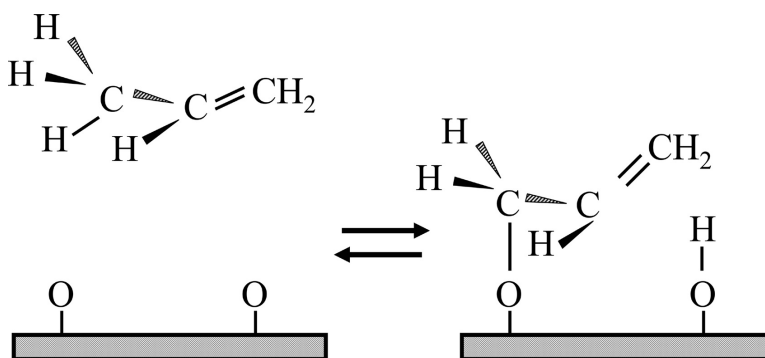


Insight into the Partial Oxidation of Propene: The Reactions of 2-Propen-1-ol on Clean and O-Covered Mo(110)

L. J. Deiner, J. G. Serafin, C. M. Friend, S. G. Weller, J. A. Levinson, and R. E. Palmer

J. Am. Chem. Soc., **2003**, 125 (43), 13252-13257 • DOI: 10.1021/ja030250q • Publication Date (Web): 02 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Insight into the Partial Oxidation of Propene: The Reactions of 2-Propen-1-ol on Clean and O-Covered Mo(110)

L. J. Deiner,^{||} J. G. Serafin,[⊥] C. M. Friend,^{*||†} S. G. Weller,[‡] J. A. Levinson,^{||} and R. E. Palmer[‡]

Contribution from the Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, The Dow Chemical Company, P.O. Box 8361, South Charleston, West Virginia 25303, Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138, and Centre for Chemical Physics, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, B15 2TT, U.K.

Received April 23, 2003; E-mail: friend@chemistry.harvard.edu

Abstract: The reactions of 2-propen-1-ol (allyl alcohol) were studied on clean and O-covered Mo(110) to understand the effect of resonance stabilization and the presence of surface oxygen on reaction selectivity. Propene is the only gaseous hydrocarbon product evolved from allyl alcohol reaction on O-covered Mo(110). Water and dihydrogen are also produced, along with a small amount of adsorbed carbon. We estimated, using X-ray photoelectron spectroscopy, that approximately 70% of the 0.11 ML of 2-propen-1-ol that reacts forms propene. In contrast, the dominant reaction pathway on the clean surface is nonselective decomposition to adsorbed carbon and hydrogen, leading to a 23% selectivity for propene formation. On both clean and O-covered Mo(110), X-ray photoelectron spectroscopy and infrared spectroscopy identify allyloxy as the reaction intermediate yielding propene. These results are discussed in the context of propene oxidation and periodic trends in reactivity.

Introduction

The reactions of radicals on surfaces form the basis of a wide range of hydrocarbon processing applications, most notably polymer synthesis.¹ Within this realm, allyl radicals have gained special attention for their role in olefin oxidation on bismuth molybdates, Ir,² and metal oxide catalysts.^{3,4} In addition, the allyl radical is thought to be a key species in the reduction of NO_x by propene over the Cu-ZSM-5 catalyst.⁵ In both partial oxidation and propene-assisted reduction of NO_x, it is proposed that allyl radical forms an allyloxy intermediate. 2-Propen-1-ol or allyl alcohol (H₂C=CH-CH₂-OH) provides a path to the potentially important allyloxy intermediate and a means for evaluating its subsequent reaction. In addition, the allyl alcohol molecule provides more general insight into reactivity trends associated with bifunctionality and with resonance stabilized radicals.

The reaction of 2-propen-1-ol has been studied previously on Ag(110),^{6,7} Rh(111)⁸ and Cu(110).⁹ On clean Ag(110),

2-propen-1-ol adsorbs reversibly. Covering the Ag(110) surface with oxygen activates the allyl alcohol molecule, which produces dihydrogen, water, acrolein, and allyl alcohol. An allyloxy intermediate is proposed.^{6,7} The same intermediate is also proposed for the reaction of allyl alcohol on Rh(111);⁸ however, CO and H₂ are produced rather than hydrocarbons. On clean and O-covered Cu(110),⁹ the reaction of allyl alcohol is proposed to proceed to various oxymetalloxy species in addition to allyloxy. Propanal, acrolein, *n*-propyl alcohol, hydrogen, propylene, and water are all evolved. From these examples, it is clear that the selectivity of the reaction of 2-propen-1-ol varies substantially with the identity of the surface and with the presence or absence of oxygen; specifically, the activity of the surface for C-H activation. The C-O bond is retained in all cases, with the exception of propylene evolution from Cu(110).

The present study examines the reactions of allyl alcohol on clean and O-covered Mo(110). Allyloxy forms on both clean and O-covered Mo(110) as reported for Ag, Cu, and Rh. The strong Mo-O bond enthalpy provides a thermodynamic driving force for C-O bond dissociation. Hence, C-O dissociation occurs, yielding propene on both clean and O-covered Mo(110). The selectivity for propene evolution also depends on the presence of oxygen. Oxygen on clean Mo(110) decreases the amount of allyl alcohol that reacts, whereas it increases the selectivity. This is in direct opposition to the trend of oxygen

^{||} Department of Chemistry, Harvard University.

