vacuum, and degassed by 3 freeze–pump–thaw cycles before use each day. Oxygen (Wesco, 99.994%) was used without further purification. The purity of the gases introduced into the ultrahigh vacuum chamber was confirmed by mass spectrometry. Direct dosers with precision leak valves allowed for controlled deposition of the ethylene glycol onto the clean Mo(110) crystal surface at a surface temperature of 85 K while the chamber pressure remained below 3×10^{-10} Torr.

Results

Temperature-Programmed Reaction Spectroscopy. Ethylene is the major gas-phase product of the ethylene glycol temperature-programmed reaction on clean Mo(110), accounting for $\sim 85\%$ of the reaction of a saturated monolayer of ethylene glycol. Gaseous dihydrogen and surface atomic oxygen are also formed in this pathway. Nonselective decomposition to adsorbed atomic carbon and oxygen and gaseous dihydrogen is a secondary reaction channel. A trace amount of water desorption ($\sim 5 \times 10^{-4}$ ML) was also detected at $\sim 350 \text{ K}$. Ethylene glycol evolution is also observed at $\sim 195 \text{ K}$ for exposures above ~ 0.8 of saturation and is attributed to ethylene glycol multilayer desorption, since this peak increases in intensity without limit as the ethylene glycol exposure is increased (Figure 1A(iv–v)).¹⁷

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(17) Intensity in this peak *prior* to saturation of the ethylene glycol monolayer is attributed to three-dimensional clustering, as has been previously observed for ethylene glycol on Ag(110).²

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All masses between 2 and 150 amu were monitored during these experiments, and no other gaseous reaction products were detected.¹¹

Ethylene is formed in two distinct states with peak temperatures of ~ 350 and ~ 390 K during temperature-programmed reaction of a saturation exposure of ethylene glycol on Mo(110) (Figure 1B(v)).^{18,19} The evolution of ethylene in both states is limited by the rate of the reaction, not desorption, since ethylene desorbs below 300 K when adsorbed on both clean and O-covered Mo(110).²⁰ Ethylene production is a sensitive function of the initial ethylene glycol coverage; at the lowest exposure studied (0.05 of saturation), nonselective decomposition is the sole reaction pathway, and no ethylene evolution is detected. However, as the coverage is increased to 0.11 of saturation, ethylene is produced in a single state with a peak maximum at ~ 365 K (Figure 1B(i)). The two distinct ethylene states are evident at ~ 0.5 of saturation and above (Figure 1B(iv,v)). A small high-temperature ethylene tail at ~ 510 K also grows in at the highest ethylene glycol exposures (Figure 1B(iv,v)). Importantly, data obtained using HOCD₂CD₂OH demonstrate that there is *no* reversible C–H bond scission along the path to ethylene formation, since C₂D₄ is formed exclusively; no C₂D₃H, C₂D₂H₂, C₂DH₃, or C₂H₄ are detected (data not shown).²¹ These data suggest that ethylene is evolved directly into the gas phase at ~ 350 K following facile C–O bond scission. Further evidence against ethylene interaction with the surface is provided by previous studies of the reactions of ethylene on clean and oxygen-precovered Mo(110), which demonstrate that any residual ethylene on these surfaces above 250 K undergoes decomposition.²⁰ We estimate that at saturation coverage ethylene is eliminated with $\sim 85\%$ selectivity, with the remaining $\sim 15\%$ of the ethylene glycol nonselectively decomposing, based on the ratio of the high-temperature CO produced during temperature-programmed reaction of ethylene glycol and methanol.²²

Dihydrogen is produced in two states, the primary one with a peak temperature of 390 K (β_2), with a pronounced shoulder at 500 K (β_1), for temperature-programmed reaction of a saturation exposure of ethylene glycol on Mo(110) (Figure 1C(v)). There is almost no change in the peak temperature of the β_2 state over the entire coverage range studied (Figure 1C(i–v)), other than a slight broadening on the low-temperature side at the highest ethylene glycol coverage. We assign the β_2 dihydrogen peak to the recombination of surface hydrogen originating from the hydroxyl hydrogens of the parent glycol molecule, by reference to previous studies of hydrogen as well as alkoxides on Mo(110), which indicate that this β_2 hydrogen peak is limited by desorption, not reaction kinetics.^{7,10,23} This

(18) Saturation coverage, θ_{sat} , is defined as the exposure beyond which the reaction product yields do not increase any further and the multilayer desorption peak at 195 K increases without bound.

(19) Identification of products was verified by comparison of cracking patterns observed during reaction with that obtained using a genuine sample of ethylene. Importantly, the entire m/e 28 signal during temperature-programmed reaction of ethylene glycol was accounted for by the observed ratio of m/e 28: m/e 27: m/e 26 in the genuine ethylene sample, confirming that no CO was produced by the reaction of ethylene glycol on Mo(110).

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(21) If reversible C–H bond scission occurred, recombination of the alcoholic hydrogens with the deuterated alkyl fragments would take place, incorporating H into some of the ethylene evolved.

(22) The selectivity estimated was based on the saturation coverage of methanol on Mo(110), previously found to be 0.25 ML.¹⁰ Over 95% of the methanol undergoes nonselective decomposition to form gaseous dihydrogen along with adsorbed carbon and oxygen on Mo(110). The carbon and oxygen subsequently recombine to form CO ~ 1200 K. Comparison of the integrated CO intensity for ethylene glycol and methanol on Mo(110) is used to estimate the amount of nonselective reaction.

