Oxidation, Reduction, and Isomerization of Allyl Alcohol and 1-Propanol over Cu₂O(100)

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The reactivity of allyl alcohol and 1-propanol has been studied with TDS and XPS on the polar, Cu⁺-terminated, Cu₂O(100) surface. Allyl alcohol reacts on the (100) surface to give selective and nonselective oxidation products (acrolein, CO, CO₂, H₂O), an isomerization product (propionaldehyde), and a reduction product (propene). 1-Propanol also reacts on the (100) surface to give selective and nonselective oxidation products (acrolein, propionaldehyde, CO, CO₂, H₂O) and a reduction product (propene). Both alcohols dissociatively adsorb to form alkoxides. The alkoxide species undergo hydride elimination on the carbon α to the oxygen to form the corresponding aldehydes. The acrolein and propionaldehyde formed from the alcohols are linked by a common surface enolate intermediate which explains the similarity in C₃ products observed from the two alcohols. A low-temperature reaction to propene is attributed to pathways involving C–O bond scission from unsaturated surface oxygenates to give a surface allyl. Hydrogenation of the resulting allyl produces propene at low temperature.

Introduction

The partial oxidation of propene $(CH_2 = CHCH_3)$ to acrolein (CH2=CHCHO) is a useful model for the class of allylic oxidation reactions of olefins. The basic steps in the propene oxidation pathway have been widely studied, but the form of the final, oxygen-containing " σ -allyl" intermediate in the propene oxidation pathway has been the subject of debate.¹⁻⁵ The reaction of allyl alcohol (CH₂=CHCH₂OH) over bismuth molybdate catalysts has been studied previously in steady-state flow reactors to demonstrate that a reaction pathway to acrolein involving a surface allyloxy intermediate (CH2=CHCH2O-) is chemically viable.3,6 The allyloxy formed by the dissociation of allyl alcohol should be characteristic of the so-called σ -allyl obtained if oxygen insertion onto the end of a π -allyl occurs prior to the final hydrogen abstraction in propene oxidation to acrolein.^{3,6} In this study we have investigated the reactivity of allyl alcohol with $Cu_2O(100)$ for comparison with studies of propene oxidation.⁷ In conjunction with the allyl alcohol studies, the reactivity of 1-propanol was also studied on Cu₂O for insight into the effects of the C=C functionality on the reaction pathway.

Alcohol decomposition has been studied extensively on metal single-crystal surfaces; however, there are only two reported studies of higher alcohols on metal *oxide* single-crystal surfaces. 1-Propanol dissociatively adsorbs on the polar ZnO(0001)–Zn surface to form surface propoxy.⁸ Propoxy then undergoes either oxidation to a carboxylate (propionate) by nucleophilic attack of lattice oxygen or dehydrogenation to propionaldehyde. 1-Propanol decomposes on the TiO₂(001)-{011} faceted surface to give propene, propionaldehyde, water, and H₂ as reaction products.⁹ This pathway also proceeds through a propoxy intermediate, with propionaldehyde produced via hydride elimination and propene by deoxygenation of the propoxy accompanied by hydride elimination.⁹

The Cu₂O(100) surface used in this study is a reconstructed, Cu⁺-terminated surface which displays a $(3\sqrt{2}\times\sqrt{2})R45^\circ$ LEED pattern with many missing spots.¹⁰ No definitive model of the structure of the reconstructed surface is available. However, the periodicity of the reconstruction suggests a relaxation of top atomic layer Cu⁺ cations, possibly associated with a weak Cu⁺-Cu⁺ bonding interaction.¹⁰ No lattice oxygen is available in the top atomic layer of the ideal $Cu_2O(100)$ surface, and the top-layer Cu^+ cations are singly coordinated to oxygen with one vacant coordination site. A more complete description of the characterization of the clean $Cu_2O(100)$ surface has been reported previously.¹⁰

Experimental Section

All experiments were performed in a dual-chamber, ultrahigh-vacuum (UHV) system equipped with X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS). Dosing was accomplished by backfilling through a variable leak valve. For all TDS experiments the sample was heated at a linear rate of 2 K/s. An Inficon Quadrex 200 was used to monitor up to 6 mass numbers simultaneously during the thermal desorption experiments. The mass spectrometer was equipped with a quartz skimmer to minimize the sampling of desorption products from the sample support hardware. All allyl alcohol and 1-propanol doses have been corrected for ion gauge sensitivity,^{11,12} and all TDS traces have been corrected for mass spectrometer sensitivity. The background pressure was less than 1.5×10^{-10} Torr throughout the thermal desorption experiments.

The identification of each reaction product in TDS was accomplished using a minimum of three m/z contributions for comparison to the cracking patterns measured experimentally in the UHV system. However, the primary m/z fragments used for monitoring the different C_3 species are 1-propanol (60), propionaldehyde (58), allyl alcohol (57), acrolein (56), and propene (41). The primary difficulty encountered with the thermal desorption data is the separation of propionaldehyde and allyl alcohol, both of which have a parent mass of 58 and many overlapping cracking fragments. Fortunately, the ratio of the 58 to 57 m/z signals for propional dehyde and allyl alcohol are quite different. The 58:57 m/z ratio is large (2.8) for propionaldehyde, and small (0.23) for allyl alcohol. Our approach is to make the maximum correction to the product signal (i.e., to report the minimum amount of product). Hence, the 58 signal from the reaction of allyl alcohols is corrected to represent the propionaldehyde reaction product by assuming all 57 signal is from allyl alcohol. Conversely, the 57 signal from 1-propanol is corrected to represent product allyl alcohol by assuming all 58 is from propionaldehyde. Therefore, the reported traces represent the

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Figure 1. Thermal desorption spectra from a 0.2-langmuir dose of allyl alcohol on $Cu_2O(100)$.

minimum amount of product formed, rather than an optimized fit to all the cracking patterns.

The Cu₂O crystal was oriented by Laube back-reflection and mechanically polished to within $\pm 0.5^{\circ}$ of the (100) surface. Sample dimensions were approximately $7 \times 5 \times 1 \text{ mm}^3$. The sample was mechanically attached to a tantalum holder which acted as an indirect heating and cooling source. A type K thermocouple was held in contact with the back of the sample through a hole in the sample holder with Aremco type 569 ceramic cement. Thus, direct measurements of the crystal temperature were possible.

All XPS spectra were collected using Mg K α radiation ($h\nu = 1253.6 \text{ eV}$) exclusively, and run at a resolution of 1.03 eV full width at half-maximum (fwhm) on Ag 3d_{5/2}. Because of the width and asymmetry of the C 1s XPS spectra obtained from allyl alcohol and 1-propanol, peak-fitting was necessary. A Gauss-Newton optimization routine employing Gaussian peaks was used.¹³ The variations in fitted peak positions which gave acceptable fits were ± 0.1 eV for the lowest and highest binding energy peaks and ± 0.2 eV for peaks at intermediate binding energies. For all fits, the *minimum* number of peaks which gave an acceptable fit were used. The peak-fitting routine was used with a fwhm of 1.6 eV for the C 1s signals. All spectra were referenced to the Cu⁺ 2p_{3/2} binding energy of 932.4 eV.¹⁴

Aldrich allyl alcohol (99+%) and HPLC grade 1-propanol (99.9%) were purified by repeated freeze-pump-thaw cycles prior to use. Matheson research-grade H₂ (99.9995%) was used as received. Since H₂ does not dissociatively adsorb on the Cu₂O-(100) surface under UHV conditions,¹⁵ H₂ was dissociated using a hot platinum filament located 15 mm from the sample face. All hydrogen doses are reported as the equivalent H₂ dose.