[⊥] The Dow Chemical Company.

[†] Division of Engineering and Applied Sciences, Harvard University.

[‡] The University of Birmingham.

(1) Fressenden, R. J.; Fressenden, J. S. *Organic Chemistry*, 6th ed.; Brooks/Cole Publishing Co.: Pacific Grove, 1998; Vol. 1.

(2) Karseboom, S. G.; Davis, J. E.; Mullins, C. B. *Surf. Sci.* **1998**, *398*, 11-27.

(3) Carter, R. N.; Anton, A. B.; Apai, G. *J. Am. Chem. Soc.* **1992**, *114*, 410-441.

(4) Carter, R. N.; Anton, A. B.; Apai, G. *Surf. Sci.* **1993**, *290*, 319-334.

(5) Matyshak, V. A.; Ukharskii, A. A.; Il'ichev, A. N.; Sadykov, V. A.; Korchak, V. N. *Kinet. Catal.* **1999**, *40*, 105-111.

(6) Solomon, J. L.; Madix, R. J. *J. Phys. Chem.* **1987**, *91*, 6241-6244.

(7) Solomon, J. L.; Madix, R. J.; Stohr, J. *J. Chem. Phys.* **1988**, *89*, 5316-5322.

(8) Brown, N. F.; Barteau, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 4258-4265.

(9) Brainard, R. L.; Peterson, C. G.; Madix, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4553-4561.

activation observed for Ag(110). On Mo(110), oxygen inhibits C–H dissociation and most likely also blocks adsorption sites for the allyloxy. The critical influence oxygen exerts over selectivity and C–H bond dissociation is discussed in the context of other Mo-catalyzed reactions, especially olefin oxidation.

Experimental Section

All experiments were performed in two stainless steel ultrahigh vacuum chambers that have been described in detail elsewhere.^{10,11} Briefly, the first chamber has a base pressure of $<3 \times 10^{-10}$ Torr, and it is equipped with a UTI 100c mass spectrometer, low-energy electron diffraction (LEED) optics, and an X-ray photoelectron spectrometer (PHI ESCA 5300) consisting of a Mg anode X-ray source and a hemispherical electron energy analyzer. The second chamber has a base pressure of $\sim 1 \times 10^{-10}$ Torr and is equipped with a quadrupole mass spectrometer (UTI model 100C), an Auger electron spectrometer, low-energy electron diffraction optics (LEED), and is interfaced with a Fourier transform infrared spectrometer (Thermo Nicolet Nexus 670).

The oxygen overlayer was prepared by directed dosing of O₂ at 100 K followed by heating ($dT/dt \approx 10$ K/s) to 500 K. This procedure yields an approximate coverage of 0.67 ML and saturates high coordination sites without inducing oxygen dissolution into the bulk.¹² Between each experiment, the crystal was cleaned by oxidation at 1200 K followed by rapid heating to ~ 2300 K to remove residual oxygen. Cleanliness was confirmed by Auger electron spectroscopy and low-energy electron diffraction.

Allyl alcohol (Aldrich, 99+%) was purified by multiple freeze–pump–thaw cycles prior to use each day. Allyl alcohol was dosed via directed dosing with the crystal positioned ~ 5 mm away from the doser. The dose was controlled by varying the exposure time to a constant flux of reagent as measured by a background pressure increase of 1×10^{-10} Torr.

Temperature-programmed reaction data were collected in multiplex mode, recording the signal of between four and eight masses per run. All experiments were performed with the crystal biased at -90 V to avoid electron-induced reaction from the mass spectrometer filament. Temperature was measured with a W/Re (5%/26%) thermocouple. Radiative heating was used to achieve the temperature ramp to 800 K (average $dT/dt \approx 10$ K/s). Electron bombardment heating was used to reach temperatures above 800 K (average $dT/dt \approx 20$ K/s). The filament was briefly flashed prior to temperature-programmed reaction data collection to avoid recording artifacts of filament outgassing.

Infrared spectra were obtained at a crystal temperature of ~ 120 K. The moving mirror path length was set to allow a 4 cm^{-1} resolution. Five hundred scans were collected per experiment, and data were recorded using a liquid nitrogen-cooled MCT-A semiconductor photodiode detector.

Results

Temperature-Programmed Reaction Studies on O-Covered Mo(110). Propene, water, and dihydrogen are evolved during the reaction of 2-propen-1-ol on O-covered Mo(110) (Figure 1). A small amount of the 2-propen-1-ol also decomposes completely, leading to the formation of CO in a broad peak centered at ~ 1000 K (data not shown). Approximately 0.03 ML of CO is evolved after nonselective decomposition. This value was calculated by comparison to temperature-programmed reaction data for clean Mo(110) saturated with methoxy which yields ~ 0.35 ML of CO.^{13,14}

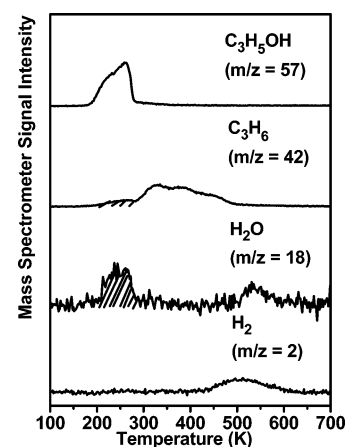


Figure 1. Temperature-programmed reaction spectra for a saturation coverage of 2-propen-1-ol on O-covered Mo(110). The shaded area indicates fragmentation of 2-propen-1-ol. The heating rate is ~ 10 K/s over the range of the data.