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conclusion, as well as the assignment of the β_1 tail at 500 K to reaction-limited dihydrogen evolution, is confirmed by temperature-programmed reaction of HOCD₂CD₂OH. The observed predominance of H₂ in the β_2 state indicates that this peak originates from the recombination of hydroxyl protons and that, therefore, facile O–H bond scission occurs below 390 K. In contrast, the reaction-limited β_1 tail at 500 K consists mainly of D₂, resulting from recombination of surface deuterium formed from dehydrogenation of a surface hydrocarbon intermediate. Finally, the saturation coverage for ethylene glycol on Mo(110) is estimated to be 0.14 ML, based on the relative dihydrogen yields observed during temperature-programmed reaction of ethylene glycol and a known coverage of methanol on Mo(110).¹⁰

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy indicates that there is a single surface intermediate with an intact C–O bond after annealing low coverages of ethylene glycol ($\theta < 0.4\theta_{\text{sat}}$) to 300 K.²⁴ The X-ray photoelectron peak with an O(1s) binding energy of 532.6 eV and resolution-limited width is assigned to oxygen in an alkoxide group by comparison with X-ray photoelectron spectra of other alcohols on Mo(110) (Figure 2A(i)).^{7,10,23} Importantly, the existence of only a single C–O bond environment and the complete absence of an X-ray photoelectron feature due to intact C–O–H groups near 533.7 eV (see below) is strongly suggestive of the existence of a single bidentate-type intermediate at these coverages. In addition, a small amount of decomposition also occurs at low coverage, based on the peak at 530.8 eV, which is ascribed to atomic oxygen by comparison to X-ray photoelectron spectra of oxygen adsorbed on Mo(110). Notably, no atomic oxygen is detected in X-ray photoelectron spectra recorded at 100 K (data not shown), showing the absence of any C–O bond scission at these lower temperatures. In agreement with the data for the O(1s) region, there is a single carbon environment at 300 K, signified by a single C(1s) peak at 286.7 eV, which is similar to that measured for other alkoxides on Mo(110) (Figure 2B(i)).^{7,10,23} The presence of atomic oxygen and the concomitant lack of atomic carbon detected in the X-ray photoelectron experiments at 300 K are consistent with temperature-programmed reaction spectra in which ethylene evolution begins below 300 K at these coverages (Figure 1B(iii)).

As the coverage of ethylene glycol on Mo(110) increases beyond $0.4\theta_{\text{sat}}$, both the O(1s) and C(1s) alkoxide peaks develop higher-binding energy shoulders after annealing to 300 K, suggesting the existence of a second surface species (Figures 2A(ii) and 2B(ii)). As the coverage is increased to saturation the new feature in the O(1s) region, centered at ~ 533.7 eV, has approximately 0.2 times the integrated area of the 532.6-eV alkoxide peak (Figure 2A(ii)).²⁵ Similarly, the C(1s) spectrum becomes highly asymmetric, displaying a shoulder centered at ~ 287.9 eV. While the intensity of this peak is sensitive to the fit, the data are well fit when the shoulder accounts for ~ 0.2 times that of the main alkoxide peak at 286.7 eV, in agreement with the O(1s) region (Figure 2B(ii)). By comparison with the X-ray photoelectron spectra for multilayers of ethylene glycol (data not shown), these new features are assigned to the oxygen and carbon of an intact C–O–H group.

(24) Approximately the same heating rate was used to anneal the surface prior to recording X-ray photoelectron and infrared spectra as was used for the temperature-programmed reaction experiments.

(25) The intensity due to the new feature is distinct from the intensity always seen as a tail to the higher-binding energy side of the O(1s) signal due to final state effects.²⁶ Intensity due to the tail is estimated by comparison to lower-coverage spectra, where no shoulder due to a second species appears.

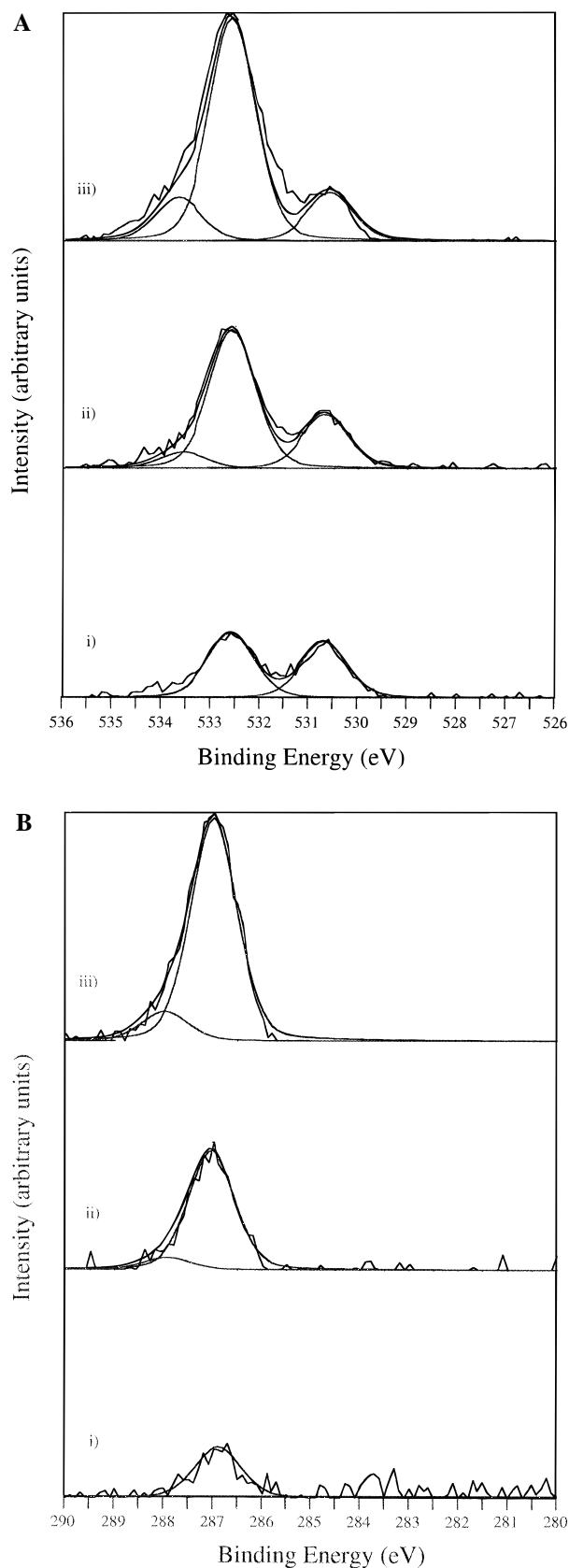


Figure 2. X-ray photoelectron spectra obtained for (A) O(1s) and (B) C(1s) regions after heating ethylene glycol to 300 K at ~ 5 K s^{-1} . Ethylene glycol was adsorbed at ~ 100 K, and the exposures shown are (i) 0.06, (ii) 0.08, and (iii) 0.14 ML (saturation). Noise below the baseline in all spectra is cut off by the Perkin Elmer curve-fitting algorithm.