Results

Thermal Desorption. Allyl Alcohol Thermal Desorption. Figure 1 shows the TDS traces obtained following a 0.2-langmuir dose of allyl alcohol at 120 K. A 0.2-langmuir dose was chosen for this illustration because at higher coverages a large, lowtemperature allyl alcohol desorption feature obscures the highertemperature features near 500 K. The operational definition of a 1-ML (monolayer) coverage is taken as the coverage where an allyl alcohol multilayer desorption feature first appears, and where the signal from reaction products saturates. A 0.65-langmuir dose corresponds to a coverage of 1 ML. Hence, the TDS data in Figure 1 correspond to an initial coverage of about 1/3 of a monolayer. CO, CO₂, H₂O, propene (CH₂=CHCH₃), propionaldehyde (CH₃CH₂CHO), and acrolein (CH₂=CHCHO) were all detected as reaction products. No bimolecular reaction products or C₂ products were detected. Allyl alcohol desorbs in three temperature ranges. At low coverages, allyl alcohol desorption is first observed at 525 K. A coverage-dependent desorption state is observed at intermediate coverages, and shifts in temperature are observed from 250 K at 0.3 ML to 210 K at 1.0 ML. For higher coverages, an allyl alcohol peak appears at 170 K (not shown in Figure 1) for doses greater than 0.65 langmuir. This feature does not saturate with increasing coverage, demonstrating that it is due to the desorption of multilayer allyl alcohol.

The desorption temperature of the 525 K allyl alcohol feature and the associated aldehydic products evolved at this temperature (CH₂—CHCHO and CH₃CH₂CHO) do not shift as a function of coverage, implying a first-order process for the rate-limiting step. The evolution of acrolein and propionaldehyde at 525 K is reaction-limited.¹⁶ The coincident desorption of acrolein and allyl alcohol at 525 K is characteristic of a rate-limiting step involving the first-order, unimolecular, decomposition of a surface alkoxide species, in this case an allyloxy (CH₂—CHCH₂O–). Assuming a preexponential of 10¹³ s⁻¹, and using the Redhead equation,¹⁷ gives an activation energy of 35.6 kcal/mol for the features at 525 K. Acrolein desorbs in an additional lower temperature peak at 310 K, with a first-order activation energy of 20.7 kcal/mol.

Propene evolves over a broad temperature range with three clear desorption features. Two desorption-limited features are visible at 170 and 215 K,¹⁸ with corresponding first-order activation energies for desorption of 11.2 and 14.2 kcal/mol, respectively. A broad propene desorption feature is also observed between 400 and 600 K, in the same temperature range as the first-order allyloxy decomposition. However, because of the width of this feature the assignment of a reaction order for the rate-limiting step is not possible.

The simultaneous desorption of CO and CO₂ occurs via a reaction-limited process^{19,20} at 680 K. No variation in the desorption temperature is observed as a function of coverage, again indicating a first-order process. The corresponding activaton energy for reaction is 46.5 kcal/mol. CO₂ desorption is also observed in a lower-temperature, reaction-limited shoulder near 590 K. The rate-limiting reaction also appears to be first order, with an activation energy of about 40 kcal/mol.

 H_2O desorbs in a broad feature with a maximum at 545 K and a higher-temperature shoulder at 675 K. H_2O thermal desorption studies have shown that the recombination of dissociated water occurs at or below 465 K on this surface,²¹ and hydrogen adsorption studies have shown that atomic hydrogen extracts lattice oxygen from this surface to form water at 500 K.¹⁵ Thus, the ratelimiting step for all the H_2O observed above 500 K involves the dehydrogenation of surface hydrocarbons. No H_2 was detected as a reaction product; however, the background of H_2 in the system was such that some H_2 may have gone undetected.

The conversion of allyl alcohol to products was coverage dependent and varied from about 40% at low coverages (0.3 ML) to about 20% at higher coverages (1 ML). The selectivity (on a C₃ basis) did not change significantly with coverage and was 15% to CO, 20% to CO₂, 25% to propene, 6% to propionaldehyde, and 34% to acrolein. The relative yields of the desorption products from a 0.2-langmuir dose of allyl alcohol are shown in Table I. From the amounts of oxygen-containing products, it is clear that lattice oxygen is extracted during the thermal desorption run.

1-Propanol Thermal Desorption. Figure 2 shows the thermal desorption traces following a 0.20-langmuir (0.33 ML) dose of 1-propanol at 120 K. As with allyl alcohol, 1 ML of 1-propanol was defined as the dose (0.61 langmuir) where the 1-propanol multilayer first appeared and the signals from the reaction products saturated. Acrolein, propionaldehyde, propene, CO, CO_2 , and H_2O were all detected as reaction products. No C_2 products or bimolecular reaction products were detected.

1-Propanol desorbs in three temperature ranges. A 1-propanol desorption peak is observed at 170 K (not shown in Figure 2) for



Figure 2. Thermal desorption spectra from a 0.2-langmuir dose of 1-propanol on $Cu_2O(100)$.

TABLE I: Relative Yields for Allyl Alcohol on Cu₂O(100)

product	rel yield	
CH2-CHCH2OH TDS (0.33 ML)		
CH2=CHCH2OH	2.27	
CH2=CHCHO	0.58	
CH ₃ CH ₂ CHO	0.11	
CH2=CHCH3	0.42	
CO	0.76	
CO ₂	1.00	
H ₂ O	0.90	
H/CH2=CHCH2OH TDS (1 ML)		
CH2=CHCH2OH	12.2	
CH2=CHCHO	0.44	
CH ₃ CH ₂ CHO	0.46	
CH2=CHCH3	1.40	
CO	0.66	
CO ₂	1.00	

doses greater than 0.61 langmuir. This feature does not saturate with increasing coverage, demonstrating that it is due to the desorption of a 1-propanol multilayer. A coverage-dependent 1-propanol peak is observed which shifts from 350 K at 0.08 ML to 200 K by 1 ML. A high-temperature desorption state at 525K is observed also, similar to that seen with allyl alcohol.

Accompanying the 525 K 1-propanol desorption signal is the reaction-limited evolution of propionaldehyde, ¹⁶ acrolein, ¹⁶ and propene.¹⁸ No coverage dependence is observed in the desorption temperatures of the 525 K 1-propanol peak or any of the associated products, implying a first-order process for the rate-limiting step. Assuming a preexponential of 10^{13} s⁻¹ and applying the Redhead equation¹⁷ gives an activation energy of 35.6 kcal/mol for the 525 K desorption features. The coincident desorption of propionaldehyde and 1-propanol at 525 K is characteristic of the first-order, unimolecular decomposition of a surface alkoxide, in this case propoxy (CH₃CH₂CH₂O–).