Table 1. Mass Spectra Fragmentation of Products of 2-propen-1-ol Reaction on Mo(110) (1×6 -O) and Clean Mo(110)^a

	<i>m/z</i> 29	<i>m/z</i> 39	<i>m/z</i> 41	<i>m/z</i> 42
products ($\Theta < \Theta_{\text{sat}}$)	0	82	100	65
products after subtraction of fragments from 2-propen-1-ol molecular peak ($\Theta < \text{multilayer}$)	0	85	100	64
products of 2-propen-1-ol on clean Mo(110)	0	85	100	61
2-propen-1-ol	100	48	8	3
propene	1	82	100	63
ethene	100	0	0	0
acetaldehyde	100	0	4	10
cyclopropane	0	78	100	100

^a All fragmentation patterns obtained from multilayer or physisorbed cracking data for authentic samples. All masses normalized to their highest intensity mass of the listed group.

Molecular desorption of 2-propen-1-ol from O-covered Mo(110) also occurs between 180 and 275 K. Sublimation of 2-propen-1-ol multilayers is observed between 135 and 180 K (data not shown). The minimum exposure necessary for multilayer sublimation (1 min for $\Delta P = 1 \times 10^{-10}$ Torr) is defined as saturation coverage. The yields of propene, water, and dihydrogen production are all at a maximum at this coverage.

At saturation coverage of 2-propen-1-ol, propene (42 amu) is evolved in an unresolved set of features beginning at 275 K, concurrent with the cessation of molecular desorption. Propene evolution continues up to 500 K. Propene was identified as the only hydrocarbon reaction product based on quantitative analysis of a comprehensive mass search between 2 and 86 amu. The mass spectrometer fragmentation pattern obtained for the product was compared to those for authentic samples of propene, ethene, cyclopropane, and acetaldehyde (Table 1). Oxygenate products were generally ruled out on the basis of the absence of a *m/z* 29 peak characteristic of oxygen-containing hydrocarbons. Cyclopropane was ruled out on the basis of the measured product ratio *m/z* 41:*m/z* 42 of $\sim 100:50$, which is very different from the ratio measured for an authentic sample of cyclopropane, $\sim 99:100$ (data not shown). There was no evidence for C₆ species since no peaks between masses 70 and 86 were detected. There was also no evidence of CO or C₂H₄ on the basis of the intensities of 26, 27, and 28 amu, which were consistent with hydrocarbon production.

(10) Xu, X.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 6779–6785.

(11) Weldon, M. K.; Friend, C. M. *Surf. Sci.* **1994**, *310*, 95–102.

(12) Queeney, K. T.; Friend, C. M. *J. Phys. Chem. B* **2000**, *104*, 409–415.

(13) Chen, D. A.; Friend, C. M. *J. Phys. Chem. B* **1997**, *101*, 5712–5716.

(14) Queeney, K. T.; Friend, C. M. *J. Chem. Phys.* **1998**, *109*, 6067–6074.

Table 2. Mass Spectra Fragmentation of Products of 2-propen-1-ol Reaction on OD-Covered 0.66 ML O on Mo(110)

	<i>m/z</i> 39	<i>m/z</i> 40	<i>m/z</i> 41	<i>m/z</i> 42
products of 2-propen-1-ol reaction on OD covered Mo(110)-(1 × 6)-O corrected for fragmentation from allyl alcohol and <i>d</i> ₁ -propene ^a	86	29	100	63
propene ^b	82	33	100	63

^a The ratio of *d*₀ propene to *d*₁ propene was 58:42. ^b Propene fragmentation pattern obtained from multilayer cracking data for authentic sample. All masses normalized to their highest intensity mass of the listed group.

The possibility of gaseous allyl radical evolution was definitively ruled out on the basis of the fact that deuterium is incorporated into the hydrocarbon produced from the reaction of 2-propen-1-ol in the presence of OD on O-covered Mo(110). OD was formed by condensing D₂O on the O-covered surface at 100 K and subsequent brief heating to 300 K. Infrared spectroscopy was used to determine that this procedure yielded adsorbed OD (data not shown). In the presence of OD, the ratio of 42:43 changes from ~100:2 to ~3:1, whereas the ratio of 42:44 remains 1:0. All masses between 39 and 44 amu were monitored in these experiments (Table 2). As such, it is clear that propene incorporates a single deuterium when it is formed on the surface containing OD. Indeed, all intensity of the masses between 39 and 43 is accounted for by a mixture of *d*₀-propene and *d*₁-propene for reaction on the OD-covered surface (Table 2). If allyl radical were evolved, then there would be unaccounted for intensity in the *m/z* 41 channel. Notably, to within the error of our measurement, there is no extra intensity in *m/z* 41.

The only other volatile products are dihydrogen and water. H₂ (2 amu) desorbs in a single peak from 450 to 600 K. A small amount of water (18 amu) evolves between 500 and 550 K.

