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O-H and C-H Bond Activation in Ethylene Glycol by Atomic Oxygen on Ag(110): Heterometallacycle Formation and Selective Dehydrogenation to Glyoxal

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Abstract: The absorption and reaction of ethylene glycol [$(CH_2OH)_2$] on clean and oxygen-covered Ag(110) surfaces have been studied with temperature-programmed reaction spectroscopy (TPRS) and high resolution electron energy loss vibrational spectroscopy (EELS). On the clean surface $(CH_2OH)_2$ was reversibly adsorbed, desorbing with an activation energy of 15 kcal/mol at 250 K from a monolayer state and at 225 K from a multilayer state with a heat of sublimation of 16 kcal/mol. Vibrational spectra of both the multilayer and monolayer were in good agreement with that of liquid $(CH_2OH)_2$, indicating that $(CH_2OH)_2$ is only weakly bonded to the Ag(110). The relative intensities of the vibrational bands in the two states strongly suggest that $(CH_2OH)_2$ is bound to the Ag(110) surface via both oxygen atoms in the monolayer state. On the partially oxidized surface, in addition to forming molecular multilayer and monolayer states, $(CH_2OH)_2$ reacts with atomic oxygen to form adsorbed ethylenedioxy ($-OCH_2CH_2O-$) and H_2O. The $-OCH_2CH_2O-$(a) species is stable up to a temperature of 350 K, where C-H bond breaking and re-formation occurs leading to the evolution of $(CH_2OH)_2$ at 365 K, glyoxal [$(CHO)_2$] at 380 K and H_2 at both temperatures. The decomposition of $-OCH_2CH_2O-$(a) is shown to proceed via surface bound $O{=}CHCH_2O-$ by the appearance of aldehydic C═O and C—H stretches at 1730 and 2730 cm^{-1}, respectively, in the vibrational spectrum following the initial stage of $-OCH_2CH_2O-$(a) decomposition. The cyclic ethylenedioxy species is shown to be more stable than the acyclic methoxy species, which decomposes by 300 K on the same surface. The added stability is due to a higher entropy of activation and may originate from a greater degree of freedom in the dialkoxide.

I. Introduction

The interaction of alcohols with adsorbed atomic oxygen on Ag and Cu single crystal surfaces is one of the best understood reaction systems in the surface science literature.[1-12] The accepted reaction mechanism involves the loss of the hydroxyl hydrogen to surface oxygen to form water plus adsorbed alkoxy intermediates.

$$2ROH + O(a) \rightarrow 2RO(a) + H_2O(g) \qquad (1)$$

The alkoxy intermediate decomposes upon heating via β-C-H (i.e., the carbon atom is beta to the surface) bond activation to yield the corresponding aldehyde for a primary alcohol or ketone for a secondary alcohol, along with the parent alcohol, hydrogen, and water from recombination reactions according to

$$R_2CHO(a) \rightarrow R_2C{=}O(g) + H(a) \qquad (2)$$

$$R_2CHO(a) + H(a) \rightarrow R_2CHOH(g) \qquad (3)$$

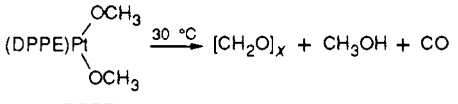
$$2H(a) \rightarrow H_2(g) \qquad (4)$$

$$2H(a) + O(a) \rightarrow H_2O(g) \qquad (5)$$

The absence of a β hydrogen in tertiary alcohols results in much different decomposition pathways which are currently under investigation.[13]

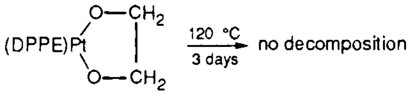
Since the reactivity of a molecule on a given surface is determined principally by the functional groups in the molecule, the surface chemistry of diols (HO-R-OH) should be very similar to that of simpler alcohols (R-OH). Nonetheless, the presence of two reactive groups raises interesting questions as to whether both hydroxyl groups react with surface oxygen, thus binding the molecule to the surface via both alcohol groups, and as to how the stability of the resultant cyclic alkyldioxy surface intermediate compares with that of the corresponding acyclic alkoxy surface species (Figure 1, structures **1** and **2**, respectively).

C-H bond activation by the surface for the alkyldioxy decompositions may be expected to be somewhat more difficult, since bringing a β-C-H bond in proximity with the surface would be hindered by the relative immobility of the other end of the molecule. This effect is analogous to one which has previously been observed in organometallic chemistry, where metallacycles are often found to be significantly more stable than their acyclic counterparts owing to the difficulty of the β-hydrogen substituents to access the metal center.[14-17] In particular, a cyclic ethylenedioxy complex of Pt is known to be strikingly more stable than the corresponding methoxy complex:[15]



$$(\mathrm{DPPE})\mathrm{Pt}\begin{matrix}\mathrm{OCH_3}\\ \\ \mathrm{OCH_3}\end{matrix} \xrightarrow{30\ ^\circ\mathrm{C}} [CH_2O]_x + CH_3OH + CO \qquad (6)$$

(DPPE = 1, 2-bis(diphenylphosphino)ethane)



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A manifestation of the importance of such steric effects on surfaces is found in a previous study of alcohol adsorption on Cu(110) surfaces, where ethylene glycol (1,2-ethanediol), $(CH_2OH)_2$, was reported to form a surface intermediate which decomposed at a temperature 40 K higher than any previously studied acyclic alkoxy surface species.[5] However, the results of this study were

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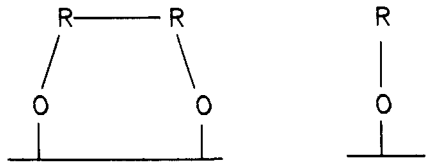

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Figure 1. Cyclic alkyldioxy species (**1**) and the corresponding acyclic alkoxy species (**2**).

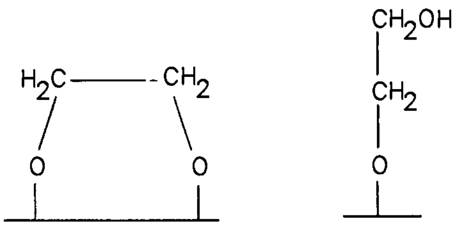

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Figure 2. Cyclic ethylenedioxy species (**3**) and the corresponding acyclic 2-hydroxyethoxy species (**4**) possible from ethylene glycol.

somewhat ambiguous in that it did not distinguish between the presence of the acyclic 2-hydroxyethoxy, $HOCH_2CH_2O(a)$, and/or the cyclic ethylenedioxy, $OCH_2CH_2O(a)$, species as surface intermediates (Figure 2). However, the fact that glyoxal (O=C-HCH=O) was formed upon decomposition whereas no glycoaldehyde ($O=CHCH_2OH$) was detected makes the existence of substantial amounts of **4** rather unlikely.

