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Surface-Mediated Isomerization and Oxidation of Allyl Alcohol on Cu(110)

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Abstract: Allyl alcohol reacts with clean and oxygen-covered Cu(110) surfaces to produce propanal, acrolein, *n*-propyl alcohol, and hydrogen under ultrahigh-vacuum conditions. Very small amounts of propylene and water are also formed. This pattern of reactivity contrasts sharply to the selective oxidation to acrolein observed on Ag(110). On the clean Cu(110) surface allyl alcohol undergoes O–H cleavage to form the surface alkoxide $CH_2{=}CHCH_2O_{(a)}$ and $H_{(a)}$. The results suggest that the olefin in this species undergoes partial hydrogenation to the surface-bound oxametallacycles $(-CH_2CH_2CH_2O-)_{(a)}$ and $(-CH(CH_3)CH_2O-)_{(a)}$ and complete hydrogenation to $CH_3CH_2CH_2O_{(a)}$. Propanal forms at 320 K via further reaction of these oxametallacycles. Evidence for a π-bonded allyl oxide $CH_2{=}CHCH_2O_{(a)}$, which is more stable than *n*-propoxide $(CH_3CH_2CH_2O_{(a)})$ toward β-hydride elimination, is presented. This allyl oxide decomposes at 370 K to form acrolein. The interaction of the double bond with the surface apparently restricts the interaction of the β-C–H bond with the surface and increases the stability of this species. Propanal, acrolein, and H_2 are formed at 435 K by a process thought to involve the thermal decomposition of $(-CH_2CH_2CH_2O-)_{(a)}$ by a β-hydride elimination pathway. This dehydrogenation pathway exhibits an activation energy 8 kcal/mol greater than for acyclic alkoxides. The conversion of allyl alcohol to propanal and propyl alcohol obviously involves the hydrogenation of the double bond which, by comparison, does not occur for propylene coadsorbed with hydrogen under similar conditions on this surface. Clearly, the hydroxyl group in allyl alcohol facilitates the hydrogenation of its olefin group by tethering the double bond to the surface at temperatures higher than the normal desorption temperature of olefins.

The reactions of monofunctional alcohols with Cu(110) surfaces have been studied in great detail.[1-3] The bonding and reactivity of olefins with this surface have also been studied, although to a lesser extent. As part of our investigation of the reactivity of difunctional molecules on single-crystal surfaces, we have studied the bonding and reactivity of allyl alcohol on Cu(110) surfaces. This molecule contains both hydroxyl and olefinic functionalities and, hence, may be expected to exhibit the reactivities already observed for each functional group alone yet may also exhibit reactivity that is an unexpected combination of these functional groups together.

Primary and secondary alcohols react on preoxidized Cu(110) surfaces below 200 K forming surface alkoxides and water.[1-3] These alkoxides dehydrogenate above room temperature to form the corresponding aldehydes (or ketones) and $H_{(a)}$. Recombination reactions involving $H_{(a)}$ and these alkoxides form the parent alcohol and H_2. Surface oxygen present during the alcohol dose enhances the amount of alkoxide formed.

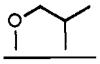
Outka and co-workers[4] observed that ethylene interacts weakly with Cu(110) surfaces: weakly bound ethylene desorbs at 210 K without reaction. Similarly, propylene is not hydrogenated by surface hydrogen on the Cu(110) surface (vide infra). Recent studies[5] of allyl oxide ($CH_2{=}CHCH_2O_{(a)}$, **1**) on the Ag(110) surface show that there is a weak bonding interaction between the π-system and the Ag(110) surface, yet $CH_2{=}CHCH_2O_{(a)}$ (**1**) decomposes on this surface yielding acrolein ($CH_2{=}CHCHO$) and H_2 with no hydrogenation of the double bond.[6] Hence, although double bonds do bind to Cu(110) and Ag(110) surfaces under ultrahigh-vacuum (UHV) conditions, monofunctional olefins are not readily hydrogenated by the Cu(110) surface, and the difunctional $CH_2{=}CHCH_2O_{(a)}$ (**1**) is not hydrogenated by the Ag(110) surface.