Temperature-Programmed Reaction Studies on Clean Mo(110). The reactions of 2-propen-1-ol on clean Mo(110) are analogous to those on the O-covered surface; however, the selectivity for propene production is lower, and the overall reactivity is higher. Furthermore, no water is produced. On clean Mo(110), the predominant reaction pathway for 2-propen-1-ol nonselective decomposition is signified by CO desorption at ~1000 K. The amount of CO evolved at high temperature (~1000 K) is ~0.17 ML, or ~6 times more than the O-covered surface, as calibrated against the CO evolution from a methoxy-saturated surface.^{13,14}

Propene, molecular alcohol, and H₂ also evolve during temperature-programmed reaction (Figure 2). As the amount of 2-propen-1-ol exposed to the surface is increased, multilayers sublime at 180 K (data not shown), with the minimum exposure required for multilayer sublimation defined as saturation. Molecular 2-propen-1-ol (57 amu) desorption is concentrated between 180 and 225 K. The cessation of most of the molecular alcohol desorption at 225 K is ~50 K lower than on the O-covered surface, and the amount of molecular alcohol evolved is ~50% of the amount evolved from the O-covered surface. No carbon-containing products other than propene and 2-propen-1-ol were detected in a comprehensive search of all masses between 2 and 80 amu during temperature-programmed reaction of a saturation exposure of 2-propen-1-ol. Quantitative analysis

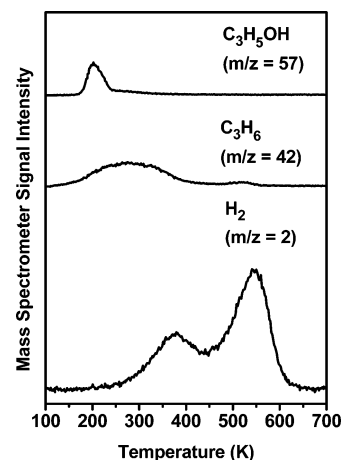


Figure 2. Temperature-programmed reaction spectra for a saturation coverage of 2-propen-1-ol clean on Mo(110). The heating rate is ~10 K/s over the range of the data.

of the mass spectrometric data identified propene as described for the O-covered surface (Table 1).

Propene is evolved in broad feature between ~180–450 K, and in a small peak in the range of 450–550 K (Figure 2). The lower temperature feature accounts for ~94% of the propene formed. Notably, the onset of propene evolution is nearly 100 K lower than for the O-covered surface. The absolute amount of propene evolved is roughly comparable on the clean and O-covered surfaces. Preadsorption of deuterium on Mo(110) prior to a saturation exposure of 2-propen-1-ol produces a mass shift associated with incorporation of a single deuterium atom in the product based on a similar analysis as performed for the O-covered surface (data not shown). In addition, H₂, HD, and D₂ are evolved. The observation that only one deuterium is incorporated in the propene product suggests that there is no reversible C–H bond activation of the propene-producing intermediate.

Dihydrogen formation occurs via two distinct processes, as signified by peaks centered at 375 and 550 K (Figure 2). The 550 K peak is approximately twice as intense as the 375 peak, which is the reverse of the observed peak intensity ratio for H desorption from clean Mo(110) (data not shown). The additional intensity of the second hydrogen peak in the reaction of 2-propen-1-ol on Mo(110) indicates that hydrogen from nonselective decomposition contributes strongly to this pathway, while hydrogen recombination accounts for most of the intensity of the first peak.

X-ray Photoelectron Spectroscopy Studies on O-Covered Mo(110). X-ray photoelectron spectroscopy data of 2-propen-1-ol on O-covered Mo(110) at 100 K provides evidence for two species with intact C–O bonds assigned to 2-propen-1-ol and 2-propenoxide (allyloxide). The O(1s) region was fit with features due to atomic oxygen (530.9 and a broad satellite at 532.5) and two overlapping peaks at 533.0 and 533.8 eV (Figure 3a, Table 3). The peaks at 533.0 and 533.8 eV are assigned to the oxygen of alkoxide and alcohol, respectively, via comparison to reference data.¹⁵ The large peak at 530.9 eV is due to the Mo–O species of the underlying oxygen layer, assigned via comparison to the spectrum of as-prepared oxygen overlayer with 0.67 ML of oxygen. The corresponding C(1s) data are also

(15) Serafin, J. G.; Friend, C. M. *Surf. Sci.* **1989**, *209*, L163–L175.

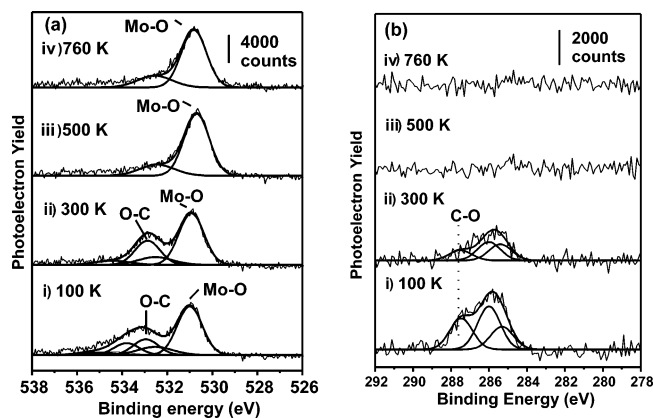


Figure 3. X-ray photoelectron data for 2-propen-1-ol on O-covered Mo(110). (a) O(1s) and (b) X-ray photoelectron data for 2-propen-1-ol on O-covered Mo(110). (b) C(1s) spectra measured after adsorption of a saturation coverage adsorbed at 100 K: (i) as deposited; and heated to: (ii) 300 K; (iii) 500 K; and (iv) 760 K. The heating rate used was 10 K/s. All spectra were obtained after cooling to ~ 100 K.