Importantly, the new O(1s) feature is *not* consistent with the appearance of surface hydroxyl groups, by reference to previous

Table 1. Vibrational Assignments for Ethylene Glycol

liquid phase HOCH ₂ CH ₂ OH ²⁷	-OCH ₂ CH ₂ O- on Mo(110) ^a (cm ⁻¹)	-OCH ₂ CH ₂ OH on Mo(110) ^a (cm ⁻¹)	assigned mode
3150–3400	NO ^b	3440, 3220	ν (OH)
2935	2913	2931	ν_{as} (CH)
2875	2857	2840	ν_s (CH)
1459	1455	(1455)	δ (CH ₂)
1087	1031	1080	ν_s (CO)
864	896	910	ν (CC)

^a Frequencies for surface species correspond to a saturated monolayer of ethylene glycol at 300 K. ^b NO = not observed.

X-ray photoelectron studies of water on Mo(110).²⁶ Moreover, the formation of surface hydroxyl groups would not account for the appearance of the new feature in the C(1s) region of the spectrum. Rather, these peaks suggest the existence of a second surface species with an intact (molecular) hydroxyl group at these higher ethylene glycol coverages, a conclusion corroborated by our infrared studies (see below).

Analysis of the thermal evolution of the X-ray photoelectron spectra of a saturation exposure of ethylene glycol on Mo(110) indicates that the two alkoxide species are observed by 250 K and one alkoxide persists to above 400 K (data not shown). Upon annealing the surface to 400 K, by which temperature ethylene evolution is almost complete, a dramatic increase in the intensity of the atomic oxygen peak is observed, together with a shift in its binding energy to 530.5 eV, at the expense of the intensity in the other two O(1s) peaks. Importantly, the 533.7 eV peak attributed to the C–O–H moiety disappears completely, while the alkoxide peak at 532.6 eV persists, indicating that a single species with an intact C–O bond is present on the surface at 400 K, as was observed in the spectra obtained by annealing a low coverage of ethylene glycol to 300 K. In addition, a peak due to atomic carbon at 283.6 eV is observed together with the alkoxide C(1s) peak at 286.6 eV. Finally, only atomic oxygen (530.5 eV) and atomic carbon (283.5 eV) remain on the surface after annealing the saturated overlayer to 750 K (data not shown). Comparison of the total C(1s) intensity after annealing to 750 K, when all the ethylene glycol has reacted, to the intensity at 250 K (at which temperature the multilayer has desorbed to leave a saturation coverage of ethylene glycol), yields an estimate of $17 \pm 5\%$ for nonselective decomposition, in good agreement with the estimate based on temperature-programmed reaction data.

Vibrational Spectroscopies. Infrared spectra indicate that a single intermediate, ethylenedioxy ($-OCH_2CH_2O-$), is formed below 300 K on Mo(110) for exposures of ethylene glycol corresponding to less than 0.6 of saturation (Figures 3A(i) and 3B(i)). The complete absence at these exposures of the O–H stretching mode at ~ 3300 – 3600 cm^{-1} , the dominant feature in the infrared spectrum of multilayers of ethylene glycol at 100 K (data not shown), indicates that O–H bond scission has occurred by 300 K. There is essentially no change in the infrared spectra at these exposures upon annealing to 350 K, a temperature at which recombinant dihydrogen evolution from the alcoholic protons has commenced, supporting the assertion from the X-ray photoelectron data that the O–H bonds break below 300 K. The infrared spectrum obtained after annealing low ethylene glycol exposures on Mo(110) to 300 K is assigned in terms of an intact $-O-CH_2-CH_2-O-$ skeleton (Table 1).

Two narrow, symmetric absorption bands are observed at 881 and 1008 cm^{-1} in the 800–1500- cm^{-1} region of the infrared spectrum of the lowest exposure of ethylene glycol (Figure 3B(i)). The 881- cm^{-1} band is assigned to a mode which has *predominantly* C–C character, by reference to the known