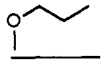
Under atmospheric pressures, however, the double bond in allyl alcohol is partially hydrogenated by heterogeneous copper catalysts. These catalysts convert allyl alcohol to propanal, acrolein, and hydrogen at 180–280 °C (eq 1).[7]

$$2CH_2{=}CHCH_2OH \xrightarrow{[Cu]} CH_3CH_2CHO + CH_2{=}CHCHO + H_2 \quad (1)$$

We report here that allyl alcohol reacts with the clean Cu(110) surface by a process that involves dehydrogenation of the hydroxyl functionality with concomitant hydrogenation of its olefin functionality to form propanal. Acrolein and dihydrogen are also formed as major products in stoichiometric amounts. Minor quantities of *n*-propanol, propylene, and water are also observed. We find that initially the O–H bond is broken to form allyl oxide ($CH_2{=}CHCH_2O_{(a)}$) and $H_{(a)}$. The surface hydrogen partially hydrogenates the double bond, suggesting the formation of surface oxametallacycles **2a** or **2b**. A small amount of the saturated *n*-propoxide **3** may also be formed at this temperature (<250 K).


2a


2b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Subsequent to partial hydrogenation of the surface allyl oxide, five distinct reaction channels occur. We suggest that three of these arise from oxametallacycles **2a** and **2b** rearranging at 320 K to liberate propanal, oxametallacycle **2b** decomposing at 390 K to form propylene and $O_{(a)}$, and oxametallacycle **2a** decomposing at 435 K via β-hydroxide elimination and hydrogenation reactions yielding propanal, acrolein, and dihydrogen.

Experimental Section

General Methods. The experimental apparatus consists of an ultrahigh-vacuum chamber equipped with low-energy electron diffraction and a cylindrical mirror analyzer used in this work for Auger electron spectroscopy (AES). A quadrupole mass spectrometer used for temperature-programmed reaction spectroscopy (TPRS)[8] and a multiplexed computerized system was used to simultaneously monitor up to 100 mass-to-charge (m/q) ratios for TPRS experiments. The mass spectrometer was programmed to rapidly switch between preset mass values

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(1) Wachs, I. E.; Madix, R. J. *J. Catal.* **1978**, *53*, 208–227. Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *95*, 190.

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

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Table I. Experimental Cracking Fractions[a]

m/q	allyl alcohol	propanal	acrolein	propyl alcohol	allyl alcohol-d_1[b]	H_2	H_2O
2	4	2	2	3	20	100	0
18	7	0	0	6		0	100
26	42	24	66	7		0	0
27	82	65	100	26		0	0
28	61	87	62	17		0	0
29	100	100	39	36		0	0
31	48	3	0	100		0	0
39	40	3	3	6		0	0
56	6	0	27	0	2	0	0
57	36	6	0	1	14	0	0
58	22	17	0	1	100	0	0
59	5	0.5		4	28	0	0
60	0			5	2	0	0

[a] Those masses not entered into the table were either not measured or not needed for deconvolution of TPRS spectra. [b] The largest entry for allyl alcohol-d_1 (58) is set equal to 100.

as the crystal was heated. The output of a single TPRS experiment consists of mass spectrometer intensities plotted as function of temperature. Heating rates were approximately 4 K/s unless otherwise stated.

The copper crystal was cleaned by argon ion bombardment at room temperature and annealed at 780 K for 2 min. Surface cleanliness was checked by AES before and after each experiment. The crystal could be cooled to 120 K and was heated from behind by radiation from a tungsten filament. Temperatures were measured by a chromel–alumel thermocouple press-fitted into a hole in the corner of the crystal.

Liquid samples of allyl alcohol, propanal, acrolein, and propyl alcohol were obtained at 96% purity. The cracking pattern of each product was determined on the experimental apparatus by two methods (Table I): (1) a small amount of the compound was leaked into the chamber, and the change in the entire mass spectrum of the gas present in the chamber was analyzed to determine the major fractions; (2) the compound was condensed onto the crystal surface held at 120 K and then thermally desorbed into the mass spectrometer. The mass spectrum of the desorbing multilayers was integrated, and the contributions due to each mass signal were determined. Both methods gave comparable results. We estimate the accuracy of these calibrations to be within 5% of the measured values.

TPRS Experiments. In a typical TPRS experiment, the clean or oxygen-covered Cu(110) surface at 120 K was exposed to multilayer quantities of allyl alcohol (2–5 langmuirs). Then the crystal was annealed to 245 K to desorb the multilayer and molecular states so that these large peaks would not interfere with the smaller product peaks. The crystal was then allowed to cool to 120–200 K before the beginning of the TPRS experiment.

Interpretation of TPRS data in this study is complicated by the similar chemical structure and, thus, similar mass spectral fragmentation patterns of the reaction products. It is not possible to select masses to monitor that are unique to each different product. The desorption spectrum of each individual product was determined by using the decomposition procedure described in the Appendix. The errors associated with the decomposed spectra are 10–20%. For this reason, no attempt is made to explain the fine features of the spectra. The major features of the spectra, however, are entirely reproducible.