Propionaldehyde and acrolein also desorb with a reactionlimited, lower-temperature shoulder near 400 K, with an associated first-order activation energy of about 27 kal/mol. Propene desorbs over a broad temperature range, with peak maxima at 310 and 525 K. The 310 K propene desorption feature is also reaction-limited,¹⁸ with a corresponding first-order activation energy of 20.7 kcal/mol.

CO and CO₂ desorb simultaneously in reaction-limited^{19,20} peaks at 580 and 720 K. Again, since no variations in these desorption temperatures are observed with coverage, the rate-limiting surface reaction steps appear to be first-order with activation energies of 39.5 and 50.7 kcal/mol, respectively. Water desorbs in a broad feature centered near 600 K. The high

 TABLE II:
 Relative Yields for 1-Propanol TDS on Cu₂O(100)

product	rel yield
CH ₃ CH ₂ CH ₂ OH T	DS (0.33 ML)
CH ₃ CH ₂ CH ₂ OH	1.61
CH ₃ CH ₂ CHO	1.87
CH2=CHCH3	0.41
CH2=CHCHO	0.10
CO	1.81
CO ₂	1.00
H ₂ O	1.72
H/CH ₃ CH ₂ CH ₂ OI	HTDS (1 ML)
CH ₃ CH ₂ CH ₂ OH	31.0
CH₃CH₂CHO	2.92
CH2=CHCH3	1.28
CH2=CHCHO	0.23
CO	1.40
CO ₂	1.00

desorption temperature of water is again due to the dehydrogenation of surface hydrocarbons. As with allyl alcohol, no H_2 is detected as a reaction product. However, some H_2 might have gone undetected due to the background of H_2 in the vacuum system.

The conversion of 1-propanol varies from 65% at lower coverages (0.33 ML) to 20% at higher coverages (1 ML). The selectivity (calculated on a C_3 basis) does not vary as a function of coverage. The selectivity to propionaldehyde was 57%, to acrolein 3%, to CO 18%, to CO₂ 10%, and to propene 12%. The relative yields of the products from a 0.2 L dose of 1-propanol are shown in Table II. From the amounts of oxygen-containing products, it is clear that lattice oxygen is extracted during 1-propanol thermal desorption.

Allyl Alcohol and 1-Propanol TDS from the H-Predosed Surface. The allyl alcohol TDS experiments were repeated on a hydrogen-predosed surface to study the effectiveness of surface hydrogen in hydrogenating the C=C double bond. Hydrogen (200-langmuir equivalent H₂ dose) was preadsorbed with 0.65 langmuir (1 ML) of allyl alcohol at 120 K. The same desorption products were observed during these experiments as were observed following allyl alcohol adsorption on the clean surface. No changes in the desorption temperatures of allyl alcohol or the reaction products were observed due to the presence of preadsorbed hydrogen.

No significant difference in the conversion of allyl alcohol to products is observed for a 0.65-langmuir allyl alcohol dose on the H-predosed (100) surface. The selectivity is 15% (±3%) to acrolein, $16\% (\pm 3\%)$ to propional dehyde, $49\% (\pm 3\%)$ to propene, 8% (\pm 3%) to CO, and 12% (\pm 3%) to CO₂. An increase in the selectivity to reduction and isomerization products (propene and propionaldehyde, respectively) and a decrease in selectivity to oxidation products (both selective and nonselective) are observed for the hydrogen-predosed surface. The increased selectivity to propene and propionaldehyde demonstrates the importance of surface hydrogen in the formation of these products via the hydrogenation of surface intermediates. Quantification of the H_2O signal was not possible because of the background H_2O generated by the predissociation of hydrogen. The relative yields of the desorption products from allyl alcohol TDS on a hydrogenpredosed surface are given in Table I.

1-Propanol TDS was also repeated on a hydrogen-predosed surface. Hydrogen (200-langmuir equivalent H_2 dose) was preadsorbed with 0.61 langmuir (1 ML) of 1-propanol at 120 K. The same desorption products are observed during these experiments as were observed following 1-propanol adsorption on the clean surface. No significant shift in the desorption temperatures of 1-propanol was observed due to predosed hydrogen. Propionaldehyde, acrolein, CO, and CO₂ all evolve in the same temperature ranges from the clean surface. However, propene desorbs primarily at 350 K, with no propene features detected



Figure 3. C 1s XPS spectra following an 8.7-langmuir dose of allyl alcohol on Cu₂O(100) at 120 K as a function of annealing temperature: (a) multilayer allyl alcohol; (b) surface in (a) heated to 170 K; (c) surface in (b) heated to 400 K; (d) surface in (c) heated to 580 K.

in the 400-600 K temperature range as observed following 1-propanol adsorption on the clean surface.

No difference in the conversion of 1-propanol to products was observed for a 0.61-langmuir dose of 1-propanol on the H-predosed (100) surface. The selectivity was 4% (\pm 3%) to acrolein, 56% (\pm 3%) to propionaldehyde, 24% (\pm 3%) to propene, 9% (\pm 3%) to CO, and 6% (\pm 3%) to CO₂. An increase in the selectivity to propene was observed on the hydrogen-predosed surface, demonstrating the importance of surface hydrogen in the formation of propene via the hydrogenation of surface intermediates. Quantification of the H₂O signal was not possible because of the background of H₂O generated by the predissociation of hydrogen. The relative yields of the products from 1-propanol TDS on a hydrogen-predosed surface are given in Table II.

XPS Experiments. Allyl Alcohol. Allyl alcohol adsorption was also studied with XPS in order to gain some insight into the surface intermediates involved in the allyl alcohol reaction pathways. For these experiments, 8.7 langmuirs of allyl alcohol was dosed onto the surface at 120 K, and the sample was heated to the desired temperature and then cooled back down to 120 K before the XPS spectrum was collected.

The C 1s spectrum of an allyl alcohol multilayer is shown as Figure 3a. Two peaks were fit to this spectrum (shown as dashed lines) at binding energies of 286.9 and 285.2 eV. The separation between these peaks is 1.7 eV, somewhat higher than a separation of 1.4 eV observed in the C 1s spectrum of gas-phase ethanol.²² By comparison to the spectra of gas-phase alcohols,²² the higher binding energy peak at 286.9 eV is assigned to the carbon bound to the hydroxyl group of molecular allyl alcohol (hereafter referred to as a "hydroxyl carbon"), while the lower binding energy peak is assigned to the vinyl carbons of molecular allyl alcohol. The ratio of the intensities of the C 1s signals of the vinyl carbons to the hydroxyl carbons is 2.2, slightly higher than the stoichiometric value of 2.0. In general, the calculated ratio for a given spectrum can vary by ± 0.2 for small changes in the peak-fitting parameters.