In this study the binding and reactions of ethylene glycol with clean and oxygen-covered Ag(110) surfaces were studied using temperature-programmed reaction spectroscopy (TPRS) and high-resolution electron energy loss vibrational spectroscopy (EELS). On clean Ag(110) surfaces $(CH_2OH)_2$ was reversibly adsorbed intact at both monolayer and multilayer concentrations. Vibrational spectra of the monolayer state support a bidentate surface species, comparable to the bonding of ethylene glycol in transition metal complexes. On the oxidized surface, $(CH_2OH)_2$ reacted with O(a) to yield water and adsorbed ethylenedioxy ($OCH_2CH_2O(a)$) species. This species was stable up to a temperature of 365 K, which, by comparison, is 65 K higher than methoxy ($CH_3O(a)$) and 100 K higher than ethoxy (CH_3CH_2O-(a)) on this surface.[1,2] The decomposition of the ethylenedioxy species proceeded via β-C–H bond breaking to yield glyoxal, ethylene glycol, and hydrogen as the only detectable products. The vibrational spectra of the ethylenedioxy species are compared in this paper with that of $(OCH_2CH_2O)^{2-}$ salts, and a bonding scheme analoguous with $(OCH_2CH_2O)^{2-}$ in transition metal complexes is proposed. The attack of $OCH_2CH_2O(a)$ by excess coadsorbed oxygen atoms yields very different chemistry, including C–C bond scission, and is the subject of a separate study.[18]

II. Experimental Section

Temperature-programmed reaction spectroscopy experiments (TPRS) were conducted in an ultrahigh vacuum chamber (base pressure = 2×10^{-10} Torr) described previously.[19] To elucidate the reactions occurring, TPRS experiments were performed using a computer-multiplexed mass spectrometer which allowed up to 200 masses to be monitored simultaneously. With this instrument a complete mass scan could be taken every 20 ms or every 4 s while monitoring either 8 or 200 masses, respectively. This mode of detection allowed high-resolution spectra to be obtained in the eight mass mode for mechanistic analysis of the reactions and complete product identification to be achieved in the 200 mass mode. A heating rate of 9 K/s was used unless otherwise noted.

Electron energy loss vibrational spectroscopy (EELS) experiments were performed on another Ag(110) crystal in a separate ultrahigh vacuum chamber (base pressure = 8×10^{-11} Torr) which has also been previously described.[20] The energy loss experiments were conducted in the specular direction with a beam energy of approximately 1 eV and with a resolution ranging from 70 to 100 cm^{-1} depending on surface conditions. All spectra were recorded at 125 K after annealing to the temperatures indicated on the figures.

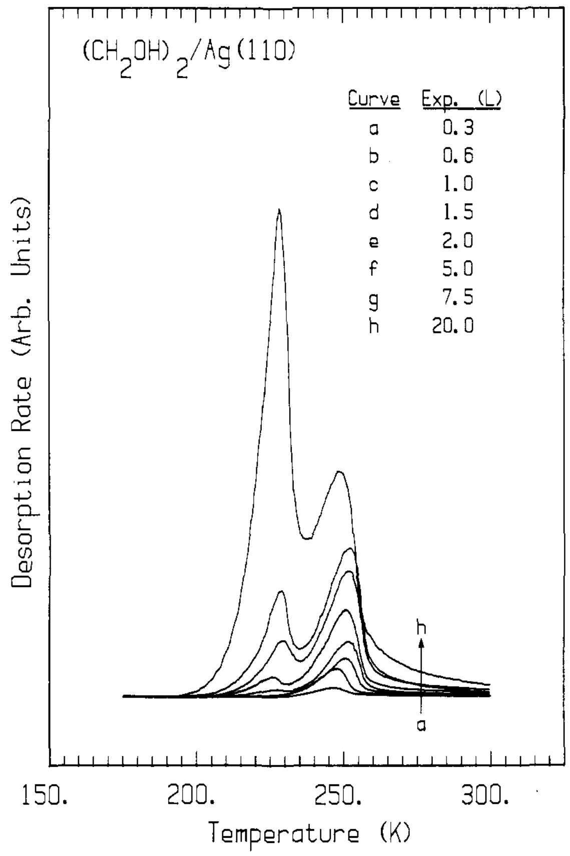

Figure 3. Temperature-programmed reaction spectrum for various exposures of ethylene glycol to the clean Ag(110) surface at 150 K. Shown is the CH_2OH (*m/e* 31) signal.

Clean Ag(110) surfaces were prepared by argon ion bombardment followed by annealing to 800 K. Residual carbon was removed by dosing oxygen and flashing the sample to oxidize the carbon to $CO_2(g)$. The cleanliness of the sample was verified by Auger electron spectroscopy (AES) and by monitoring the relative sizes of the CO_2 and O_2 peaks in a temperature-programmed desorption (TPD) experiment after an oxygen dose. A "clean" surface was defined as one where no contaminants are observable by AES and which possesses an uncorrected CO_2/O_2 desorption peak area ratio ≤ 0.05. Surface order was verified by sharp (1×1) low-energy electron-diffraction (LEED) patterns. Reagent grade $(CH_2OH)_2$ was distilled and then degassed with freeze–pump–thaw cycles. $(CD_2OH)_2$ (ICN, 99 atom % D) was used after degassing. Oxygen (Matheson, extra dry) and $^{18}O_2$ (Bio Rad, 99.1% ^{18}O) were used as received. Sample purity was checked by leaking the samples into the chamber and measuring their cracking patterns with the mass spectrometer and comparing the results with published spectra.[21] In addition, the purity of the glycols was routinely checked by condensing the samples on the clean Ag(110) surface and measuring their cracking patterns in the desorption of a multilayer, since this method maintained a lower background pressure. All exposures were calculated with uncorrected ion gauge readiangs and are expressed in Langmuirs (1 L = 10^{-6} Torr·s). Directed dosing, which provided enhancement factors of approximately 100 and 1000 for gases and condensables, respectively, was employed throughout this study. Note that for ethylene glycol 1 L = 2.6×10^{14} molecules/cm^2 exposure.

III. Results and Discussion

A. Ethylene Glycol Adsorption on Clean Ag(110). 1. Temperature-Programmed Desorption (TPD).

On the clean Ag(110) surface $(CH_2OH)_2$ is reversibly absorbed and suffers no detectable decomposition, as evidenced by the absence of any other desorption

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Table I. Vibrational Frequencies (cm^{-1}) of $(CH_2OH)_2$/Ag(110)

vibrational mode[a]	liquid[b]	$(Ni_2(EG)_4Cl_2)Cl_4$[c]	$(CH_2OH)_2$/Ag(110) multilayer	$(CH_2OH)_2$/Ag(110) monolayer
ν(OH)	3275 s (b)	3230 vs (b)	3290 s (b)	3310 w (b)
ν_{as}(CH)	2935 s	2935 s	2900 m (b)	2890 m (b)
ν_s(CH)	2875 s	2870 s		
$\nu(CH_2)$	1459 m	1460 m	1450 m	1450 sh
δ(COH)	1405 m (vb)	1405 w	1410 sh	1410 m
$\rho_w(CH_2)$	1332 w	1307 m	nr	nr
$\rho_t(CH_2)$	1212 w	1210 m	nr	nr
ν_s(CO)	1087 vs	1061 s	1090 s	1080 s
ν_{as}(CO)	1038 vs	1024 s	nr	nr
$\rho_r(CH_2)$	887 s	889 s	870 m	880 w
ν(CC)	864 m	879 s		
τ(OH)	700 s (b)	680 m (b)	710 s (b)	700 m (b)
δ(CCO)	478 w	555 m	nr	nr
τ(CC)	360 w	nr	nr	nr

[a] ν = stretch; ν_{as} = asymmetric stretch; ν_s = symmetric stretch; δ = in-plane bending; ρ_w = wag; ρ_t = twist; ρ_r = rock; τ = torsion; v = very; w = weak; s = strong; b = broad; sh = shoulder; nr = not resolved. [b] Reference 23. [c] Reference 24; EG = $(CH_2OH)_2$.