Table 3. Peak Fits for O(1s) Region of X-ray Photoelectron Spectroscopy Data for 2-propen-1-ol on O-covered Mo(110)^{a,b}

	100 K		
binding energy (eV)	533.8	533.0	530.9
area	2.4	3.2	9.9
assignment	alcohol	alkoxide	Mo–O
	300 K		
binding energy (eV)	532.9	530.9	
area	4.9	10.5	
assignment	O–C	Mo–O	
	500 K		
binding energy (eV)	530.9		
area	12.5		
assignment	Mo–O		
	760 K		
binding energy (eV)	530.9		
area	11.6		
assignment	Mo–O		

^a Area in 10^3 cts·eV/s. ^b Satellite peaks are not included.

consistent with intact C–O bonds at 100 K, based on the substantial intensity above 286 eV (Figure 3b).

By 300 K, the high binding energy portion of the O(1s) peak (533.8 eV) disappears, suggesting that all intact alcohol desorbs or undergoes O–H bond cleavage. Mo–O from the oxygen overlayer (530.9, 532.5 eV) and C–O in the alkoxide (533.0 eV) remain visible in the O(1s) region. The intensity in the C(1s) region diminishes consistently with the observation of desorption in temperature-programmed reaction.

The O(1s) data indicate that there are no intact C–O bonds after heating 2-propen-1-ol on O-covered Mo(110) to 500 K. Only the Mo–O peak at 530.9 eV and the associated shoulder remain. Heating to 760 K does not significantly change the binding energy of this feature; however, the formation of water between 500 and 550 K leads to a decrease in the integrated intensity of $\sim 7\%$ (Figures 1 and 3a; Table 3). Comparison of the O(1s) peak from the 760 K spectrum to that of a reference spectrum for 0.66 ML of O on Mo(110) indicates that the reaction deposits approximately 0.10 ML of oxygen. Since no oxygenates other than water leave the surface, 0.10 ML is approximately the amount of 2-propen-1-ol that reacts. Temperature-programmed reaction data indicate that the amount of nonselective decomposition is 0.03 ML. Hence, the reaction of

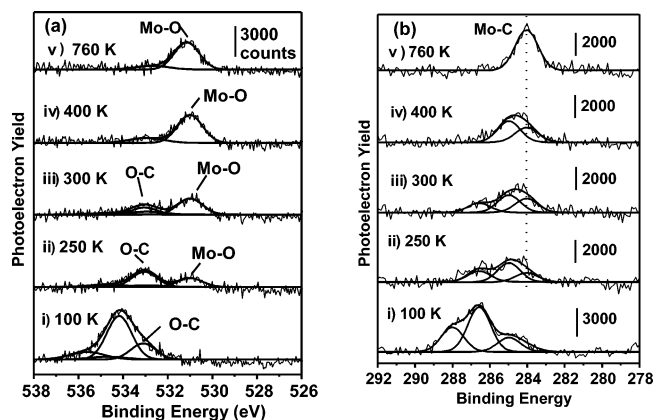


Figure 4. X-ray photoelectron data for 2-propen-1-ol on Mo(110). (a) C(1s) and (b) O(1s) spectra measured after adsorption of a saturation coverage adsorbed at 100 K: (i) as deposited; and heated to: (ii) 250 K, (iii) 300 K, (iv) 400 K, and (v) 760 K. The heating rate used was 10 K/s. All spectra were obtained after cooling to ~ 100 K.

2-propen-1-ol on O-covered Mo(110) has $\sim 70\%$ selectivity for propene formation. The amount of carbon from nonselective decomposition is less than the spectrometer detection limit of 0.07 ML (Figure 3biii, iv)

X-ray Photoelectron Studies on Clean Mo(110). X-ray photoelectron spectroscopy data indicates that the majority of C–O bonds of 2-propen-1-ol remain intact upon adsorption at 100 K on clean Mo(110) on the basis of the preponderance of intensity above 286 eV in the C(1s) region (Figure 4). There is no detectable atomic oxygen at 100 K in the O(1s) region, indicating little if any C–O dissociation (Figure 4).

As the surface is heated from 250 to 400 K, there is clear evidence for C–O bond scission: a peak due to atomic oxygen appears at 531 eV and intensity near 284 eV grows (Figure 4a,b). Nevertheless, there are some intact C–O bonds remaining after heating to 300 K, based on the persistence of peaks around 533 and 287 eV. After heating to 400 K, there is no evidence for intact C–O bonds in the X-ray photoelectron spectra (Figure 4a,b).