Sample Preparation. Acrolein, propanal, and propyl alcohol were stored over $MgSO_4$ and degassed by several freeze–pump–thaw cycles prior to use. Allyl alcohol was dried over $MgSO_4$ and vacuum transferred to a dry sample tube to prevent $MgSO_4$-initiated decomposition.

Sample purity was monitored by checking the desorption spectra for extraneous peaks, which would indicate a contaminant. It was not possible to dry allyl alcohol completely since it forms an azeotrope with water.

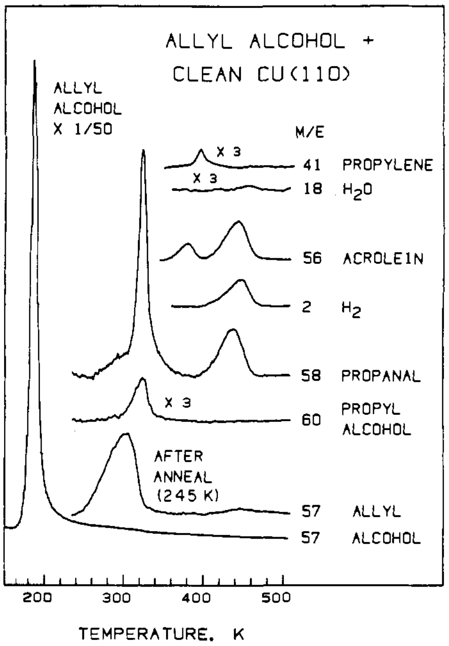

Figure 1. Temperature-programmed reaction spectra for a saturation dose of allyl alcohol on a clean Cu(110) surface heated at 4 K/s. These spectra have been corrected for overlapping cracking fractions and scaled to show the relative amounts of each product as described in the appendix. The m/q values shown are the masses tracked for each.

Allyl Alcohol-d_1 (OD). Temperture-programmed reaction spectroscopy was used to study the reaction of allyl alcohol-d_1 with the clean Cu(110) surface. Decomposition of the TPRS curves, however, was complicated by several factors, which are clarified here prior to presentation of the results: First, samples of all of the expected product isotopes were not readily available, and thus it was not possible to determine the fragmentation patterns of these compounds in the mass spectrometer used here. It was necessary, therefore, to assume that the d_1 and d_2 product fragmentation patterns were essentially the same as their d_0 counterparts except that the parent masses were shifted by one or two mass units, respectively. Second, it was not always possible to pick a single m/q value that uniquely represented each compound (e.g., m/q = 58 for both propanal-d_0 and allyl alcohol-d_1; m/q = 60 for propyl alcohol and propanal-d_2, etc.). However, this problem was circumvented in instances in which only one of the two possible compounds was produced at a given temperature. For instance, the reaction of allyl alcohol-d_0 with Cu(110) produces very little allyl alcohol at 435 K. Thus, in the reaction of allyl alcohol-d_1 with this surface, most or *all* of the m/q = 58 signal at 435 K must be due to propanal-d_0 and not to allyl alcohol-d_1. In the case of m/q = 60, however, relative assignments to propyl alcohol-d_0 and propanal-d_2 were impossible. Third, the allyl alcohol-d_1 starting material was not very isotopically pure. We estimated the purity of the allyl alcohol to be 80% d_1 by assuming the fragmentation pattern of pure allyl alcohol-d_1 paralleled that of pure allyl alcohol-d_0 except for corresponding shifts of 1 amu of certain fragments.

Despite these complications, several specific conclusions can be reached. In particular, most of the deuterium originating in the allyl alcohol-d_1 (OD) starting material ends up on one of the C_1 or C_2 carbons in the propanal-d_1 product. Also since difficulties in product identification mainly concern minor products (e.g., propyl alcohol-d_0 vs propanal-d_2), the deuterium mass balance was excellent.