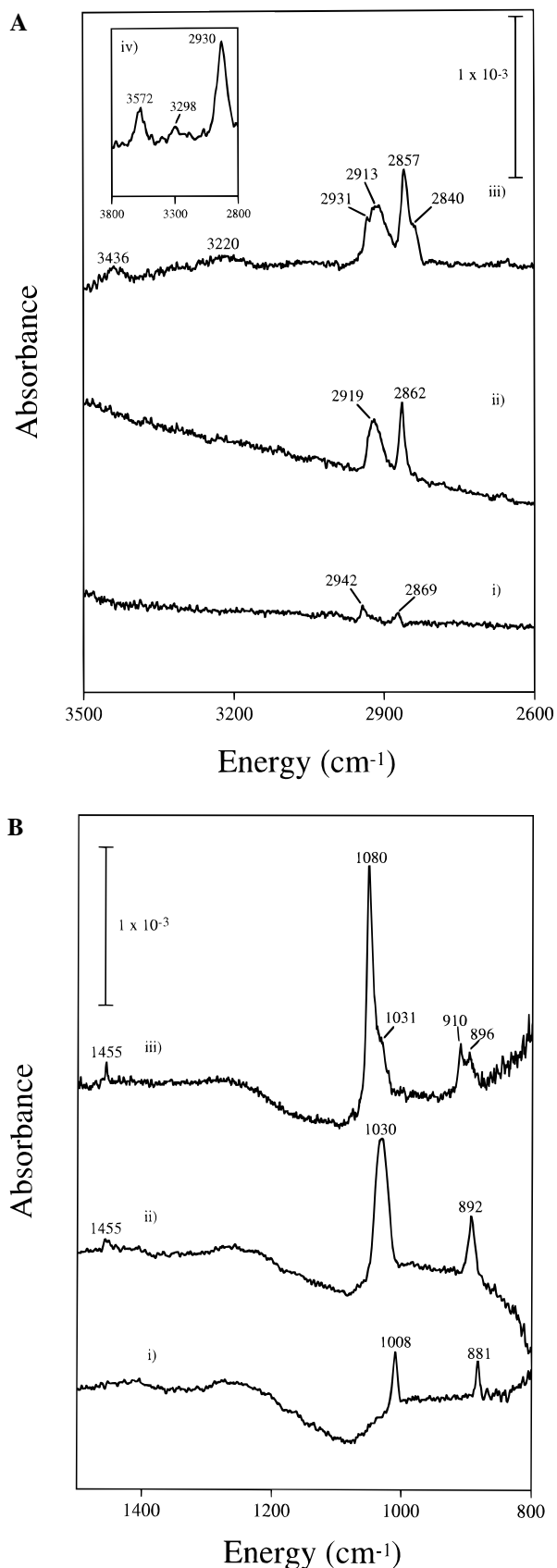


Figure 3. Infrared spectra of ethylene glycol on Mo(110) obtained after annealing to 300 K for (A) the C–H and O–H stretching region and (B) the C–O and C–C stretching region. The coverages correspond to (i) 0.04, (ii) 0.08, and (iii) 0.14 ML (saturation). The inset labeled (iv) is the C–H and O–H stretching region of the electron energy loss spectrum of a surface prepared identically to that in parts a and b(iii). infrared spectrum of ethylene glycol (Table 1).²⁷ However, we suggest that a substantial component of C–O motion is also

associated with this mode, by analogy with the parent molecule²⁷ and by reference to a recent study in which it was demonstrated that a mode at 875–880 cm^{-1} in the (qualitatively similar) ethoxide species ($\text{CH}_3\text{CH}_2\text{O}^-$) adsorbed on Mo(110) consists of approximately equal amounts of C–C and C–O motion.²⁸ Importantly, given the above normal mode description, the adsorbate symmetry cannot be trivially deduced based on this mode alone, since it is surface-dipole allowed for all C–C bond orientations.

The feature at 1008 cm^{-1} in the infrared spectrum of the lowest exposure of ethylene glycol is assigned (predominantly) to the *symmetric* C–O stretching mode of an ethylenedioxy intermediate (Figure 3B(i)). There are two possible assignments for the 1008- cm^{-1} feature: either the symmetric (in-phase) or the asymmetric (out-of-phase) C–O stretching modes, observed at 1087 and 1038 cm^{-1} , respectively, in the condensed glycol. On first inspection, one might assign this band to $\nu_a(\text{C}-\text{O})$, by direct analogy with the condensed-phase molecule. However, in the aforementioned study of ethoxide adsorbed on Mo(110), a pronounced perturbation of the C–O stretching mode was observed upon formation of the alkoxide. Specifically, the mode assigned predominantly to $\nu(\text{C}-\text{O})$ at 1068 cm^{-1} in the parent molecule was observed to shift down to 1020 cm^{-1} for $\text{CH}_3\text{CH}_2\text{O}-\text{Mo}$. Furthermore, assignment of the 1008- cm^{-1} feature to the out-of-phase C–O stretch is inconsistent with the rest of the infrared data, since the exclusive observation of this mode would be indicative of a geometry wherein the C–C bond was normal to the surface, which is inconsistent with the bidentate ethylenedioxy geometry suggested by analysis of the O–H stretching region and supported by X-ray photoelectron data (Figure 4a). Conversely, the in-phase C–O stretching mode would predominate when the C–C bond axis is parallel to the Mo(110) plane, since the asymmetric C–O mode would be effectively screened out by the metal image dipole.

Further support for these assignments is provided by analysis of the C–H stretching region of the infrared spectra (Figure 3A(i)). The features at 2869 and 2942 cm^{-1} are assigned to the in-phase symmetric and out-of-phase asymmetric C–H stretching modes, respectively, given the exact correspondence with the condensed-phase data (Table 1). Importantly, the symmetric C–H mode has a dipole moment that is perpendicular to the C–C bond axis, so that the observation of this mode is consistent with a predominantly parallel geometry of the dialkoxy intermediate, as suggested above. In contrast, the asymmetric C–H mode is infrared inactive for C_{2v} adsorbate symmetry (the highest possible adsorbate symmetry group with the C–C axis parallel to the surface plane), because the dipole moment is zero when the $-\text{O}-\text{C}-\text{C}-\text{O}-$ plane is normal to the metal surface. However, if no mirror plane exists in the adsorbate, i.e. the symmetry is C_2 or lower, this mode becomes surface dipole allowed (Figure 4b). Interestingly, the above description is consistent with the known geometry of ethylene glycol in the condensed phase.²⁷

As the ethylene glycol exposure is increased to 0.6 of saturation, there is little change in the infrared spectrum obtained after annealing to 300 K,²⁴ other than a uniform increase in the intensity of all features observed at lower exposures, together with a slight upshift in the frequency of $\nu_s(\text{C}-\text{O})$ and $\nu(\text{C}-\text{C})$ and concomitant decrease in the frequencies of the C–H stretching modes (Figures 3A(ii) and 3B(ii)). All infrared features persist after heating to 300 K for all ethylene glycol coverages above 0.6 of saturation (Figures 3A(iii) and 3B(iii),

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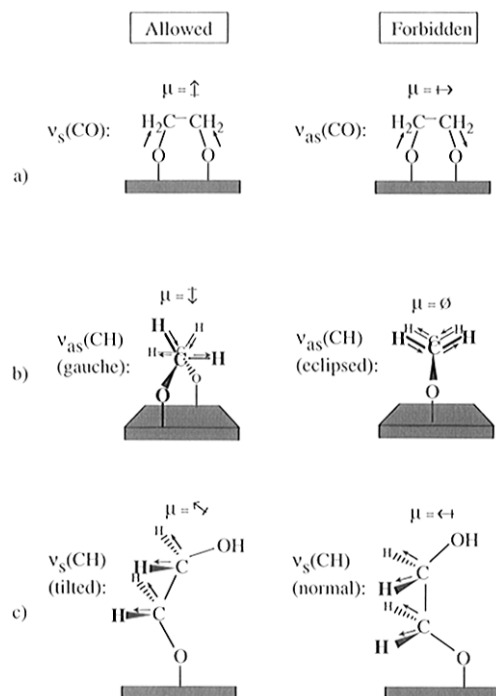