products and the absence of adsorbed carbon and/or oxygen species after desorption according to either O_2 titrations or AES. TPD spectra obtained after adsorption of $(CH_2OH)_2$ on the clean Ag(110) surface at 150 K are shown in Figure 3. At very low exposures a single state with a desorption peak at 245 K is populated (curve a). As the exposure is increased this peak grows in intensity and shifts to slightly higher temperatures up to an exposure of 1.0 L (curve c). Above this exposure the peak temperature remains fixed at 250 K, indicative of a first-order desorption process. Another state with a desorption peak at 225 K is also populated and also shifts to slightly higher temperatures with coverage. This state cannot be saturated and is therefore attributed to multilayer formation. From plots of log (desorption rate) versus reciprocal temperature for the leading edge of the low-temperature peak, a heat of sublimation of 16 kcal/mol was estimated for the multilayer state. The state at 250 K saturates after about a 10-L exposure and is therefore attributed to the (sub)monolayer adsorption state of molecular ethylene glycol. Assuming first-order kinetics, as suggested by the 250 K peak symmetry, and a normal first-order preexponential factor of 10^{13} s^{-1}, the desorption activation energy for this state was estimated to be 15 kcal/mol.[22] Extensive clustering of the $(CH_2OH)_2$ molecules on the clean Ag(110) surface is suggested by the fact that the low-temperature state, clearly due to multilayer formation at high exposures, forms before the saturation of the monolayer state occurs, and by the EELS results discussed below.

2. Vibrational Spectroscopy (EELS). Electron energy loss vibrational spectra (EELS) obtained after the adsorption of ethylene glycol (EG) on the clean Ag(110) surface at 120 K are shown in Figure 4 and listed in Table I along with the infrared frequencies (IR) and assignments for $(CH_2OH)_2$ in the liquid phase[23] and in the complex $(Ni_2(EG)_4Cl_2)Cl_4$.[24] Figure 4A shows the vibrational spectrum after an exposure of the clean surface at 125 K to 20 L of $(CH_2OH)_2$ during which multilayers were formed (see Figure 3). All of the observed losses can be assigned as follows from the liquid-phase IR: O–H stretch (3290 cm^{-1}); C–H stretches (2900 cm^{-1}); H–C–H in-plane bend (1450 cm^{-1}); C–O–H in-plane bend (1410 cm^{-1}); symmetric C–O stretch (1090 cm^{-1}); H–C–H rock + C–C stretch (870 cm^{-1}); O–H torsion (710 cm^{-1}). In all cases, the frequencies agree to within 25 cm^{-1}. Notable by its absence is a loss corresponding to the asymmetric C–O stretch which has a very strong adsorption band in the liquid-phase IR spectrum at 1038 cm^{-1}. Annealing to 225 K desorbed the multilayer state, thus isolating the 250 K desorption state previously assigned to monolayer adsorption (see Figure 3). The resultant spectrum (Figure 4B, Table I) is very similar to

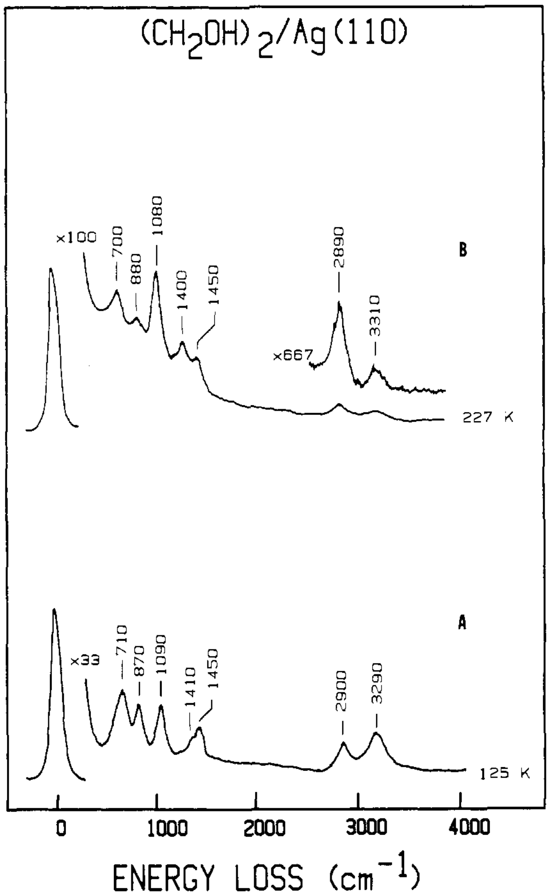

Figure 4. Vibrational spectra of ethylene glycol adsorbed on the clean Ag(110) surface at 125 K. Figure 2A shows the vibrational spectrum for multilayers of $(CH_2OH)_2$ formed after a 25-L exposure. Figure 2B shows the vibrational spectrum after annealing to 230 K to isolate the monolayer state. Frequencies and assignments are tabulated in Table I.

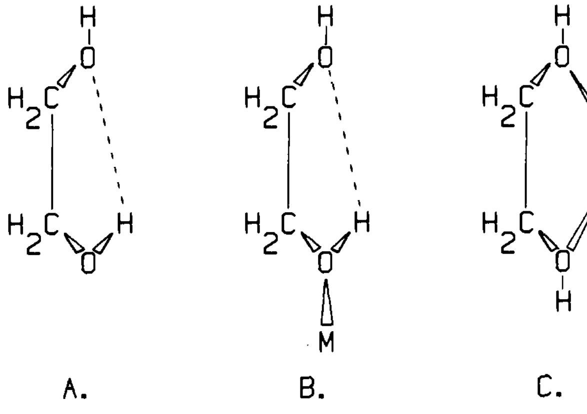

Figure 5. Bonding modes of ethylene glycol: (a) ligand (gauche conformation); (b) monodentate; (c) bidentate. Dashed lines indicate an intramolecular hydrogen bond.

that of the multilayer state (Figure 4A) except for some changes in the relative intensities of the losses. In particular, the losses due to C–O stretching (1080 cm^{-1}) and the C–O–H in-plane bend (1400 cm^{-1}) both become relatively more intense with respect to other losses in the monolayer spectrum. Also noteworthy is the fact that the losses due to the C–H stretching modes (2890 cm^{-1}) become more intense than those due to the O–H stretching modes (3310 cm^{-1}) in the monolayer spectrum. These changes in relative intensities between the multilayer and the monolayer state suggest either that in the monolayer state ethylene glycol is no longer randomly oriented as it most probably is in the multilayer state or that the intramolecular dynamic dipoles in $HOCH_2CH_2OH$

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are significantly affected by the presence of the surface-oxygen bonds in the monolayer state. Extensive clustering of the ethylene glycol molecules is also evident even in the monolayer state O–H stretch (3310 cm^{-1}) which is very close to that of the liquid phase (3275 cm^{-1}) where extensive intermolecular hydrogen bonding takes place, and not to the gas-phase value of 3677 cm^{-1} for the nonhydrogen bonded O–H stretch and 3644 cm^{-1} for the intramolecular hydrogen-bonded O–H stretch[25] (see Figure 5A).