Heating the surface to 170 K results in the desorption of the multilayer, leaving chemisorbed species on the surface. The resulting C 1s spectrum is shown in Figure 3b. A 10% decrease in the total C 1s signal was observed after heating to 170 K. Three peaks were fit to this spectrum at binding energies of 288.0, 286.4, and 285.1 eV. The peak at 285.1 eV is again assigned to the vinyl carbons. The peak at 288.0 eV is assigned to the oxygenated carbon of a surface carboxylate (i.e., acrylate) by comparison to results for acrylic acid adsorption on Cu₂O(100).²³

The peak at 286.4 eV is 0.5 eV lower in binding energy that observed for the hydroxyl carbon in the allyl alcohol multilayer. However, the binding energy of this feature (286.4 eV) is lower

than expected for either a carboxylate species $(288.0 \text{ eV})^{23}$ or the formyl group of a chemisorbed aldehyde (287.2 eV),¹⁶ suggesting a surface species with only a single C–O bond. A similar decrease in the C 1s binding energy has been reported for the formation of surface alkoxides by alcohol dissociation on ZnO(0001)–Zn and Cu₂O.^{8,24,25} The thermal desorption and XPS results are consistent with a 286.4-eV peak due to the oxygenated carbons of surface allyloxy species (CH₂=CHCH₂O–).

In summary, the peak at 286.4 eV is characteristic of a surface alkoxide and is assigned to allyloxy species. The peak at 288.0eV is characteristic of an acrylate species, and the peaks at 285.1eV is assigned to the vinyl carbons of either acrylate or allyloxy species. The largest signal is due to the vinyl carbon peak at 285.1 eV, with the ratio of areas of the peaks approximately 1:2.5:8 for the 288.0, 286.4, and 285.1 eV peaks, respectively.

A useful measure for the stoichiometry of the adsorbed species is obtained by comparing the intensity of the C 1s signals of all the nonoxygenated carbons due to vinyl groups, alkyl carbons, or hydrocarbon fragments (designated C_xH_y) to the intensity of all the oxygenated carbons of carboxylates and alkoxide species (designated CO₂). This C_xH_y/CO_z ratio gives a measure of the extent of oxidation or reduction of the C₃ backbone of the adsorbate. The spectrum shown as Figure 2b has a corresponding C_xH_y/CO_z ratio of 2.4, only slightly higher than the expected stoichiometric value of 2.0 for alkoxide and carboxylate surface species.

Further heating to 400 K removes the 210–250 K allyl alcohol desorption feature and low-temperature propene and acrolein. A decrease of about 40% in the overall intensity of the C 1s signal is observed compared to that at 170 K. The resulting C 1s XPS spectrum is shown in Figure 3c. Three peaks are fit to this spectrum at binding energies of 287.8, 286.2, and 284.9 eV. The peak assignments are as given above. The C_xH_y/CO_z ratio for the spectrum shown as Figure 3c is 3.2. The increase in the C_xH_y/CO_z ratio demonstrates that some reduction of surface oxygenates occurs, suggesting that the peak at 284.9 eV contains contributions from surface hydrocarbon fragments as well as the vinyl carbons of acrylate and allyloxy species. Despite an overall decrease in the C 1s signal, no change was noted in the relative sizes of the oxygenate peaks. The intensities appear in the ratio of 1:2.4:11 for the 287.8-, 286.2-, and 284.9-eV peaks, respectively.

Further heating to 580 K leaves only those surface species eventually leading to CO, CO_2 , and H_2O . A decrease of about 80% in the C 1s signal was observed compared to that for 400 K. The resulting C 1s spectrum is shown in Figure 3d. Four peaks are fit to this spectrum at binding energies of 287.8, 286.2, 285.0, and 284.0 eV. The new peak at 284.0 eV is in the same binding energy range as reported for graphitic carbon¹⁴ and is assigned to surface carbon from dehydrogenated surface species. The very small features characteristic of allyloxy (286.2 eV) and acrylate (287.8 eV) are thought to be due to the readsorption of allyl alcohol during the XPS measurements since allyloxy decomposition is observed at 525 K in TDS and acrylate decomposition occurs in this same temperature range.²³ Similarly, the majority of the 285.0-eV contribution is accounted for by the expected stoichiometry of the allyloxy and acrylate due to readsorption. Hence, the major contribution to the C 1s signal not due to readsorption is a feature at 284.0 eV due to surface carbon. Further heating to 1000 K results in a carbon-free surface.

In addition to examining the C 1s features, the Cu L_3VV feature was also examined. Previous studies on copper oxides have shown that a clear differentiation between Cu⁰, Cu⁺, and Cu²⁺ can be made by shifts in the kinetic energy of the Cu L_3VV Auger feature or the binding energies and shake-up structure of the Cu 2p photoemission features.²⁶ Several Cu L_3VV spectra are shown in Figure 4 which correspond to the C 1s spectra described above. Figure 4a shows the Cu L_3VV feature after heating 7.8 langmuirs of allyl alcohol to 400 K. The only features in the spectrum are



Figure 4. Cu L_3VV of Cu₂O(100) surface as a function of temperature following allyl alcohol adsorption. All spectra were taken at 120 K. (a) Surface heated to 400 K. (b) Surface heated to 580 K. (c) Surface heated to 100 K.



Figure 5. C 1s XPS spectra following an 8.1-langmuir dose of 1-propanol on Cu₂O(100) at 120 K as a function of annealing temperature: (a) multilayer 1-propanol; (b) sample in (a) heated to 170 K; (c) sample in (b) heated at 430 K; (d) sample in (c) heated to 600 K.

due to Cu⁺. Heating of the surface to 580 K results in the growth of features with binding energies of 334.9 and 332.3 eV indicative of Cu⁰, as shown in Figure 4b. Continued heating of the surface to 1000 K results in the diffusion of oxygen from the bulk to reoxidize the surface.¹⁰ The presence of Cu⁰ at the intermediate temperatures is consistent with the thermal desorption results which show that lattice oxygen is removed during the TDS experiments.

1-Propanol. Adsorbed 1-propanol was also studied with XPS to help identify the surface intermediates in the reaction pathway. For these experiments, 8.1 langmuirs of 1-propanol was dosed on the surface at 120 K. The XPS experiments were done as described above for allyl alcohol.

The C 1s XPS spectrum of a 1-propanol multilayer is shown in Figure 5a. Two peaks are fit to this spectrum (shown as dashed lines) at binding energies of 286.9 and 285.4 eV. The separation between the high and low binding energy peaks is 1.5 eV, in good agreement with the separations observed for molecular allyl alcohol (1.7 eV) and gas-phase ethanol (1.4 eV).²² The assignment of these peaks is similar to the assignments for the allyl alcohol multilayer. The peak at higher binding energy (286.9 eV) is assigned to the oxygenated (hydroxyl carbon) carbon of molecular 1-propanol, while the lower binding energy peak (285.4 eV) is assigned to the alkyl carbons in the ethyl group of molecular 1-propanol. The C_xH_y/CO_z ratio for the multilayer is 2.0, the expected stoichiometric value.