Figure 4. The molecular motions used to deduce the orientation of adsorbates derived from ethylene glycol on Mo(110) at 300 K. The following comparisons are illustrated: (a) the in-phase (observed) and out-of-phase (not observed) C–O stretches in the bidentate species, which allows for assignment of the observed $\nu_s(\text{CO})$ peak consistent with a C–C bond axis parallel to the surface; (b) the out-of-phase asymmetric C–H stretch in the bidentate species for a planar O–C–C–O skeleton with eclipsed hydrogens (infrared inactive) and a gauche conformation (infrared active), showing that the appearance of this mode in the infrared spectrum indicates a gauche conformation of the bidentate species; and (c) the symmetric C–H stretch in a monodentate species with its C–C axis normal to the surface (infrared inactive) and inclined away from the surface normal (infrared active), demonstrating that the appearance of this peak in the monodentate infrared spectrum indicates a tilted C–C bond axis.

Table 1). In addition, a new infrared absorption band is apparent at 1455 cm^{-1} , which is assigned to the in-phase methylene scissors mode that is observed at 1459 cm^{-1} in condensed ethylene glycol (Table 1). Once again, the observation of this feature is indicative of a predominantly parallel orientation of the C–C bond with respect to the surface plane.

While the infrared peaks corresponding to the bidentate species remain relatively unperturbed as the ethylene glycol coverage is increased, at saturation coverage a second species is detected in the infrared spectrum (Figures 3A(iii) and 3B(iii), Table 1). The new features are assigned to a monodentate, acyclic 2-hydroxyethoxide moiety ($-\text{OCH}_2\text{CH}_2\text{OH}$) in which the C–C bond is inclined with respect to the surface plane. The “chemical similarity” between the bidentate species, the sole intermediate at low coverage, and this second species is suggested by the observation of a second set of modes at high coverage, shifted by $\sim 10\text{--}20\text{ cm}^{-1}$ in frequency from the corresponding bidentate modes. However, an important difference is apparent on inspection of the $3100\text{--}3700\text{-cm}^{-1}$ region of the infrared spectrum at saturation coverage; two bands are observed at 3220 and 3436 cm^{-1} that are attributed to the O–H stretching vibrations of associated and (largely) unassociated OH moieties, respectively, by reference to the wealth of condensed-phase literature of such functional groups. In general, such $\nu(\text{OH})$ features may arise either from surface hydroxyl groups or from intact OH groups within molecular (e.g. alcoholic) species. However, the C(1s) X-ray photoelectron

data indicate that the OH groups belong to a molecular species. The possibility that the $\nu(\text{OH})$ features belong to a species with two intact OH groups can be eliminated based on the persistence of these infrared peaks up to 300 K. Intact ethylene glycol desorbs below 200 K, which is consistent with the low desorption temperature observed for species containing intact OH bonds on Mo(110), including molecular water²⁶ as well as other intact alcohols.^{23,29} Furthermore, assignment of the $\nu(\text{OH})$ features to a monoalkoxide species is consistent with the presence of *both* hydrogen-bonded and non-interacting OH groups, since the length and lack of rigidity of the monoalkoxide surface moiety would allow some OH groups on adjacent monodentate species to interact with each other, giving rise to the lower-frequency (hydrogen-bonded) $\nu(\text{OH})$ peak. The fact that some intact OH groups do *not* interact with neighboring OH groups, as indicated by the presence of a higher-frequency $\nu(\text{OH})$ peak, is supported by the relatively low concentration of these species as compared to the bidentate species.

Conclusive support for the identification of the $\nu(\text{OH})$ modes is given by the electron energy loss spectrum in Figure 3A(iv). The high-frequency region of this spectrum clearly demonstrates the existence of two peaks in the $\nu(\text{OH})$ region, one at 3572 cm^{-1} and one at 3298 cm^{-1} . The increased intensity of these peaks relative to the $\nu(\text{CH})$ peak (one peak at 2930 cm^{-1}), in comparison with the infrared data, may be attributed to contributions from both impact and resonance scattering, which may add intensity to such high-frequency adsorbate modes. Indeed, the fact that the electron energy loss peaks appear at slightly different frequencies than the corresponding infrared peaks, though still in regions corresponding to unassociated and hydrogen-bonded molecular O–H bonds, is also consistent with the enhancement of a subset of the overlayer hydroxyl modes by such non-dipolar scattering mechanisms.³⁰

The appearance of a new $\nu_s(\text{CH})$ mode in the infrared spectrum, attributable to the monodentate species, requires that the C–C bond of this moiety be inclined with respect to the surface normal in order for this mode to be experimentally observed (Figure 4c). Importantly, both the in-phase and out-of-phase components of the C–O stretching modes of such a (tilted) monodentate species are surface-dipole allowed and should therefore *in principle* be observable. However, it is widely recognized that strong dipole–dipole coupling can occur between co-adsorbates, resulting in an upshift in the frequency of the absorbance band (for a predominantly perpendicular dipole).³¹ In addition, there may be appreciable intensity borrowing by high-frequency oscillators from the lower frequency sites in an inhomogeneous overlayer, resulting in a further upshift in the absorbance maximum and a decrease in the band width, since essentially all the intensity appears in the highest frequency modes in a given spectral region. Indeed, this is precisely what is observed for all alkoxides studied to date on Mo(110). For example, on a Mo(110) surface populated with both $\text{CD}_3\text{O}-$ and $\text{CH}_3\text{O}-$ species, the two $\nu(\text{CO})$ peaks are indistinguishable at all but the lowest coverages, despite being separated by more than 30 cm^{-1} in the condensed-phase parent molecules.³² By analogy, we propose that similar dipole–dipole coupling occurs at ethylene glycol coverages approaching

(29) Serafin, J. G. Ph.D. Thesis, Harvard University, 1989.

(30) Slight differences in the base temperatures used for initial adsorption and/or spectral collection in infrared and electron energy loss experiments might also contribute to the differences in the O–H stretch frequencies in the two types of experiments. The O–H stretch frequency is known to be sensitive to chemical environment; thus, small differences in surface concentration or temperature might lead to a shift.