In all phases ethylene glycol exists predominantly in the gauche conformation with one internal hydrogen bond[25] (Figure 5A). In complexes, $(CH_2OH)_2$ acts as a normal OH-donor ligand, coordinating via one (monodentate) or both (bidentate) oxygen atoms.[24] In monodentate complexes, the ligand retains is conformation (Figure 5B), while in bidentate complexes, the ligand itself must modify its conformation with both OH groups trans to the central C–C bond and the CH_2OH groups gauche to one another (Figure 5C).[24] Carrying this analogy over to the monolayer ethylene glycol species on Ag(110), the observed vibrational spectrum can most easily be explained in terms of $(CH_2OH)_2$ bound to the Ag(110) surface via both oxygen atoms in a bidentate or chelating configuration, as depicted in Figure 5C. This geometry would position the O–H bonds parallel or nearly parallel to the surface and the C–O bonds almost perpendicular to the surface, thus giving the least amount of surface image–dipole reduction to the intensity of the symmetric C–O stretching mode and the C–O–H in-plane bending modes and the greatest such reduction to the O–H and C–C stretching, O–H torsional, H–C–H scissoring, and H–C–H rocking modes, in agreement with the monolayer vibrational spectrum. This geometry would also explain the absence of the asymmetric C–O stretch in the monolayer spectrum as it would not be dipole active in such a geometry. This does not, however, explain the absence of the asymmetric C–O stretch in the multilayer spectrum, since retainment of this orientation for several layers seems unlikely.

A characteristic feature in the IR spectra of ethylene glycol complexes is a down-shifted C–O stretch when compared with that of the free ligand. This shift is exemplified in the bidentate complex $(Ni_2(EG)_4Cl_2)Cl_4$, which shows a symmetric C–O stretch 26 cm^{-1} below and an asymmetric C–O stretch 14 cm^{-1} below that for ethylene glycol in the liquid phase. For $(CH_2OH)_2$ on Ag(110) the C–O stretch was also measured to be 10 cm^{-1} lower in the monolayer state than it is in the multilayer state (see Figure 4 and Table I), but the consistent detection of such small changes in peak position were at the level of detectability with our spectrometer.

B. Ethylene Glycol Adsorption on Oxygen-Covered Ag(110). 1. Temperature-Programmed Reaction Spectroscopy (TPRS). The temperature-programmed reaction spectrum following an exposure of 20 L of ethylene glycol to the Ag(110) surface predosed with 0.25 ML of $^{18}O(a)$ is shown in Figure 6. For this exposure, which is in substantial excess of one monolayer, the majority of the $(CH_2{}^{16}OH)_2$ desorbed intact, but some reacted completely with the $^{18}O(a)$ as evidenced by the evolution of $H_2{}^{18}O$ at 180 and 220 K, and of H_2 and $(CH^{16}O)_2$ at 365–380 K. Following heating to 450 K, both AES and O_2 titrations showed the surface to be clean. In order to avoid deconvolution of common mass cracking fragments, only the parent fragments are shown (at the expense of signal strength for larger molecules, i.e., $HOCH_2CH_2OH$ and $O{=}CHCH{=}O$). Deconvoluted spectra using the most abundant fragment for each species show identical results with improved signal to noise.

The reaction of $(CH_2{}^{16}OH)_2$ with $^{18}O(a)$ resulted in the incorporation of all of the oxygen-18 into $H_2{}^{18}O$ which desorbed at 180 and 220 K. From previous studies of water adsorption on this surface, both of these desorption states are known to evolve from molecularly bound H_2O.[26,27] No $H_2{}^{16}O$, nor any other ^{16}O-containing species other than $(CH_2{}^{16}O)_2$ and $(CH^{16}O)_2$, was evolved. $(CH_2{}^{16}OH)_2$ was evolved at 230, 255, and 365 K. The peaks at 230 and 255 K were also present in the desorption spectrum for ethylene glycol from the clean Ag(110) surface (see Figure 3) and have been previously assigned to desorption from molecular multilayer and monolayer adsorption states, respectively. The $(CH_2{}^{16}OH)_2$ peak at 365 K was accompanied by H_2 evolution at the same temperature and followed by the further evolution of H_2 and $(CH^{16}O)_2$ at 380 K. The two-peaked hydrogen desorption spectrum suggests that the surface species formed initially by the reaction of ethylene glycol with surface oxygen is sequentially dehydrogenated. The two most likely surface species which account for this observation are the 2-hydroxyethoxy intermediate $(HOCH_2CH_2O(a))$, where dehydrogenation could take place at the OH group and then at both CH_2 groups simultaneously (or vice versa), and the ethylenedioxy intermediate $(OCH_2CH_2O(a))$, where dehydrogenation could take place at one CH_2 group followed by the other. In order to differentiate deprotonation at the CH_2 groups from deprotonation at the OH groups in $(CH_2OH)_2$, the reaction of $(CD_2OH)_2$ with O(a) was investigated. Figure 7 shows the reaction spectrum following an exposure of 20 L of $(CD_2OH)_2$ to the Ag(110) surface covered with 0.25 ML of oxygen atoms. Masses 1 to 200 amu were checked and showed only the parent and corresponding cracking fractions assignable to the species shown in Figure 7. This experiment clearly shows that both OH groups in $(CD_2OH)_2$ are deprotonated by surface oxygen to form H_2O and leave behind the deuterated glycolate intermediate, $OCD_2CD_2O(a)$. That this is the only species present after the desorption of H_2O and molecularly adsorbed $(CD_2OH)_2$ is supported by the fact that $(CD_2OD)_2$, $(CDO)_2$, and D_2 are the only species evolved upon further heating of the sample, with no evidence of H_2, HD, $(CD_2OH)_2$, or $HOCD_2CD_2OD$ formation. The mechanism involving sequential C–H (C–D) bond-breaking in the decomposition of $OCH_2CH_2O(a)$ $(OCD_2CD_2O(a))$ is further supported by the observed 10–15 K shift to higher temperature of both the reaction-limited peaks for $OCD_2CD_2O(a)$ decomposition compared

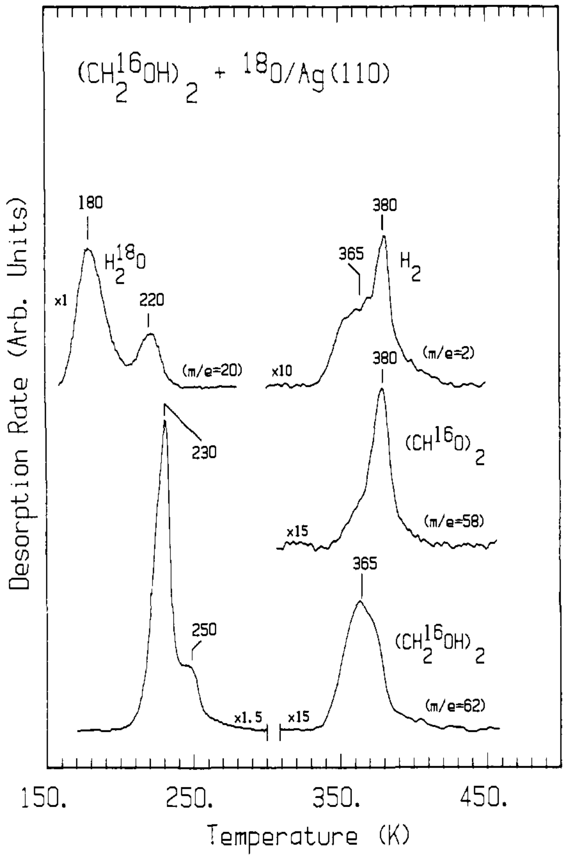

Figure 6. Temperature-programmed reaction spectra after a 20-L dose at 150 K of $(CH_2{}^{16}OH)_2$ to the Ag(110) surface covered with 0.25 ML of $^{18}O(a)$. The *m/e* values used to monitor each product were 62 $(CH_2OH)_2$, 58 $(CHO)_2$, 18 (H_2O), and 2 (H_2).