Heating to 170 K results in the desorption of the multilayer. A 40% decrease in the overall C 1s intensity is observed. The resulting C 1s spectrum is shown in Figure 4b. Three peaks are fit to this spectrum at binding energies of 287.8, 286.4, and 285.0 eV in an area ratio of 1:3.7:10, respectively. The assignment of these peaks is similar to the assignments for allyl alcohol. The highest binding energy peak (287.8 eV) is assigned to the oxygenated carbon of surface propionate (CH₃CH₂COO⁻) by comparison to results for propionic acid decomposition on Cu₂O-(100).²³ The intermediate binding energy feature (286.4 eV) is in a range similar to the allyloxy peak from allyl alcohol and is assigned to the oxygenated carbon of surface propoxy (CH₃-CH₂CH₂O₋). The lowest binding energy peak (285.0 eV) is assigned to the alkyl carbons from surface propionates and propoxy species. The $C_x H_y/CO_z$ ratio for the spectrum shown as Figure 4b is 2.2.

Heating to 430 K removes the 200–350 K 1-propanol desorption feature as well as the low-temperature propene, acrolein, and propionaldehyde. A 50% decrease in the C 1s signal is observed. The resulting spectrum is shown in Figure 4c. Three peaks are fit to this spectrum at binding energies of 287.8, 286.3, and 284.8 eV, in an intensity ratio of 1:3.6:13.6. The C_xH_y/CO_z ratio is 3.0 for the spectrum shown as Figure 4c. The increase in the C_xH_y/CO_z ratio demonstrates that some reduction of surface oxygenates occurs, suggesting that a contribution to the 284.8eV peak is from hydrocarbon fragments.

Further heating to 600 K desorbs all the C3 products and leaves only those surface species eventually leading to CO, CO₂, and H_2O . A decrease in the C 1s signal of about 50% is observed compared with the 430 K spectrum. The resulting C 1s spectrum is shown in Figure 4d. Three peaks were fit to this spectrum at binding energies of 286.3, 285.0, and 284.0 eV. As with alkyl alcohol, the 284.0-eV contribution is assigned to surface carbon from dehydrogenated surface species. The peak at 286.3 eV characteristic of an alkoxide species is thought to be due to readsorption of 1-propanol during the XPS experiment since alkoxide decomposition is observed at 525 K in TDS. Similarly, the 285.0-eV contribution is accounted for by the expected stoichiometry of the propoxy due to readsorption. Hence, the major contribution to the C 1s signal not due to readsorption is the feature at 284.0 eV due to surface carbon. Further heating to 1000 K resulted in a carbon-free surface.

As with allyl alcohol, examination of the Cu L_3VV Auger features (not shown) shows that some Cu⁰ is detected at the surface after heating to 600 K, illustrating the removal of lattice oxygen. The presence of Cu⁰ in XPS is consistent with the thermal desorption results which demonstrate that lattice oxygen is removed during 1-propanol TDS experiments. Heating to 1000 K results in the diffusion of oxygen from the bulk to reoxidize the surface.

Discussion

Molecular Alcohol Adsorption/Desorption. The desorption of molecular alcohols in TDS is observed from surface species resulting from both molecular and dissociative adsorption. Desorption from molecular multilayers is clearly observed at 170 K for both allyl alcohol and 1-propanol in TDS. Alcohol desorption by alkoxide-hydrogen recombination with alkoxide decomposition as the rate-limiting step is also observed at 525 K for both alcohols. For this recombination channel, the characteristic simultaneous desorption of alcohols and aldehydes is observed in TDS.²⁷ The observation in XPS of oxygenated C 1s binding energies shifted lower than for the molecular alcohols (286.9 eV from multilayer vs 286.4 eV for alkoxide) is also characteristic of alcohol dissociation on oxides to surface alkoxides.^{8,24,25} However, the desorption of the C₃ alcohols between 200 and 400 K is less easily characterized.

Other thermal desorption studies of C_3 alcohols have reported the desorption of molecular surface alcohols between 200 and 300 K. On Cu(110)²⁷ and TiO₂(001)- $\{011\}^9$ the desorption of molecular surface 1-propanol has been observed between 200 and 300 K. As reported above for Cu₂O(100), coverage-dependent alcohol desorption features were observed in the 200–400 K range: 250–210 K for allyl alcohol (0.3–1.0 ML) and 350–200 K for 1-propanol (0.08–1.0 ML). A comparison to the results for Cu(110) and TiO₂(001)- $\{011\}$ suggests that the majority of the desorption from Cu₂O(100) which occurs below 300 K for near-monolayer coverages originates from molecular adsorbates. However, the XPS results are of little value in confirming this assignment.

Molecular alcohols on $Cu_2O(100)$ might be expected to show intermediate C 1s binding energies for the "hydroxyl" carbons (286.9 eV as seen for the alcohol multilayers) between those expected for the oxygenated carbons of surface carboxylates (288.0 eV) and alkoxides (286.4 eV). In the XPS results reported above for $Cu_2O(100)$, no molecular contribution (286.9 eV) is reported for either alcohol after desorption of the multilayer at 170 K. We note, however, that it is possible to peak-fit these C 1s spectra for 1-propanol and allyl alcohol with four peaks characteristic of molecular, alkoxide, and carboxylate contributions. However, the variation in BE's for intermediate peaks of ± 0.2 eV made a three-peak fit equally reasonable. Thus, the XPS data can be interpreted as consistent with the presence of both molecular alcohols and alkoxides on the surface between 200 and 400 K, but provide no real confirming evidence in support of such an assignment. We wish to emphasize, however, that peak-fitting with a high binding energy contribution due to carboxylate species is required to give an adequate fit.

C₃ Reaction Pathways. Alkoxide Decomposition. For both alcohols investigated, the rate-limiting step for the alcohol and aldehyde desorption features at 525 K are attributed to the firstorder unimolecular decomposition of surface alkoxides. In this pathway, the alcohols are dissociatively adsorbed to yield surface alkoxides via the loss of the acidic proton at the OH group. The formation of aldehydes from surface alkoxides (i.e., acrolein from allyloxy and propionaldehyde from propoxy) occurs via hydride elimination from the carbon α to oxygen. The C-H bonds on the oxygenated (α) carbons are activated, with lower bond dissociation energies than in the absence of the oxygen heteroatom.²⁷ The rate-limiting hydride elimination step releases hydrogen to the surface which recombines with some of the remaining surface alkoxides to produce the parent alcohols. This reaction pathway has been observed for a number of alcohols on different metal and metal oxide surfaces. Examples most directly related to the present study include the production of acrolein from allyl alcohol through an allyloxy intermediate on Cu(110)²⁸ and the production of propionaldehyde from 1-propanol through a propoxy intermediate on ZnO(0001)-Zn (at 490 K),8 TiO2(001)-{011} (at 580 K),⁹ and Cu(110) (at 340 K).²⁷ The 525 K decomposition temperature of propoxy on $Cu_2O(100)$ is intermediate between that observed for propoxy on ZnO⁸ and TiO₂,⁹ and considerably higher than that observed over Cu(110).27 In general, the reported decomposition temperatures and the activation energies for the unimolecular decomposition of surface alkoxides on metal oxide surfaces are higher than the values reported over metals. The reactions involving surface alkoxides may be summarized as follows:

$$RCH_2OH(g) \rightleftharpoons RCH_2O(ad) + H(ad)$$
 (1)

$$\operatorname{RCH}_2\operatorname{O}(\operatorname{ad}) \to \operatorname{RCHO}(g) + \operatorname{H}(\operatorname{ad})$$
 (2)