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saturation, so that only a single intense $\nu(\text{CO})$ band is resolved for the monodentate species despite the tilted C—C axis.

Complementary temperature-programmed reaction studies of isotopically mixed layers allow investigation of the relative reactivities of the mono- and bidentate species. Infrared studies of ethylene glycol- d_0 were used to establish the conditions for saturation of the bidentate population. Temperature-programmed reaction experiments were then performed on an overlayer in which the bidentate state was selectively populated with ethylene glycol- d_4 and the monodentate state with ethylene glycol- d_0 using the conditions established by the infrared experiments (data not shown).³³ Both C_2D_4 and C_2H_4 were produced in *both* the 350 and 390 K states previously identified for the isotopically pure sample. Therefore, both the mono- and bidentate surface species contribute to both states of ethylene evolution. However, the ratio for low- to high-temperature ethylene from the bidentate (deuterated) intermediate is $\sim 1.3:1$, as compared to a ratio of $\sim 1.1:1$ for the monodentate (undeuterated) intermediate, indicating a slight preference for reaction of initially bidentate moieties in the early stages of ethylene evolution.

Additional information on the mechanism of ethylene production is given by the temperature evolution of the infrared spectra, which demonstrates conversion of the monodentate intermediate to bidentate as the reaction of ethylene glycol on Mo(110) proceeds. Specifically, as the temperature is raised to 325 K in the midst of ethylene evolution, the intensity of the monodentate modes is severely attenuated, while the intensity of the bidentate modes remains essentially constant (Figures 5A(ii) and 5B(ii)). In conjunction with the above temperature-programmed reaction data, which demonstrate that both the mono- and bidentate moieties give rise to similar ethylene formation features, the infrared data suggest that the monodentate species reacts via a bidentate intermediate to produce ethylene. The bidentate species is thus repopulated over the early part of the reaction. Furthermore, as the annealing temperature is raised to 350 K, only the bidentate species is apparent in the infrared spectrum, despite the observation of continued ethylene evolution from (initially) monodentate species during temperature-programmed reaction (Figures 5A(iii) and 5B(iii)). These data are consistent with the conversion of mono- to bidentate, concomitant with the progress of the reaction.

Discussion

Ethylene glycol predominantly reacts on Mo(110) to evolve gas-phase ethylene; the selectivity for this reaction over nonselective decomposition increases as a function of ethylene glycol coverage, reaching $\sim 85\%$ at saturation. Our X-ray photoelectron and infrared studies show that, at low ethylene glycol coverage, the sole surface intermediate for ethylene production is a bidentate, dialkoxide species adsorbed with C_2 (or lower) symmetry. At coverages greater than 0.4 of saturation, a second surface intermediate is formed, identified as a monoalkoxide species with one intact O—H bond. The two species coexist at 300 K such that the monoalkoxide:dialkoxide ratio is $\sim 2:3$ at saturation coverage.³⁴ As the surface temperature is raised above 300 K, the bidentate species begins to react,

(33) Infrared spectroscopy was used to calibrate the exact dose required just to saturate the bidentate state, and this dose was used to populate that state fully with only $\text{HOCD}_2\text{CD}_2\text{OH}$. Sufficient nondeuterated ethylene glycol was then dosed to saturate the monodentate state. Infrared data for the mixed overlayer were not collected.

(34) This ratio was calculated from the relative intensities of the 533.7- and the 532.6-eV X-ray photoelectron peaks in Figure 2A(iii), taking into account the contribution of the monoalkoxide species to the intensity in the 532.6-eV alkoxide peak, assumed to be equal to the total intensity of the 533.7-eV peak.

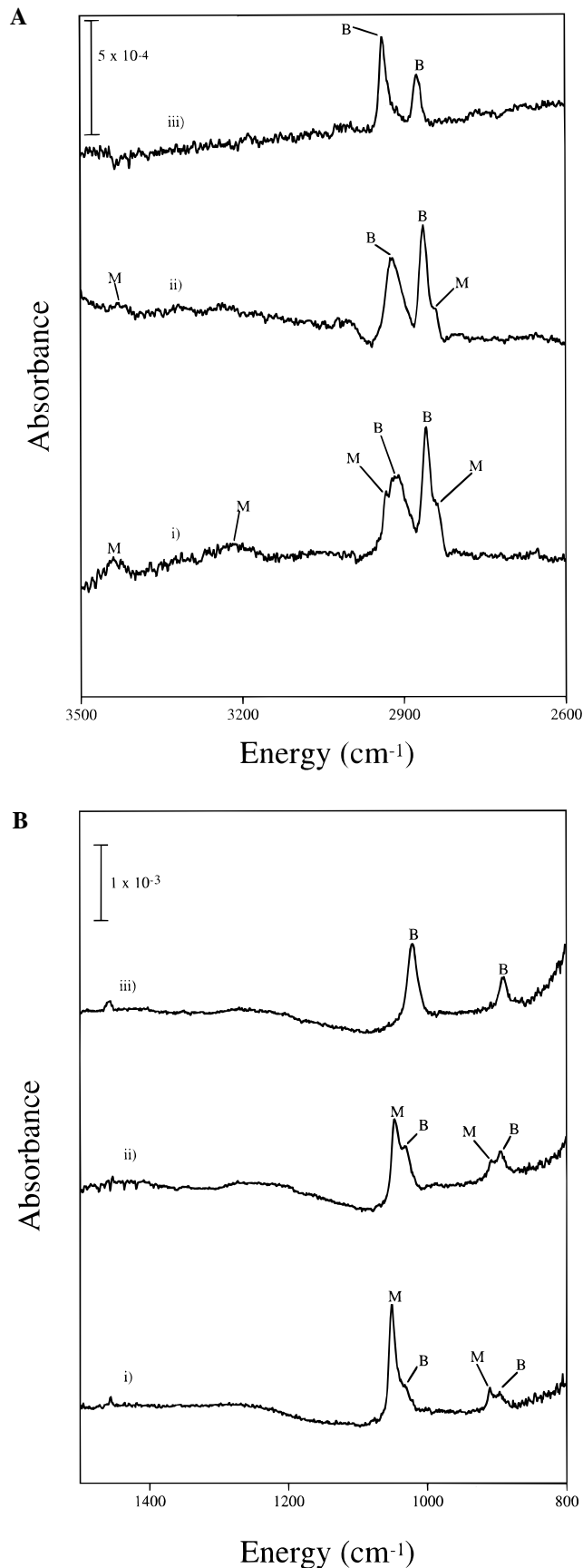


Figure 5. Infrared spectra of the temperature evolution of a saturation coverage of ethylene glycol on Mo(110) for (A) the C—H and O—H stretching region and (B) the C—O and C—C stretching region. The spectra shown were recorded at ~ 120 K after annealing a multilayer dose to (i) 300, (ii) 325, and (iii) 350 K. Peaks labeled “M” and “B” are those attributed to the monodentate and the bidentate species, respectively; their frequencies are listed in Table 1.