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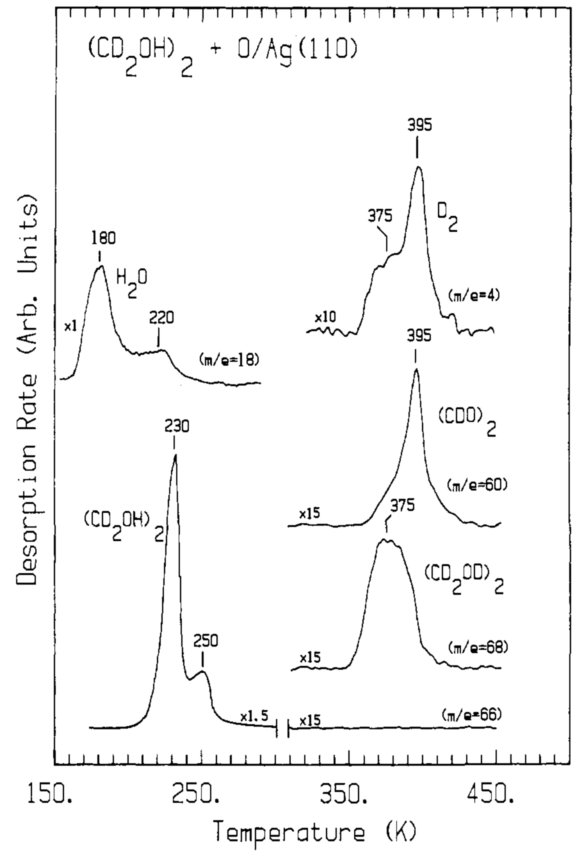

Figure 7. Temperature-programmed reaction spectra after a 20-L dose at 150 K of $(CD_2OH)_2$ to the Ag(110) surface covered with 0.25 ML of oxygen atoms. The masses used to monitor each comound were 68 $(CD_2OD)_2$, 66 $(CD_2OH)_2$, 60 $(CDO)_2$, 18 (H_2O), and 4 (D_2).

to those for $OCH_2CH_2O(a)$ decomposition. The overall reaction mechanism is then as follows: below 170 K $(CH_2OH)_2$ reacts with atomic oxygen to form water and adsorbed ethylenedioxy species:

$$HOCH_2CH_2OH(g) \rightarrow HOCH_2CH_2OH(a) \tag{8}$$

$$HOCH_2CH_2OH(a) + O(a) \rightarrow HOCH_2CH_2O(a) + OH(a) \tag{9}$$

$$HOCH_2CH_2O(a) + OH(a) \rightarrow OCH_2CH_2O(a) + H_2O(a) \tag{10}$$

At 170–300 K, molecularly adsorbed water and ethylene glycol desorb:

$$H_2O(a) \rightarrow H_2O(g) \tag{11}$$

$$HOCH_2CH_2OH(a) \rightarrow HOCH_2CH_2OH(g) \tag{12}$$

and at 325–425 K, the ethylenedioxy species decompose via an 2-oxoethoxy surface intermediate:

$$OCH_2CH_2O(a) \rightarrow O{=}CHCH_2O(a) + H(a) \tag{13}$$

$$OCH_2CH_2O(a) + H(a) \rightarrow HOCH_2CH_2O(a) \tag{14}$$

$$HOCH_2CH_2O(a) + H(a) \rightarrow HOCH_2CH_2OH(g) \tag{15}$$

$$O{=}CHCH_2O(a) \rightarrow O{=}CHCH{=}O(g) + H(a) \tag{16}$$

$$2H(a) \rightarrow H_2(g) \tag{17}$$

The existence of both the ethylenedioxy $(OCH_2CH_2O(a))$ and the short-lived 2-oxoethoxy $(O{=}CHCH_2O(a))$ intermediates were verified by vibrational spectroscopy, as discussed below. Surprisingly, the formation of glycoaldehyde $(HOCH_2CH{=}O$, *m/e* 60), as might be expected by the simple recombination of $O{=}CHCH_2O(a)$ with H(a), was not observed. Very similar results have been previously observed on Cu(110).[5] On that surface ethylene glycol forms a strongly bound intermediate, decomposing by 390 K (some 35 K higher than methoxy decomposition on that surface[4] to yield only glyoxal along with ethylene glycol and hydrogen via recombination reactions. Although the details of the decomposition pathways on Cu(110) were not fully explored, the similarity of the overall chemistry obtained on that surface to what we have observed on Ag(110) strongly suggests that similar mechanisms apply to both surfaces.

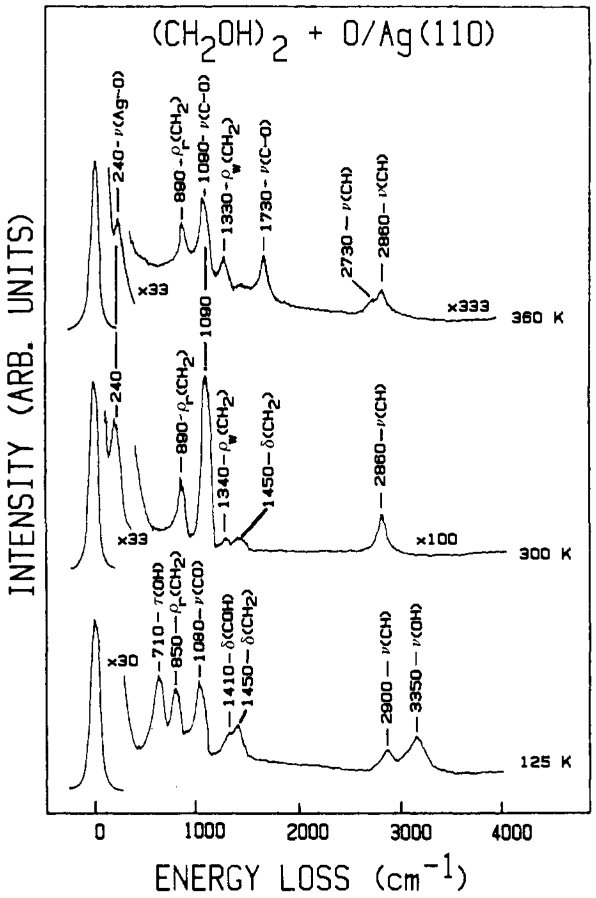

Figure 8. Vibrational spectra after a 20-L exposure of $(CH_2OH)_2$ at 125 K to the Ag(110) surface covered with 0.25 ML of O(a). Also shown are the vibrational spectra following annealing of the surface to 300 and 360 K.

Table II. Vibrational Frequencies of 20 L of $(CH_2OH)_2$ + 0.25 mL of O(a)/Ag(110)

vibrational mode[a]	liquid[b]	$K_2[OCH_2CH_2O]$[c]	$(CH_2OH)_2$/Ag(110)–O		
			125 K	300 K	360 K
ν(OH)	3275 s (b)		3350 s (b)		
ν_{as}(CH)	2935 s	2899 vs			2730 w[d]
ν_s(CH)	2875 s	2833 s	2900 m (b)	2860 m	2860 m
$\delta(CH_2)$	1459 m	1445 s	1450 m	1450 w	nr
δ(COH)	1405 m (vb)		1410 sh		
$\rho_w(CH_2)$	1332 w	1370 s	nr	1340 w	1330 w
$\rho_t(CH_2)$	1212 w	1290 m	nr	nr	nr
ν_s(CO)	1087 vs	1093 s	1090 s	1090 vs	1090 s 1730[e]
ν_{as}(CO)	1038 vs	1042 s	nr	nr	
$\rho_r(CH_2)$	887 s	883 m	850 m	890 m	890 m
ν(CC)	864 m	858 sh			
τ(OH)	700 s (b)		710 s (b)		
δ(CCO)	478 w		nr		
τ(CC)	360 w	nr	nr	nr	nr
ν(Ag–O)			nr	240 vs	240 vs

[a] See Table I for explanation of notation. [b] Reference 23. [c] Reference 28. [d] 2730-cm^{-1} loss due to ν(CH) of aldehyde group in $O{=}CHCH_2O(a)$; see text. [e] 1730-cm^{-1} loss due to ν(C=O) of $O{=}CHCH_2O(a)$; see text.