Note that reaction 1 involves the loss of an acidic proton, while reaction 2 involves a hydride elimination from the surface alkoxide. The two equations as written are not meant to specify the nature of the surface hydrogen formed by the two reactions. Previous investigations of the interaction of atomic hydrogen with this surface suggest the possibility of forming both OH and hydridic (Cu^+-H) surface moieties.^{15,16}

Allyloxy Decomposition, 525 K. Besides the allyl alcohol and acrolein desorption signals observed at 525 K from allyloxy decomposition in Figure 1, two other C₃ products are observed which are not typically associated with allyloxy decomposition: propionaldehyde (a net isomerization product from allyl alcohol) and propene (a net deoxygenation product from allyl alcohol). The simultaneous evolution of these two additional products with the alkoxide decomposition suggests that alkoxide decompositions are the rate-limiting steps in their production. Also, the formation of the saturated aldehyde (propionaldehyde) from allyl alcohol demonstrates that the C=C bond can be hydrogenated.

Several possible pathways and surface intermediates can be imagined for the reaction-limited production of propionaldehyde from allyl alcohol at 525 K. The first possibility is the hydrogenation of the allyloxy double bond at or below 525 K to yield a surface propoxy which subsequently produces propionaldehyde via the same unimolecular decomposition observed for propoxy from 1-propanol at 525 K. Schematically, this reaction scheme is described by

$CH_2 = CHCH_2O(ad) + 2H(ad) \rightarrow CH_3CH_2CH_2O(ad)$ (3)

in combination with reaction 2 above.

While a pathway involving allyloxy hydrogenation to propoxy seems plausible, this reaction pathway is *not* consistent with the TDS data described above for the C₃ alcohols. One consequence of the hydrogenation of allyloxy to propoxy (reaction 3) followed by the unimolecular hydride elimination from propoxy to form propionaldehyde (reaction 2) is that reaction 2 must be accompanied by the recombination reaction of the alkoxide with surface hydrogen (the reverse of reaction 1) to give 1-propanol as a product. No 1-propanol desorption is observed in the TDS data for the reactions of allyl alcohol with the clean or hydrogen predosed $Cu_2O(100)$ surface.

Our inability to detect 1-propanol as a reaction product in the allyl alcohol TDS studies *is not* simply the result of low coverages of propoxy and/or surface hydrogen. 1-Propanol formation from the decomposition of surface propoxy at 525 K can be seen easily from coverages as low as 0.01 ML of propoxy in 1-propanol TDS runs. The parent mass fragment of 60 for 1-propanol *does not* overlap with fragments from the other C₃ oxygenates seen in allyl alcohol TDS. Note that the parent mass fragment for acrolein is 56 and that for allyl alcohol and propionaldehyde is 58. Hence, the large excess of allyl alcohol and the production of propionaldehyde and acrolein *do not* compromise our ability to detect 1-propanol at a m/z of 60. These results clearly indicate that reaction 3 is not operable to any significant extent under our thermal desorption conditions since no 1-propanol is observed.

It is clear that propionaldehyde is not formed via the hydrogenation of allyloxy to propoxy. Hence, the TDS data indicate that the decomposition of allyloxy is the rate-limiting step to produce propionaldehyde at 525 K. The likely route to propionaldehyde from allyloxy is by hydrogenation of the acrolein product formed by the unimolecular decomposition of the allyloxy. In fact, the formation of both propionaldehyde *and* propene from the reaction of acrolein and surface hydrogen has been observed over a wide temperature range (500 K and lower) during TDS studies of acrolein and preadsorbed hydrogen on this same surface.¹⁶ This pathway has been attributed to the reduction of acrolein to a surface enolate intermediate, which is subsequently hydrogenated to propionaldehyde or propene.¹⁶ The proposed reaction pathways involving surface enolates are described below.

We also note that Brainard et al. have observed the production of propionaldehyde from allyl alcohol over Cu(110).²⁸ Their experimental data is consistent with the presence of alkoxides and oxametallacycles as reaction intermediates. The oxametallacycles are proposed as reaction intermediates because acrolein and propionaldehyde are evolved at temperatures higher than those where alkoxide decomposition occurs on Cu(110). However, for allyl alcohol on Cu₂O(100), the reaction-limited production of C₃ products coincident with allyloxy decomposition (but not at *higher* temperatures) suggests that no oxametallacycles are required to explain the observed products.

Propoxy Decomposition, 525 K. Besides the 1-propanol and propionaldehyde desorption signals at 525 K from propoxy decomposition in Figure 2, two other unsaturated C₃ products are observed which are not typically associated with propoxy decomposition: acrolein (a net dehydrogenation product from 1-propanol) and propene (a net dehydration product from 1-propanol). The simultaneous evolution of these two additional products with the alkoxide decomposition demonstrates that alkoxide decompositions are the rate-limiting steps in their production. However, no allyl alcohol is observed as a product from 1-propanol, suggesting that dehydrogenation of a surface propoxy to allyloxy is not the operable pathway to the unsaturated products. We note that for the amount of acrolein formed from 1-propanol the discrimination of a related amount of allyl alcohol (by comparison to the 525 K allyloxy decomposition feature in allyl alcohol TDS) from the large yield of propionaldehyde would be difficult because of the overlap in the cracking patterns. However, since the simultaneous desorption of C3 aldehydes and propene in this temperature range (and below) is observed for the reaction of propionaldehyde with Cu₂O(100) which yields acrolein and propene with no evidence of an allyloxy intermediate,¹⁶ it is reasonable to conclude that the common surface intermediate responsible for the intersection of the aldehyde reaction pathways is involved in this alcohol decomposition as well. Hence, propoxy decomposition at 525 K is the rate-limiting step in the production of all the C₁ products formed at 525 K, but acrolein and propene are thought to be products of subsequent reactions of the propionaldehyde formed by propoxy decomposition. As with propionaldehyde and propene formed from allyl alcohol, the subsequent reactions of the primary aldehyde (propionaldehyde) formed at 525 K by alkoxide (propoxy) decomposition are believed to proceed through a surface enolate intermediate.¹⁶ The enolatemediated chemistry for all temperature ranges is described below.