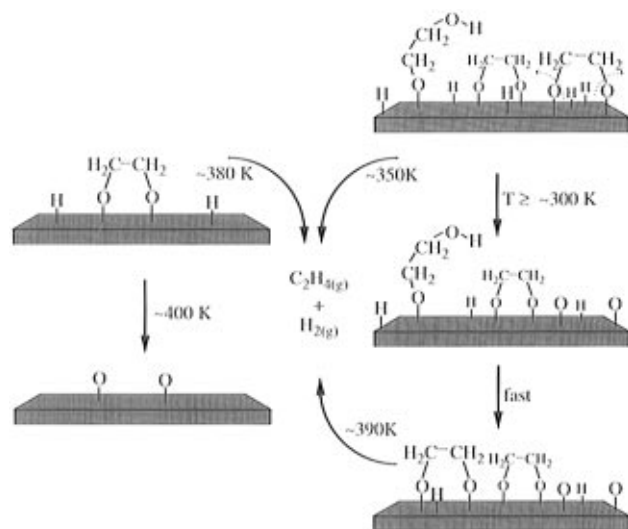


Figure 6. Proposed reaction scheme for ethylene glycol on Mo(110).

which we propose reduces steric crowding on the surface and thus allows for conversion of the monodentate to the bidentate (Figure 6). Importantly, this study is the first to utilize the high resolution of infrared spectroscopy to identify *both* the mono- and bidentate species on the same surface.

The presence of two distinct surface species at saturation coverage of ethylene glycol is indicated by *both* X-ray photoelectron and infrared reflection absorption spectroscopies. At low ethylene glycol coverages the O(1s) and C(1s) regions of the X-ray photoelectron spectra are consistent with the presence of a surface dialkoxide. The low-coverage infrared spectrum can also be assigned completely to a single bidentate species. As the exposure of ethylene glycol is increased, higher-binding energy shoulders appear in both the O(1s) and C(1s) X-ray photoelectron regions and are assigned to the oxygen and carbon in intact C–O–H groups. The existence of an intact OH group in a second intermediate at higher coverages of ethylene glycol is verified by the appearance of two peaks in the $\nu(\text{OH})$ region of the infrared and electron energy loss spectra and by a second set of peaks in the $\nu(\text{CH})$, $\nu(\text{CO})$, and $\nu(\text{CC})$ regions of the infrared spectrum. These and other infrared and X-ray photoelectron spectroscopy features described above identify the two surface species present at saturation coverage of ethylene glycol as (1) a bidentate moiety ($-\text{OCH}_2\text{CH}_2\text{O}-$) of C_2 (or lower) symmetry with its C–C bond axis parallel to the surface and (2) a monodentate species ($-\text{OCH}_2\text{CH}_2\text{OH}$) with its C–C bond axis inclined away from the surface normal. Although preferential population of the bidentate species at low ethylene glycol coverages is expected on Mo(110), based on the availability of surface sites and the facile reactivity of alcoholic O–H bonds, population of the monoalkoxide species occurs as the paired surface sites required for bidentate bonding are depleted at higher ethylene glycol coverages.

The conversion of the monodentate to the bidentate form prior to ethylene elimination is clearly indicated by analysis of both the reaction products formed and the evolution of surface intermediates as the reaction progresses. Since no oxygen-containing products are evolved, the intact OH group in the monodentate alkoxide must interact with the surface to undergo a second O–H bond scission before evolving ethylene. Our temperature-programmed reaction studies of coadsorbed $-\text{OCD}_2\text{CD}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{OH}$ clearly show that ethylene is eliminated with virtually the same temperature profile from both surface intermediates. This observation suggests that the monodentate species reacts through the bidentate species. Infrared and X-ray photoelectron data further corroborate this

model by demonstrating the depletion of the monodentate state over the course of the reaction to leave only one alkoxide intermediate, spectroscopically indistinguishable from the bidentate species formed at low coverages.

Since conversion of the monodentate to a bidentate species is favored over all other reaction pathways involving direct C–O bond scission, C–O bond scission must be more facile for the dialkoxide than for the monoalkoxide. Simple C–O bond scission in the monoalkoxide intermediate would yield the transient radical product, $\cdot\text{H}_2\text{C}-\text{CH}_2\text{OH}$. Such a species is proposed to rearrange to form acetaldehyde on Rh(111);⁵ the lack of any production of acetaldehyde or its subsequent decomposition products in our study eliminates this as a pathway for monodentate ethylene glycol reaction on Mo(110). Alternatively, the hydroxyethyl radical could undergo a reaction analogous to the formation of ethylene from adsorbed ethoxide,³⁵ eliminating one hydrogen to form $\text{CH}_2=\text{CHOH}$. However, in addition to the intrinsic instability of its vinyl alcohol product, this pathway is also disfavored due to the higher temperature of the analogous reaction for ethoxide on Mo(110) (400 K) relative to the temperature of ethylene elimination from ethylene glycol. Likewise, hydrogenation of the alkoxide carbon of the 2-hydroxyethoxide to form gas-phase ethanol does not occur, consistent with the absence of hydrogenation to form ethane from ethoxide on Mo(110).³⁵ Hence, none of these reactions is more favorable for the monodentate species than formation of the bidentate alkoxide, with subsequent double C–O bond scission to eliminate ethylene.