2. **Vibrational Spectroscopy (EELS).** Vibrational spectra following an exposure of 20 L of $(CH_2OH)_2$ at 125 K to the Ag(110) surface covered with 0.25 ML of oxygen atoms are shown in Figure 8 for three different annealing temperatures. The assignments of these spectra are tabulated in Table II along with

Table III. Arrhenius Activation Parameters for the Decomposition of Ethylenedioxy and 2-Oxoethoxy on Ag(110)

reaction[a]	E_a (kcal/mol)	log A	k_H/k_D[b]
$OCH_2CH_2O(a) \rightarrow O{=}CHCH_2O(a) + H(a)$	17.5 ± 0.8	10.6 ± 0.5	
$OCD_2CD_2O(a) \rightarrow O{=}CDCD_2O(a) + D(a)$	19.5 ± 0.7	11.4 ± 0.5	3.3
$O{=}CHCH_2O(a) \rightarrow O{=}CHCH{=}O(g) + H(a)$	21.0 ± 0.9	11.7 ± 0.5	
$O{=}CDCD_2O(a) \rightarrow O{=}CDCD{=}O(g) + D(a)$	23.1 ± 0.6	12.8 ± 0.3	2.7
$CH_3O(a) \rightarrow CH_2{=}O(g) + H(a)$	17.6[c]		
$CH_3O(a) \rightarrow CH_2{=}O(g) + H(a)$	22.1 ± 0.1[d]	12.7 ± 0.2[d]	

[a] See text. [b] Extrapolated to 300 K. [c] Results on Ag(110) from ref 1; E_a was calculated assuming first-order kinetics and log A = 13. [d] Results on Cu(110) from ref 2; the kinetic parameters were calculated by the method of heating rate variation.[34]

the assignments for $(CH_2OH)_2$ in the liquid phase[23] and for the dialkali metal 1,2-ethanedioxy complex $K_2[OCH_2CH_2O]$.[28] The spectrum at 125 K for the oxygen-covered surface is very similar to that of the clean surface at this temperature due to the presence of multilayers in both cases (see Figure 4). Annealing the sample to 300 K desorbs any molecularly bound $(CH_2OH)_2$ and H_2O formed by the reaction of $(CH_2OH)_2$ and O(a) and leaves behind only the intermediate(s) responsible for $(CH_2OH)_2$, $(CHO)_2$, and H_2 formation between 350 and 400 K. Temperature-programmed reaction spectroscopy (TPRS) experiments discussed in the previous section show that at 300 K the only species present on the surface is the ethylenedioxy ($OCH_2CH_2O(a)$ intermediate. The vibrational spectrum at 300 K agrees with this result. The disappearance of losses corresponding to O–H stretching (3350 cm^{-1}), C–O–H in-plane bending (≈1410 cm^{-1}) and O–H torsional (≈710 cm^{-1}) vibrational modes by 300 K show that both O–H bonds are broken in the species formed by the reaction of $(CH_2OH)_2$ with O(a). Conversely, the persistence of losses in the regions associated with C–C, C–O, and C–H stretching modes (890, 1090, and 2860 cm^{-1}, respectively) indicates that the rest of the molecule remains intact. The clear absence of the O–H stretch also rules out the unlikely event of intramolecular hydrogen migration from carbon to oxygen after the initial loss of the hydroxyl hydrogens to the surface oxygen.

A comparison of the electron energy loss spectrum at 300 K with the IR spectrum of potassium glycolate ($K_2[OCH_2CH_2O]$) further confirms the existence of the $OCH_2CH_2O(a)$ species and allows for the complete assignment of the observed losses as follows: C–H stretching (2900 cm^{-1}); H–C–H in-plane bending (1450 cm^{-1}); CH_2 wagging (1340 cm^{-1}); symmetric C–O stretching (1090 cm^{-1}); CH_2 rocking + C–C stretching (890 cm^{-1}); and symmetric Ag–O stretching (240 cm^{-1}). The fact that the strong adsorption band at 1042 cm^{-1} which is assigned to the asymmetric C–O stretch in $K_2[OCH_2CH_2O]$ has no counterpart in the $OCH_2CH_2O(a)$ EEL spectrum suggests that this species is bound through both oxygen atoms possessing at least C_2 symmetry with the symmetry plane perpendicular to the Ag(110) surface. Assuming that the dipole scattering mechanism is in effect for the C–O stretching mode, this configuration would give this mode a cancelling surface-image dipole and, thus, a very low intensity. For this same reason the intense loss at 240 cm^{-1} is assigned to the symmetric Ag–O stretch of $OCH_2CH_2O(a)$. This value compares well with the Ag–O stretching frequency of O_2, H_2CO, and CO_3 on Ag(110) where this mode occurs at 240, 250, and 270 cm^{-1}, respectively.[29–31]

In the previous section it was also suggested that $OCH_2CH_2O(a)$ decomposed via a $O{=}CHCH_2O(a)$ intermediate (eq 13–17). The 20 K difference in the peak temperatures of $(CH_2OH)_2$ and $(CHO)_2$ evolution made it possible to stabilize this short-lived intermediate by flashing the sample up to 360 K and quickly cooling it to 125 K. Aldehydes (R—CH=O) are characterized by a strong IR adsorption band at 1730–1740 cm^{-1} due to the C=O stretching vibration and by a medium-weak band at ≈2720 cm^{-1} due to the C–H stretching vibration.[32] For example, in acetaldehyde these bands occur at 1752 and 2731 cm^{-1}, respectively.[32] The vibrational spectrum following the 360 K anneal clearly shows the presence of an aldehyde species by the emergence of two new losses at 1730 and 2730 cm^{-1}. The remaining losses still have their counterparts in the 300 K spectrum of the glycolate species. The simplest single chemical species which can account for these observations is 2-oxoethoxy, $O{=}CHCH_2O(a)$. Vibrational mode assignments for the $O{=}CHCH_2O(a)$ intermediate can be made as follows by comparing the 360 K spectrum with the R—CH=O group assignments,[32] and to $OCH_2CH_2O(a)$ assignments (this work): C—H stretching of CH_2 group (2860 cm^{-1}); C—H stretching of CH=O group (2730 cm^{-1}); C=O stretching (1730 cm^{-1}); CH_2 wagging (1330 cm^{-1}); C—O stretching (1090 cm^{-1}); CH_2 rocking + C—C stretching (890 cm^{-1}); and Ag—O stretching (240 cm^{-1}). Note, however, that the possible coexistence of both the 2-oxoethoxy and ethylenedioxy intermediates at 360 K makes the strict assignment of modes other than those clearly belonging to the aldehydic group tentative.