We note also that propene has been observed as a reaction product from 1-propanol over the TiO₂(001)-{011} surface.⁹ For TiO₂, propene is produced coincident with propoxy decomposition at 580 K. Deoxygenation of surface propoxy to produce a propyl species has been proposed, with a subsequent by β -hydride elimination reaction to produce propene.⁹ Although propene production by this pathway from 1-propanol on Cu₂O(100) cannot be ruled out, the formation of propene between 400 and 550 K via an enolate intermediate is consistent with the previously observed chemistry of propionaldehyde and acrolein on this same surface.¹⁶

Enolate-Mediated Pathway. Propene, acrolein, and propionaldehyde have been reported previously as reaction products between 250 and 500 K during TDS studies of both C3 aldehydes, acrolein and propionaldehyde, over Cu₂O(100).¹⁶ Thus, given the evidence against interconversion between alkoxide surface intermediates (allyloxy and propoxy), the production of C₃ compounds other than the primary aldehyde formed by hydride elimination from the primary alkoxide can be explained by the subsequent reactions of the aldehydes. Note that the effects of surface hydrogen in the H-preadsorption runs show the same type of variation in selectivity for the alcohols in this study as for the aldehydes in the previous study.¹⁶ Higher coverages of surface hydrogen increase the selectivity to propene for the reaction of both 1-propanol [this study] and propionaldehyde,¹⁶ while it increases the selectivity to propene and propionaldehyde from allyl alcohol [this study] and acrolein.¹⁶ Hence, the effects of hydrogen on the selectivity of the alcohol reactions suggest that their behavior is controlled by the subsequent reactions of the aldehydes formed from the alcohols.

The formation of all three products between 250 and 500 K has been attributed to a reaction pathway involving a common surface enolate intermediate.¹⁶ The production of propene, acrolein, and propionaldehyde over such a wide temperature range on this surface has been attributed to both reactions at different surface sites and multiple reaction pathways for the ambidentate surface enolate intermediate. The surface enolate intermediate proposed to explain the intersection in the reaction pathways of acrolein and propionaldehyde on this surface¹⁶ are believed to be formed from propionaldehyde via a Lewis acid catalyzed reaction similar to Brönsted acid catalyzed keto-enol tautomerization in solution. A process similar to solution-phase (1,4) conjugate addition where cations act as Lewis acids at position 1 is postulated to give rise to the enolate intermediate during the reaction of preadsorbed hydrogen and α,β unsaturated acrolein. The aldehydes may be regained from the enolate intermediate by the reverse reactions. An additional pathway involving enolatehydrogen reaction to an unstable enol can also produce propionaldehyde by tautomerization of the enol to propionaldehyde. The reaction-limited production of propene is believed to be the result of hydrogen addition to the enolic carbon coupled with C-O bond scission.¹⁶

In TDS studies of the reaction of deuterium-labeled propionaldehyde, the addition of surface hydrogen to the C_3 backbone of propionaldehyde in the propene formation reaction has been clearly demonstrated.¹⁶ The reaction of acrolein to propene also clearly involves the addition of surface hydrogen.¹⁶ However, besides simply providing surface hydrogen for these reactions, one might reasonably expect that the increased selectivity to propene in the presence of preadsorbed hydrogen is also due to the extraction of lattice oxygen by preadsorbed hydrogen to form highly reducing/strongly oxophilic surface oxygen vacancies which promote the deoxygenation reactions. However, previous work on the low-temperature adsorption of atomic hydrogen on this surface (300 K and below) suggests that hydride formation rather than hydroxyl group formation dominates.¹⁵ TDS studies of adsorbed atomic hydrogen produce H₂:H₂O in a 30:1 ratio. Ultraviolet photoemission shows that spectral changes associated with hydroxyl formation exhibit intensities well below those observed from as little as 0.05 ML of dissociated water. The surface reduction to Cu⁰ necessarily associated with the formation of water following H adsorption is below the detection limits of XPS. The majority of the water formed when adsorbed atomic hydrogen extracts lattice oxygen occurs near 500 K,¹⁵ above the temperature where the majority of propene is formed from the two alcohols. This rather unexpected chemistry for adsorbed hydrogen is believed to occur because lattice oxygen at the Cu₂O-(100) surface is restricted to the second atomic layer (or lower) and has the full bulk coordination. Hence, it appears that the role of preadsorbed surface hydrogen in affecting the selectivity in the alcohol reaction pathways is primarily due to the increase in surface hydrogen concentration. Oxygen vacancy formation and surface reduction occur to a much greater extent from the adsorbed alcohols at temperatures above 500 K where dehydrogenation of the hydrocarbons and subsequent "burn-off" of surface carbon clearly give rise to metallic copper in XPS.

The proposed enolate-mediated chemistry connecting the reaction pathway between acrolein and propionaldehyde has been discussed in detail elsewhere¹⁶ and is consistent with the C_3 products observed in all temperature ranges for reactions and of the C_3 alcohols on Cu₂O(100). The enolate species can be formed by the initial dehydrogenation of the alkoxides to form the corresponding aldehyde, followed by the reaction of the aldehydes to surface enolates. The proposed alcohol reaction pathway to C_3 products, including the enolate-mediated chemistry linking



Figure 6. Overall alcohol reaction pathway to C₃ products involving alkoxide, enolate, and allyl intermediates.

the two aldehydes and propene, is shown in Figure 6. Additional details of the proposed enolate-mediated chemistry are given in ref 16.

The formation of propene, propionaldehyde, and acrolein by the reaction of surface enolates between 225 and 400 K is reasonable on the basis of the previously described chemistry (above and in ref 16) on $Cu_2O(100)$. However, the ability of the alcohol reaction systems to access this chemistry between 225 and 400 K seems puzzling since the hydride abstraction from allyloxy (to form acrolein) or propoxy (to form propionaldehyde) occurs at higher temperatures near 500 K. However, earlier studies of aldehyde adsorption on this same $Cu_2O(100)$ surface have demonstrated a long-term history dependence of the desorption traces due to as yet unidentified surface defects, and this indicates more than a single type of surface adsorption site.¹⁶ These slowly evolving differences in surface condition which affect the energetics of aldehyde desorption are indistinguishable in XPS (either in the Cu/O ratio or as a change in oxidation state) and give rise to no changes in the LEED periodicity.¹⁶ The presence of more than a single type of surface site, one of which catalyzes the decomposition of surface alkoxides at lower temperatures, can explain the ability of the C3 alcohols to access the proposed enolate-mediated chemistry at temperatures below 500 K.

There is one apparent contradiction between the enolatemediated portion of the reaction pathways of the alcohols (proposed above) and that observed previously for the reactions of aldehydes.¹⁶ The observation that no propionaldehyde is produced from allyl alcohol between 225 and 400 K is in apparent contradiction with an enolate-mediated pathway in this temperature range for the production of acrolein. One would expect both aldehydes to be produced from a surface enolate as seen in the aldehyde studies previously.¹⁶ We note, however, that the propionaldehyde (m/z = 58) signal shown in Figure 1 has had the maximum possible contribution due to allyl alcohol removed. Thus, the desorption trace shown in Figure 1 represents the minimum amount of propionaldehyde formed. However, the cracking patterns of alcohols in our skimmer-equipped mass spectrometer vary with pressure. A decrease of only 5% in the cracking pattern correction for allyl alcohol to the 58 m/z signal (a variation within the values observed as a function of pressure for allyl alcohol) would give rise to an apparent propionaldehyde signal between 225 and 400 K. Thus, the absence of propionaldehyde between 225 and 400 K in allyl alcohol TDS may be due to the way in which the data is processed and not because propionaldehyde is not formed.