In fact, since the monodentate ethylene glycol intermediate does not undergo any direct C–O bond scission, no direct comparison can be made between the temperatures for C–O bond scission in the two species. However, a useful comparison can be made between the dialkoxide ethylene glycol intermediate and the monoalkoxide methoxide and ethoxide species on Mo(110); decomposition of the ethylene dialkoxide species by C–O bond scission to form ethylene begins below 300 K and peaks at ~ 350 K, while C–O bond scission in both methoxide and ethoxide on Mo(110) does not occur until ~ 400 K.¹⁰ The enhanced reactivity of the dialkoxide species suggests that bonding via both oxygens may lead to additional C–O bond weakening or less structural rearrangement in the transition state for ethylene elimination. Furthermore, formation of a C–C π bond adds to the thermodynamic favorability of ethylene elimination in the dialkoxide pathway. Electronic structure calculations comparing mono- and bidentate species are needed to evaluate the contributions of these structural and bonding effects to the relative ease of deoxygenation in mono- and dialkoxides.

The reactivity of ethylene glycol is distinctly different on this surface than on all other surfaces studied, consistent with facile C–O bond scission of other alcohols on Mo(110). In all previous studies of ethylene glycol on transition metal surfaces, the C–O bonds were retained, and the bidentate alkoxide was found to have comparable or decreased reactivity compared to similar monoalkoxide species. However, in both the surface and organometallic complexes of ethylene dialkoxide studied previously, the increased reactivity of the monodentate over the bidentate moiety refers specifically to β -hydrogen elimination. For example, on Rh(111) the temperature for reaction of the proposed bidentate ethylene glycol intermediate is approximately the same as that for ethanol. Decarbonylation of the dialkoxide has begun by 260 K and decomposition is complete by just over 300 K, with the exact sequence of decarbonylation/dehydrogenation unresolved.⁵ In comparison, ethanol decar-

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bonylation and dehydrogenation is complete by 270 K on Rh(111), though no alkoxide intermediate is observed in this case.³⁶ On oxygen-precovered Ag(110), entropic considerations were invoked to rationalize the higher temperature, and thus lower reactivity, of glyoxal formation from ethylene glycol reaction relative to that for methoxy decomposition on the same surface.² Similarly, ethoxide undergoes C–H scission to form acetaldehyde at significantly lower temperatures than that observed for glyoxal formation from ethylene glycol on Ag(110).³⁷ Likewise, the methoxide ligand in the organometallic compound (DPPE)Pt(OCH₃)₂ loses a β -hydrogen to form formaldehyde, whereas the analogous (DPPE)Pt(OCH₂CH₂O) bidentate ethylene glycolate complex undergoes no such reaction.³⁸ The bidentate ligand is apparently less susceptible than its monodentate counterpart to β -hydrogen elimination, since the rigidity of the bidentate ligand hinders the access of its β -hydrogens to the metal. However, on Mo(110) C–O bond scission generally dominates over β -hydrogen elimination, as in the case of 1-propanol, in which competition between C–O bond breaking to form gaseous propene and β -hydrogen elimination to initiate nonselective decomposition results in a 3:2 branching ratio in favor of propene elimination. Indeed, since no C–H bonds are broken in the ethylene elimination reaction of ethylene glycol on Mo(110), the inhibition of β -dehydrogenation in the dialkoxide clearly increases the selectivity for ethylene elimination over nonselective decomposition involving β -C–H cleavage.⁷ The apparent lack of β -dehydrogenation in the monoalkoxide is likely due to the favorability of bidentate formation over direct monoalkoxide reaction pathways, as discussed above.

Since the two surface intermediates are shown to proceed through the same reaction pathway, the two distinct states for ethylene evolution at higher coverages are proposed to arise from competition between steric and oxygen-induced effects on the surface. The higher temperature of the ethylene evolution peak at \sim 390 K, with a peak maximum \sim 25 K higher than the single ethylene peak at the lowest coverage, is attributed to inhibition of reaction by the oxygen deposited on the surface in conjunction with initial ethylene elimination. Previous studies have shown that alcohols on oxygen-covered Mo(110) react at higher temperatures than they do on the clean surface.^{26,29,39}

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For example, methoxide on clean Mo(110) nonselectively decomposes at \sim 400 K, while on the oxygen-covered surface the majority of the reaction, to produce gaseous methyl radicals, occurs at 500 K.³⁹ A similar increase in reaction temperature is observed for ethylene glycol on Mo(110) as oxygen is deposited during the course of temperature-programmed reaction. However, at ethylene glycol coverages near saturation, the reactivity of the bidentate species increases, as evidenced by the appearance and growth of the lower temperature (\sim 350 K) ethylene peak. This increase in reactivity is attributed to intermolecular interactions, perhaps involving dipole–dipole repulsion, which lead to a higher propensity toward C–O bond scission in the bidentate species. Notably, ethylene is formed at an intermediate temperature, \sim 365 K, at the lowest coverage (\sim 0.11 of saturation), where intermolecular and oxygen buildup are both less significant, illustrating the importance of these effects.

Conclusions

Ethylene glycol reacts on Mo(110) to form gas-phase ethylene with \sim 85% selectivity. At low coverages, ethylene glycol forms two Mo–O bonds to adsorb in a bidentate (–OCH₂CH₂O–) configuration below 300 K. At saturation coverage, two distinct intermediates are present on the surface, both the bidentate and a monodentate (–OCH₂CH₂OH) species. In contrast to previous studies of ethylene glycol reactivity on other metal surfaces, we find that the reactivity of the bidentate species is *not* less than that of the monodentate species. In fact, due to both the stability of the bidentate intermediate and the greater predilection for ethylene formation over potential monodentate reaction pathways, the bidentate species is identified as the more reactive species on a surface composed of both intermediates.

Acknowledgment. The group at Harvard gratefully acknowledges the support of the Department of Energy under grant DE-FG02-84-ER13289, as well as support for K. T. Queeney from a National Science Foundation Graduate Fellowship. C. R. Arumainayagam gratefully acknowledges partial support from a Cottrell College Science Award of Research Corporation and a Brachman Hoffman fellowship from Wellesley College.

JA953987R

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