The amount of oxygen deposited through 2-propen-1-ol reaction on clean Mo(110) is estimated to be ~ 0.22 ML, based on the integrated area of the O(1s) peak for atomic oxygen measured after heating a saturation dose of 2-propen-1-ol to 760 K. The integrated area of the atomic oxygen peak is $\sim 30\%$ of that for the as-prepared oxygen overlayer with a coverage of 0.67 ML. Since temperature-programmed reaction data indicate that no oxygenates leave the surface between 100 and 760 K, the amount of 2-propen-1-ol that reacts on clean Mo(110) is also ~ 0.22 ML, or approximately double the amount that reacts on the O-covered surface. Comparison of the area of the C(1s) peak at 760 K to that of the C(1s) region of a reference spectrum of 0.25 ML CO on Mo(110) yields an estimate of the amount of carbon deposited from 2-propen-1-ol reaction of ~ 0.5 ML. Since each alcohol molecule undergoing complete decomposition yields three carbon atoms and one oxygen atom, it follows that 0.17 ML of 2-propen-1-ol decomposes nonselectively, i.e. there is $\sim 23\%$ selectivity for propene formation.

Reflectance Absorbance Infrared Spectroscopy Studies on O-Covered Mo(110). 2-Propen-1-oxy (allyloxy) is identified as the predominant intermediate prior to the formation of propene on the basis of reflectance absorbance infrared spectra

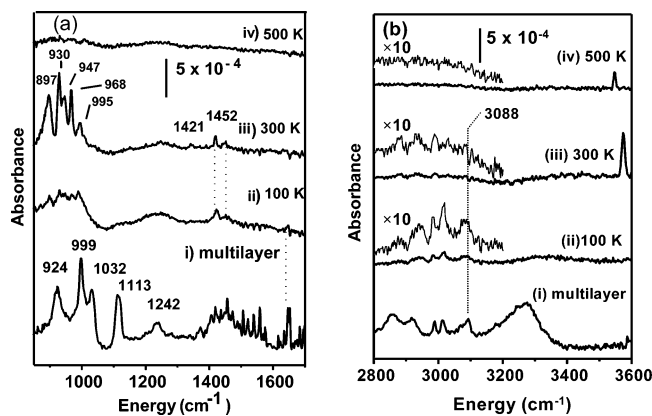


Figure 5. Infrared spectra collected after adsorption of 2-propen-1-ol on O-covered Mo(110) for regions between (a) 850–1700 cm^{-1} and (b) 2800–3750 cm^{-1} : (i) as deposited at 100 K; and after heating to: (ii) 300 K; and (iii) 500 K. All spectra were obtained at ~ 100 K and are ratioed to data obtained after heating to 760 K.

Table 4. Vibrational Assignments of 2-propen-1-ol on Clean and O-Covered Mo(110)^a and Comparison to η^3 -Allyl from Allyl Bromide on Cu(100)

vibrational mode	O-covered Mo(110)	clean Mo(110)	η^3 -allyl on Cu(100) ^a
$\rho_{\omega}(\text{CH})$	995	—	995
$\nu(\text{CCC})_{\text{sym}}$	968	968	968
CH_2 out-of-plane wag	947	945	948
CH_2 out of plane wag	930	933	937
$\nu(\text{C}-\text{O})$	897	897	—
$\rho_{\omega}(\text{CH}_2)$	—	—	886

^a Data collected after heating to 300 K and then cooling to 100 K for scan.¹⁶

in conjunction with the conclusion that there are intact C–O bonds on the surface up to 300 K. Features attributed to 2-propen-1-ol on O-covered Mo(110) for regions between (a) 850–1700 cm^{-1} and (b) 2800–3750 cm^{-1} : (i) as deposited at 100 K; and after heating to: (ii) 300 K; and (iii) 500 K. All spectra were obtained at ~ 100 K and are ratioed to data obtained after heating to 760 K. The heating rate is the same as in temperature-programmed reaction.

in conjunction with the conclusion that there are intact C–O bonds on the surface up to 300 K. Features attributed to 2-propen-1-ol on O-covered Mo(110) for regions between (a) 850–1700 cm^{-1} and (b) 2800–3750 cm^{-1} : (i) as deposited at 100 K; and after heating to: (ii) 300 K; and (iii) 500 K. All spectra were obtained at ~ 100 K and are ratioed to data obtained after heating to 760 K. The heating rate is the same as in temperature-programmed reaction.

These are the signature out-of-plane wagging and C–C–C symmetric stretching modes of the allyl skeleton as previously observed for η^3 -allyl on Cu(110) (Table 4).¹⁶ The peak at 897 cm^{-1} is assigned primarily to the $\nu(\text{C}-\text{O})$ of 2-propenoxy, although it is likely to couple to skeletal modes on the basis of analysis of density functional theory calculations and gas-phase spectra for the related molecule, 3-buten-1-ol.¹⁷ Furthermore, a similar peak with a strong $\nu(\text{C}-\text{O})$ component has been identified using isotopic labeling for 2-buten-1-ol on O-covered Mo(110).¹⁸ The $\nu(\text{C}=\text{C})$ at 1653 cm^{-1} and $\nu(\text{C}-\text{H})$ at 3078 cm^{-1} , expected for 2-propenoxy, are observed at 100 K for the saturation coverage spectrum (Figure 5). After heating to 300 K, these features are no longer visible above the noise. The lack of $\nu(\text{C}=\text{C})$ is most likely due to low surface concentration, but it is also possible that the surface intermediate reorients so as to reduce the component of the dynamic dipole perpendicular to the surface, thus decreasing the intensity. In addition to the 2-propenoxy modes, the 300 K spectrum contains a feature at 3578 cm^{-1} assigned to $\nu(\text{O}-\text{H})$ of adsorbed hydroxyl.