Low-Temperature (170 K) Reaction Pathway to Propene from Allyl Alcohol. Only allyl alcohol yields reaction products below 225 K. The presence of desorption-limited propene at 170 and

215 K demonstrates that some propene is formed by a facile reaction at or below 170 K. Further, the formation of propene at or below 170 K demonstrates that some C-O bond scission occurs at very low temperatures and possibly upon adsorption. A similar reaction pathway to propene below 215 K has been observed for the reaction of acrolein with preadsorbed hydrogen.¹⁶ Note that no low-temperature propene (<215 K) is observed during 1-propanol TDS or during the decomposition of propionaldehyde.¹⁶ It is believed that this low-energy pathway to C-O bond scission to produce the olefin is attributable to the stability of an allylic species which could be formed from allyl alcohol and alternatively via acrolein hydrogenation at the carbonyl carbon coupled with C-O bond scission.¹⁶ The lower stability of the propyl radical which would be formed by C-O bond cleavage of 1-propanol appears to limit the low-temperature deoxygenation reactions from the saturated alcohol or aldehyde. The temperature at which propene is formed suggests the formation of propene from a π -allyl rather than a σ -allyl. It is not possible from our data to make a clear distinction between the deoxygenation of allyloxy, the dehydroxylation of the molecular allyl alcohol, or the reduction of acrolein to give the low-temperature allylic precursor to propene. The low-temperature pathway to propene is included schematically in the overall alcohol reaction pathway to C_3 products shown in Figure 6.

Nonselective Oxidation Pathway. The nonselective oxidation of the C3 alcohols shows the same general characteristics reported for the nonselective oxidation of other C3 oxygenates (aldehydes and carboxylic acids). Heating from 170 to 500 K during the allyl alcohol or 1-propanol XPS experiments results in an increase in the $C_x H_y/CO_z$ ratio, indicating some initial deoxygenation in this temperature range. The reduction of oxygenate species leads to the formation of surface hydrocarbon fragments. At higher temperatures, hydrocarbon fragments are dehydrogenated to surface carbon. This dehydrogenation is evidenced by the appearance of surface carbon in XPS (at 284.0 eV) and the desorption of water above 500 K at temperatures which are well above those required to remove dissociatively adsorbed water (465 K^{21}) or surface hydrogen (500 K^{15}). Similar behavior has been observed for the nonselective oxidation of surface carboxylates²³ and adsorbed aldehydes.¹⁶ The subsequent production of CO and CO_2 then occurs by the extraction of lattice oxygen by surface carbon (characteristic of a burn-off reaction) with the associated surface reduction to Cu⁰. Reoxidation of the surface occurs by diffusion of oxygen from the bulk to the surface above 800 K. Thus, the general picture of the nonselective oxidation pathways of 1-propanol and allyl alcohol is similar to that of the C₃ aldehydes and carboxylic acids.

The observation of C 1s contributions in XPS characteristic of surface carboxylates suggests that such intermediates play a role in the nonselective oxidation of the alcohols. The highest temperature CO and CO₂ desorption features observed for allyl alcohol and 1-propanol are in similar temperature ranges as those observed previously for acrylate (from acrylic acid) and propionate (from propionic acid) surfaces species, respectively. The firstorder activation energies fall within 2-4 kcal/mol of those observed for the corresponding carboxylate surface intermediates. However, the carboxylates produce a factor of roughly 1.5-2 times more CO_2 than CO_{23} In contrast, the alcohols produce roughly 2-4 times as much CO than CO2 in the highest-temperature carbon oxide reaction channels. Hence, a similarity is observed in the reaction temperatures, while the relative CO to CO₂ selectivity varies significantly.

In studies of the reactions of various oxygenates with the ZnO-(0001)-Zn surface, Vohs and Barteau²⁴ have shown that carboxylate surface intermediates derived from alcohols which must consume lattice oxygen to produce the surface carboxylate intermediate give a higher ratio of CO to CO₂ than observed from carboxylates formed directly from the carboxylic acid, presumably because of a higher extent of local surface reduction. Such an effect could also explain the higher ratio of CO to CO₂ production from C3 alcohols (above) when compared to that for the reactions of the related C $_3$ carboxylic acids²³ since the alcohols are less oxidized reactants.

Since aldehydic selective oxidation products are formed from each alcohol, another reasonable pathway could involve the subsequent nonselective oxidation of the aldehydic products. A comparison to the nonselective oxidation products formed directly from the C₃ aldehydes¹⁶ shows that the highest temperature CO and CO₂ features from allyl alcohol are produced in a similar temperature range as observed from acrolein, although the lower temperature channels to CO and CO₂ from the alcohol show little correspondence to that of acrolein. Similarly, the lowest temperature CO₂ desorption channel for 1-propanol is near one seen for the nonselective oxidation of propionaldehyde. Once again, the ratio of CO:CO₂ production is significantly different. but for those cases where the evolution of CO and CO₂ occurs at similar temperatures to those observed from the C3 aldehydes, this variance may again be the result of differences in the local extent of surface reduction for the different reactants.

The kinetics of nonselective carbon oxide formation, if not the relative CO and CO_2 product distributions, suggest that the reactions of surface carboxylates and the further oxidation of product aldehydes are viable pathways to the nonselective oxidation products observed from the C_3 alcohols. Previous studies of the reactions of C3 carboxylates23 and aldehydes16 demonstrate that in both cases the oxygenates are first reduced, dehydrogenated to surface carbon, and then combusted via a burn-off reaction. The intermediate hydrocarbon fragments involved in this process are unknown. By comparison, for the alkoxide surface species which represent the primary intermediate in the reaction pathways for the alcohols following dissociative adsorption, we cannot eliminate the possibility that deoxygenation of alkoxide species as well leads to nonselective carbon oxide formation by similar pathways.

Conclusions

Allyl alcohol and 1-propanol both adsorb dissociatively on $Cu_2O(100)$ to form allyloxy and propoxy surface intermediates. respectively. The surface alkoxides form aldehydic selective oxidation products via first-order, unimolecular, hydride elimination reactions from the carbon α to oxygen to yield acrolein from allyloxy and propionaldehyde from propoxy. The activation energy for this reaction is essentially identical for both the allyloxy and propoxy surface intermediates. No evidence is seen for the formation of oxametallacycle surface intermediates such as those reported for the reaction of allyl alcohol over Cu(110).28

Other C3 products observed include propene from both alcohols, as well as propionaldehyde from allyl alcohol and acrolein from 1-propanol. These additional C_3 products are attributed to an enolate-mediated reaction pathway which facilitates the interconversion of the saturated and unsaturated C₃ aldehydes and gives rise to propene via a hydrogenation reaction coupled with C-O bond scission. Interconversion between allyloxy and propoxy species via hydrogenation or dehydrogenation of the C₃ backbone is not observed.

In addition to the chemistry observed for alkoxide and enolate surface intermediates, a low-temperature reaction pathway to desorption-limited propene at 215 K and below is observed for allyl alcohol but not for 1-propanol. This low-temperature pathway is attributed to the deoxygenation of the unsaturated surface oxygenate to produce an allyl intermediate which is subsequently hydrogenated to propene.

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