3. C–H Bond Activation Kinetics of Ethylenedioxy and 2-Oxoethoxy. The kinetics of 1,2-ethanedioxy decomposition (eq 13) and of 2-oxoethoxy decomposition (eq 16) were tracked by following the evolution of ethylene glycol at 365 K and of glyoxal at 380 K, respectively. Since ethylene glycol is not a direct product of $-OCH_2CH_2O-(a)$ β-hydrogen removal but is formed only after hydrogen surface diffusion and two sequential reactions with a second $-OCH_2CH_2O-(a)$ species, its evolution will be a direct measure of the initial dehydrogenation step only if the subsequent steps (eq 14 and 15) occur at a much faster rate than the initial C–H bond cleavage (eq 13). Since molecularly adsorbed ethylene glycol desorbs rapidly by 250 K on this surface (this work) and hydrogen atom diffusion on Ag(110) is very rapid as shown by its facile recombination below 200 K,[33] the evolution of ethylene glycol at 365 K is solely controlled by the rate of ethylenedioxy decomposition, i.e., the rate of hydrogen atom production. This deduction is further supported by the fact that the surface species 2-hydroxyethoxy ($HOCH_2CH_2O(a)$) could not be isolated in the 360 K anneal (as implied by the absence of a loss in the O–H stretch region), and is consistent with ethylenedioxy decomposition being the rate-determining step in ethylene glycol formation at 365 K. Furthermore, the fact that the kinetics of hydrogen and ethylene glycol formation are the same (as evidenced by their co-evolution at 365 K) rules out any recombination step as the rate-limiting step. On the other hand, glyoxal is a direct product of β-hydrogen removal from $O{=}CHCH_2O-$, and its evolution at 380 K is a direct measure of the kinetics for that process since the desorption of molecular glyoxal, itself, occurs at 250 K on this surface (unpublished results) and therefore cannot be rate-limiting at 380 K. We thus conclude that the Arrhenius parameters determined are for reactions 13 and 16, respectively.

Arrhenius activation parameters for the decomposition of both $OCH_2CH_2O(a)(OCD_2CD_2O(a))$ and $O{=}CHCH_2O(a)$-$(O{=}CDCD_2O(a))$, eq 13–17, were obtained by the method of heating rate variation.[34] Twelve different flash desorptions were performed at different heating rates varying from 0.9 to 11.5 K/s after the Ag(110) surface had been predosed with 0.25 ± 0.06 ML of O(a) at 300 K and saturated with ethylene glycol (≈20

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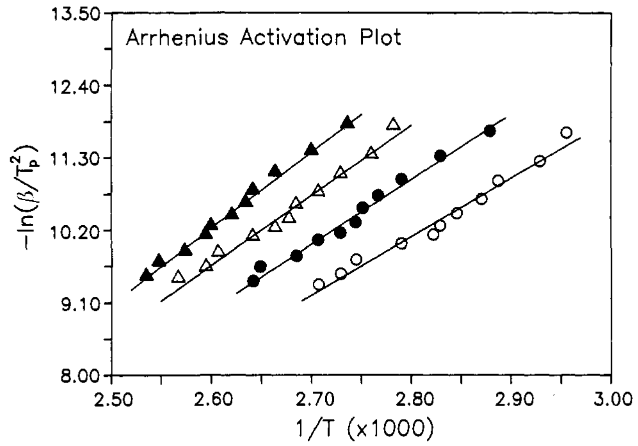

Figure 9. Arrhenius activation plot for the reaction of $HOCH_2CH_2OH$ (open figures) and $HOCD_2CD_2OH$ (closed figures) with Ag(110) covered with 0.25 ML of O(a). Shown are the plots for the evolution of ethylene glycol associated with the initial dehydrogenation of ethylenedioxy to form ethoxy-2-al (o) and for the evolution of glyoxal from the dehydrogenation of 2-oxoethoxy (Δ).

L of exposure) at 150 K. In addition, prior to each flash desorption the sample was heated to 275 K to desorb molecularly adsorbed $(CH_2OH)_2$ and water, thus isolating the ethylenedioxy species. The resultant Arrhenius plots are shown in Figure 9 and the calculated activation parameters are listed in Table III. For comparison, kinetic parameters for methoxy decomposition on both Ag(110) and Cu(110) have been included (no kinetic data are available for ethylene glycol on Cu(110)). If we assume that methoxy decomposes via the same transition state on both Ag(110) and Cu(110), then the assumption of a preexponential factor of 10^{13} s^{-1} made in ref 1 for methoxy decomposition on Ag(110) seems valid, and we may compare both the preexponential factor and activation energy for this process to our results. Such comparison suggests that the added stability of the ethylenedioxy species ($-OCH_2CH_2O-$) over that of the corresponding acyclic methoxy species (CH_3O-) is largely entropic in nature. Whereas methoxy exhibits the normal first-order preexponential factor of 10^{13} s^{-1} which corresponds to no net change in entropy between methoxy in the adsorbed state and in the transition state, i.e., $\Delta S = 0$ cal/K·mol, $-OCH_2CH_2O-$ decomposition (eq 13) exhibits a preexponential factor of $10^{10.6\pm0.5}$ s^{-1}, which in turn corresponds to a value of ΔS of approximately −10.4 cal/K·mol. This negative value for ΔS suggests that the transition state formed in going from ethylenedioxy to 2-oxoethoxy, which involves bringing one of the CH_2 groups in $-OCH_2CH_2O-$ in close proximity with the surface in order for C–H bond scission to occur, has much less freedom than the adsorbed $-OCH_2CH_2O-$ species. Currently, we can only speculate on the origin of this difference in the entropy of activation, but it is quite possible that the difference arises from sharply contrasting modes of bonding between mono- and dialkoxides. It is quite likely that the methoxy species prefers a binding site of high coordination with the oxygen atom bound to the long bridge site in the trough of the Ag(110) surface, analogous to atomic oxygen on this surface.[35] Such a site would severely restrict rotational motion of the methoxy species about the surface normal and a small entropy of activation would arise. On the other hand, the dialkoxide is able to chelate a single silver atom and retain appreciable rotational freedom about both the surface normal and an axis normal to the close-packed direction. Loss of free rotation about the surface normal alone would correspond to a ΔS of ≈ -5 cal/K·mol.[36] Thus we attribute at least a portion of this difference in activation entropy between alkoxides and dialkoxides to differences in bonding (see Figure 10).

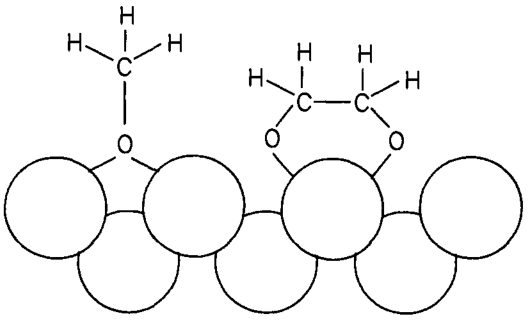

Figure 10. Likely bonding sites for methoxy and ethylenedioxy on the Ag(110) surface.

The enhanced stability of the cyclic ethylenedioxy series over its acyclic counterpart, methoxy, is the surface analogue of a phenomenon which has been previously observed in organoplatinum chemistry (see ref 15, and eq 7 and 9) for these and several other species.[14-17] Molecular orbital calculations on cyclic complexes of this type have suggested that β-hydride elimination from such a complex requires enough rearrangement and distortion from the equilibrium geometry to represent a moderately large energy barrier,[17] which accounts for the added stability over their acyclic counterparts. This same reasoning may be carried over to surfaces to explain the added stability of the ethylenedioxy species relative to methoxy on Ag(110). It is interesting to note, however, that on the Ag(110) surface the stability of the cyclic $-OCH_2CH_2O-$ surface species relative to the acyclic CH_3O- surface species is not as dramatic as that observed in platinum complexes (see eq 7 and 8 and ref 15). This difference is most likely due to the absence of uncoordinated adjacent metal atoms in the complexes, whereas on a surface the cyclic species almost certainly has several sites available for β-hydride elimination to take place. Furthermore, our kinetic data strongly suggest that on the Ag(110) surface the difference in the stability between alkoxides and dialkoxides is largely entropic.