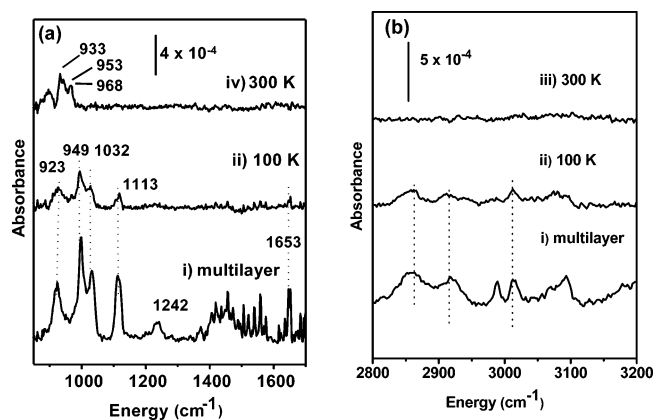


Figure 6. Infrared spectra after adsorption of 2-propen-1-ol on Mo(110) in the regions between (a) 850–1700 cm^{-1} and (b) 2800–3200 cm^{-1} (i) multilayer coverage; (ii) saturation coverage at 100 K; and (iii) saturation coverage heated to 300 K. All spectra ratioed to the surface heated to 760 K. The heating rate is the same as in temperature-programmed reaction.

No hydrocarbon intermediates are detected on the surface at 500 K using infrared spectroscopy. The $\nu(\text{O}-\text{H})$ mode at 3553 cm^{-1} is the only feature visible in the spectrum of allyl alcohol annealed to 500 K (Figure 5). This feature's intensity decreases as a result of a decrease in the coverage stemming from reaction to form propene and water. There is a 25 cm^{-1} frequency decrease observed between 300 and 500 K.

Reflectance Absorbance Infrared Spectroscopy Studies on Clean Mo(110). Reflectance absorbance infrared spectroscopy of 2-propen-1-ol on clean Mo(110) provides evidence for 2-propenoxy as a common reaction intermediate for propene formation on both the clean and O-covered surfaces. After annealing to 300 K, the 897 cm^{-1} , 933, 945, and 968 cm^{-1} features, identified on the O-covered surface as 2-propenoxy modes, are visible on the clean surface (Figure 6). Since X-ray photoelectron spectroscopy suggests that there may be other hydrocarbon species present on the clean surface at 300 K, there may be contributions to these peaks due to other intermediates. As expected, the $\nu(\text{O}-\text{H})$ mode is also absent from the clean surface spectrum, indicating that its formation requires surface oxygen.

Discussion

Our results indicate that allyl alcohol forms an allyloxy intermediate beginning at 100 K which then decomposes by C–O bond scission and C–H bond formation to yield gas-phase propene above 200 K. The evolution of propene from allyloxy is the reverse of propene oxidation; hence, our studies of the reaction of 2-propen-1-ol provide insight into this partial oxidation process.^{19–21}

The partial oxidation of propene entails the loss of hydrogen by the olefin followed by formation of a C–O bond, the reverse of the formation of propene from 2-propen-1-ol. Whether the reaction runs forward toward propene formation or in reverse toward oxygenate evolution, it is likely to proceed through the same allyloxy and transient allyl radical intermediates.²⁴ Indeed,

(16) Celio, H.; Smith, K. C.; White, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 10422–10423.

(17) Shishkov, I. F.; Shlykov, S.; Rousseau, B.; Peng, Z. H.; Van Alsenoy, C.; Geise, H. J.; Kataeva, O. N.; Herrebout, W. A.; Van der Veken, B. *J. Phys. Chem. A* **2001**, *105*, 1039–1049.

(18) Levinson, J. A.; Kretzschmar, I.; Sheehy, M. A.; Deiner, L. J.; Friend, C. M. *Surf. Sci.* **2001**, *479*, 273–286.

(19) Ressler, T.; Wienhold, J.; Jentoft, R. E.; Neisius, T. *J. Catal.* **2002**, *210*, 67–83.

(20) Kaddouri, A.; Del Rosso, R.; Mazzocchia, C.; Gronchi, R.; Fumagalli, D. *J. Therm. Anal. Calorim.* **2001**, *66*, 63–78.

(21) Nieto, J. M. L.; Fierro, J. L. G.; Tejuca, L. G.; Kremenc, G. *J. Catal.* **1987**, *107*, 325–337.

(22) Bol, C. W. J.; Friend, C. M. *J. Phys. Chem.* **1995**, *99*, 11930–11936.

the low temperature for C–O dissociation of allyloxy relative to, for example, 1-propoxy— ~ 200 K versus 375 K—correlates with the difference in their respective homolytic C–O bond strengths and is therefore consistent with formation of a transient radical.²⁵ Homolytic bond dissociation in methoxy bound to O-covered Mo(110) has been directly observed.¹⁴ Further, the balance between the rates of C–H, C=C, and C–O activation determines the selectivity of the reaction in both directions. As in the reaction of 2-propen-1-ol studied herein, the selective oxidation of propene requires a balance in terms of oxophilicity of the surface. On catalysts in which the lattice oxygen is weakly bound and hence highly reactive, total oxidation is favored over partial oxidation.²¹ Partial oxidation occurs more readily on catalysts in which the oxygen is more tightly bound and hence less reactive toward C–H and C=C activation.²¹ However, if the surface binds oxygen too tightly, oxygenates are not likely to be evolved.²⁶ In the industrial production of acrolein and acrylic acid from propene, water vapor is added to the reaction mixture to improve selectivity.²⁶ It is thought that the role of water is two-fold: it maintains a high oxidation state for the catalyst, preventing the formation of strongly bound oxygenates, and it blocks active sites which would otherwise lead to total oxidation to CO₂.²⁶ In addition, adsorbed OH from water may prevent indiscriminant C–H bond dissociation.

In our model studies and related work on single-crystal metals, we likewise observe the balance among the various types of bond activation as a determinant for reaction selectivity. Molybdenum metal is highly oxophilic and thus can readily activate O–H and C–O bonds, accounting for the high overall rate of reaction on clean Mo(110). However, clean Mo also induces facile C–H and C–C bond dissociation, which leads to nonselective decomposition. The presence of surface oxygen on Mo(110) mitigates C–H bond activation, resulting in greater selectivity for propene formation and less nonselective decomposition on O-covered Mo(110). This is true even though the Mo is still nearly zerovalent. In addition, the reactivity decreases, possibly due to a decrease in OH bond activation as a result of site blocking by oxygen. In other words, the alkoxide competes with oxygen for high coordination sites. This phenomenon of passivation of the Mo surface by oxygen has also been observed on other surfaces, e.g. for ethyl and 2-propyl formed from ethyl iodide and 2-propyl iodide on Rh(111).²²

In contrast, oxygen has the opposite effect—of activating bonds—on less reactive surfaces that have been studied. For example, Ag(110) does not induce 2-propen-1-ol reaction, but oxygen on Ag(110) activates allyl alcohol allowing for acrolein formation.^{6,7} The inert nature of Ag(110) and Cu(100) also allows for C–C bond coupling rather than C–H bond dissociation in related systems. For example, 1,5-hexadiene is formed from allyl bromide on Cu(100)¹⁶ and allyl chloride on Ag(110).³

The temperature required for reaction also plays a strong role in determining selectivity as seen by comparison of the reactions of 2-propen-1-ol and 2-propen-thiol on Mo(110). For allyl alcohol on clean Mo(110), the selectivity for propene formation is $\sim 23\%$, less than half the selectivity observed for 2-propen-thiol on clean Mo(110).²³ Both species initially react through X–H (X = O or S) bond cleavage, yielding allyloxy from 2-propen-1-ol and 2-propen-thiolate formation for the sulfur analogue. The carbon–sulfur bond in 2-propen-thiolate is weak enough to allow substantial C–S bond activation by 120 K and propene formation from 160 to 250 K. In contrast, the majority of C–O bonds of allyloxy remain intact at 120 K with some persisting on the surface up to 400 K leading to propene evolution, which continues through 550 K. The generally higher temperature of C–O versus C–S bond activation allows the allyloxy intermediate to persist on the surface to higher temperatures than for the 2-propen-thiolate intermediate. At these higher temperatures, C–H and C–C bond activation, to yield nonselective decomposition products, effectively competes with propene evolution.

Finally, the rate of C–H bond formation after C–O bond scission—the reverse of the first step in propene activation—also affects the selectivity for propene formation from 2-propen-1-ol. After homolytic bond cleavage, hydrogen must be transferred from the surface or from adsorbed OH to the allyl radical for propene evolution to occur. The rate of hydrogen transfer depends on H availability (a function of hydrogen coverage and diffusion rate) and also on the strength of bonding to the surface. The need for carbon–hydrogen bond formation decreases the selectivity for propene formation from 2-propen-1-ol below what one would expect from its low C–O bond strength. In fact, the selectivity for propene formation from 2-propen-1-ol on clean Mo(110) is lower than for 1-propanol and 2-propanol on clean Mo(110).^{25,27} These results suggest that the presence of adsorbed OH, possibly due to addition of water, would promote propene formation from allyloxy. The same reasoning indicates that adsorbed OH would inhibit propene dissociation.

Conclusions

The reactions of allyl alcohol on clean and oxygen-covered Mo(110) proceed through an allyloxy intermediate which either yields propene or nonselective decomposition. The selectivity for propene formation is found to increase with oxygen coverage, illustrating the mitigating effects of oxygen on nonselective reaction of the hydrocarbon framework. Further, the selectivity for propene formation decreases with C–O bond cleavage temperature.

Acknowledgment. We gratefully acknowledge funding support from the Department of Energy under Grant No. DE-FG02-84-ER13289. In addition, L.J.D. thanks the Department of Defense for financial support under the National Defense Science and Engineering Graduate Fellowship program.

JA030250Q

(23) Wiegand, B. C.; Friend, C. M.; Uvdal, P.; Napier, M. E. *Surf. Sci. Lett.* **1996**, 355, L311–L318.

(24) Carrazan, S. R. G.; Rives, V.; Vidal, R. *Spectrochim. Acta, Part A* **1996**, 52, 1107–1118.

(25) Wiegand, B. C.; Uvdal, P.; Serafin, J. G.; Friend, C. M. *J. Phys. Chem.* **1992**, 96, 5063–5069.

(26) SalehAlhamed, Y. A.; Hudgins, R. R.; Silveston, P. L. *J. Catal.* **1996**, 161, 430–440.

(27) Wiegand, B. C.; Uvdal, P.; Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, 113, 6686–6687.