The kinetics of the decomposition of 2-oxoethoxy, unlike those which were measured for ethylenedioxy, exhibited a more "normal" preexponential factor of $10^{11.7\pm0.5}$ s^{-1}. Therefore, its relatively high decomposition temperature seems to be enthalpic in nature, and, indeed, the measured activation energy of 21.0 ± 0.9 kcal/mol is some 3.5 kcal/mol greater than that for methoxy decomposition on this surface. This result seems odd since the stability of acyclic alkoxy species has been shown to correlate with the strength of the C–$\underset{\sim}{H}$ bond being activated by the surface,[5] and the strength of the C–H bond in the CH_2 group of $O{=}CHCH_2O{-}(a)$ is almost certainly weaker than those in methoxy owing to the electron-withdrawing properties of the carbonyl group. A possible explanation of this added stability might be that the carbonyl group interacts with the surface in a way which stabilizes the intermediate and/or inhibits C–H bond scission at the CH_2 group. We have recently observed structural ordering of the C≡C bond in $HC{\equiv}CCH_2O-$ on Ag(110) which lends plausibility to this suggestion.[37]

IV. Conclusions

Ethylene glycol $(CH_2OH)_2$ is reversibly adsorbed on the clean Ag(110) surface and desorbs by 260 K. The vibrational spectra of multilayer and monolayer $(CH_2OH)_2$ are in good agreement with that of the liquid-phase IR, indicating that little perturbation of the bonding in $(CH_2OH)_2$ occurs upon adsorption, although differences in the relative intensities of the vibrational bands between the two adsorption states suggest that the monolayer species is bound to the surface via both oxygen atoms.

On the oxidized surface, ethylene glycol reacts with O(a) to yield adsorbed water and ethylenedioxy ($OCH_2CH_2O(a)$). The $OCH_2CH_2O(a)$ species is stable up to a temperature of 350 K, where C–H bond-breaking and re-formation occur, leading to the evolution of $(CH_2OH)_2$ at 365 K, glyoxal $(CHO)_2$ at 380 K, and H_2 at both temperatures. This cyclic surface intermediate is more stable than the methoxy species on the same surface. This added stability seems to be due to entropic effects ($\Delta S = -10.4$ cal/

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K·mol), suggestive of a transition state which has much less freedom than the adsorbed $-OCH_2CH_2O-$ species. No evidence of glycoaldehyde ($HOCH_2CHO$) production was found. The decomposition of ethylenedioxy is shown to proceed via an $O{=}CHCH_2O(a)$ intermediate by the appearance of new vibrational bands at 1730 and 2730 cm^{-1} assignable to aldehydic C=O and C—H stretches. The presence of coadsorbed oxygen atoms during the decomposition of $OCH_2CH_2O(a)$ results in very different chemistry and is the subject of a separate study.[18]

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Registry No. $(CH_2OH)_2$, 107-21-1; Ag(110), 7440-22-4; oxygen, 17778-80-2.

Photolysis of Amminepentacarbonylchromium in Hydrogen-Containing Matrices: Characterization of an H–H Stretching Vibration in Matrices

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Abstract: Irradiation of $Cr(CO)_5NH_3$ (I) in argon matrices doped with dihydrogen gives good yields of $Cr(CO)_5(H_2)$ (II). The high yields are obtained because the ammonia can be removed from I by photons the frequencies of which are not absorbed by II. The carbonyl bands of the infrared spectrum of II are perturbed by the presence of the nearby ammonia that had been ejected in the photodecomposition of I. Thus, the spectrum of II is somewhat altered from what is observed when II is formed from $Cr(CO)_6$ (III). With use of FTIR, adequate amounts of $Cr(CO)_5(H_2)$ have been prepared from both I and III so that most of the vibrational features between 4300 and 450 cm^{-1} have been observed, including the H–H stretch. The H–H stretching vibration gives rise to three absorptions at 3087, 3027, and 2997 cm^{-1}. The band at 3027 cm^{-1} exhibits a width at half height of 32 cm^{-1}, nearly twice the width of the other two bands. The relative prominence of the broad band at 3027 cm^{-1} correlates with the size of the host atom. In xenon and krypton matrices this band is most prominent, while in argon and, in particular, in argon doped with ammonia the two sharper bands are most prominent. Although the H–D stretch and the D–D stretch exhibit some unresolved splittings, the splittings are not nearly as large as that exhibited by dihydrogen, even allowing for the greater reduced masses of the heavier isotopomers. Mass-dependent splittings are also observed in the $Cr–H_2$ stretching vibration. The unusual bredth of the H–H stretching vibration at 3027 cm^{-1} is ascribed to the large torsional amplitude of diprotium. No theory explains the splittings that are observed in both the H–H and the $M–H_2$ stretching vibrations. Dynamic effects probably play a role in the splittings because the corresponding modes in the spectra of the heavier isotopomers are not split nearly as much.

It has been possible to synthesize a number of metal carbonyl dihydrogen complexes in inert gas matrices by irradiating stable 18-electron precursors with ultraviolet light.[1-4] Typically a carbonyl ligand is lost, and dihydrogen can compete with this carbonyl group for the vacated coordination site. The carbonyl group remains in the cage of any newly formed dihydrogen complex and can recoordinate if the dihydrogen vacates the coordination site. This reversal places a limit on the synthetic yield of the dihydrogen complex in a matrix because the ultraviolet photons that are used to remove the original carbon monoxide ligand are frequently capable of also causing the dihydrogen to be ejected. With prolonged irradiation, a photostationary state is established. Thus, in the matrix experiments that have been reported from this laboratory, the concentration of dihydrogen adducts has never been large enough for the observation of some key spectroscopic features, in particular the H–H stretching vibration.

A novel synthetic strategy was developed for dihydrogen complexes of the group 6 pentacarbonyls when it was recognized that the bonding between dihydrogen and the metal results in a significant d orbital splitting because of both σ and π interactions. The first observed optical transition for $Cr(CO)_5(H_2)$ occurs at 364 nm.[5] Reasoning that if an 18-electron precursor complex absorbed to the red of this transition, then it might be activated with light that the dihydrogen complex would not absorb. A whole class of colored $LM(CO)_5$ complexes exist in which L is a ligand that is capable of only σ bonding. Accordingly, $M(CO)_5NH_3$ for W and Cr were synthesized and matrix isolated in the presence of H_2. Irradiation with visible light produced large quantities of molecular hydrogen adducts. Here, we report the first observation of the H–H stretching vibration that has been observed at such low temperature and show evidence for the interaction of the ejected NH_3 with the carbonyl fragment. Subsequent to the initiation of this project, an FTIR was purchased and the enhanced signal-to-noise has made it possible to observe the H–H stretch of $Cr(CO)_5(H_2)$ formed from $Cr(CO)_6$. This has proven to be essential for the assignment of causes for the complexities that are herein reported.

Experimental Section

$Cr(CO)_5NH_3$ was prepared from $Cr(CO)_6$ by irradiating a dry THF solution with a medium pressure mercury lamp while bubbling NH_3 through the solution.[6] The crude product was concentrated and deposited onto an alumina column through which was passed hexane. This procedure stripped off the bulk of unreacted $Cr(CO)_6$. Subsequently, the

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