Results

Products of the Reaction of Allyl Alcohol on Clean Cu(110). Allyl alcohol desorbs from a multilayer state at 190 K. When this state is removed by annealing to 245 K, the formation of allyl alcohol ($CH_2{=}CHCH_2OH$), propanal (CH_3CH_2CHO), acrolein ($CH_2{=}CHCHO$), and H_2 is observed (Figure 1) above 275 K. Propyl alcohol, propylene, and water are also produced in small amounts. The products are produced in five reaction channels: (1) allyl alcohol desorbs at 295 K, although the exact temperature and magnitude of this peak are influenced by the temperature to which the crystal is annealed prior to the TPRS experiment; (2) a large amount of propanal and a small amount of propyl alcohol desorb at 320 K; (3) acrolein forms at 370 K; (4) a small amount of propylene forms at 390 K; (5) propanal, acrolein, hydrogen, and water form at 435 K. Submonolayer doses of allyl alcohol onto the clean Cu(110) surface give similar results except that the 295 K allyl alcohol peak decreases with decreasing allyl alcohol exposure. It is important to note that no H_2 or H_2O is evolved below 400 K.

The low-temperature propanal peak (320 K) is half as wide (12.5 K fwhm) as expected for peaks resulting from first-order reaction kinetics at this temperature. The fwhm for the decomposition of *n*-propoxide to propanal on this surface was determined to be 36 K, which is nearly 3 times that exhibited by the propanal peak observed by the decomposition of allyl alcohol (vide supra). Clearly, the kinetics by which propanal is produced from allyl alcohol at 320 K differ considerably from those by which propanal

Table II. Relative Yields of Products from the Reaction of Allyl Alcohol with the Clean Cu(110) Surface

	peak temp, K		
product	290-320	370-390	435
allyl alcohol	*a*		10
propanal	100		44
propyl alcohol	11		
acrolein		11	36
H_2			33
H_2O			3
propylene		3	

[a] The amount of allyl alcohol desorbing at 290-320 K is highly sensitive to the annealing temperature prior to TPRS.

is produced from propyl alcohol.

Ethylene and CO_2 are not produced during the reaction on clean or oxygen-covered surfaces. Auger spectroscopy showed no significant amounts of carbon or oxygen remaining on the surface after TPRS experiments.

Mass Balance. Table II shows the relative yields of products shown in Figure 1. These yield data reveal the relative quantities of carbon, hydrogen, and oxygen on the surface at any point during the course of this reaction. Initially, allyl alcohol is dosed onto the surface, and the ratios of C, H, and O are the same as in pure allyl alcohol: C_3H_6O. Desorption of allyl alcohol at 290 K and propanal at 320 K does not disturb this ratio since propanal is an isomer (C_3H_6O) of allyl alcohol. Formation of propyl alcohol (C_3H_8O) at 320 K requires, however, that the surface C:H ratio be greater than 3:6 above 320 K. At 370 K, however, acrolein is produced in the same amount as propyl alcohol at 320 K. Since acrolein (C_3H_4O) has two fewer hydrogens than allyl alcohol, the elemental composition of the surface species at ~380 K must again be C_3H_6O. The formation of propyl alcohol and acrolein (370 K) thus appear linked. Further, since propoxide is unstable above 350 K, the only compounds that could reasonably exist on the surface at this temperature and that have this empirical formula are propanal, allyl alcohol, and oxametallacycles **2a** and **2b**. Since unreacted propanal and allyl alcohol desorb much below this temperature, oxametallacycles **2a** and **2b** are the most likely candidates.

Desorption of propylene (C_3H_6) at 390 K does not perturb the C:H ratio of 3:6. The oxygen-to-carbon ratio, however, is probably slightly greater than 1:3 after this reaction, though very little propylene is formed so this effect is small.

Allyl alcohol, propanal, acrolein, H_2O, and H_2 desorb at 435 K. Except for a slight excess of oxygen, the elemental composition for the sum of these products exactly matches the empirical formula C_3H_6O. Propanal and allyl alcohol both have this empirical formula, and the sum of the amount of hydrogen (33%) and water (3%) produced matches the amount of acrolein produced. The amount of water produced also accounts for the amount of oxygen left behind during the desorption of propylene (3%), such that the overall mass balance is excellent.

Thus, these arguments suggest that the species remaining on the surface at 380 K have the elemental composition of C_3H_6O. Similarly, the overall stoichiometry of the precursors to the reaction-limited products produced at 435 K also has this elemental composition and is accompanied by a small amount of coadsorbed atomic oxygen. Thus, oxametallacycles **2a** or **2b** are reasonable precursors for this reaction, since they not only have the correct stoichiometry, but they can also directly form the products observed.

Oxygen-Covered Cu(110). The total product yield resulting from the coadsorption of allyl alcohol increases with increasing coverage of oxygen on the Cu(110) surface as shown in Figure 2. The yield of each product is plotted as a function of oxygen coverage in Figure 3. Notably, the low-temperature propanal peak decreases sharply as the low-temperature acrolein peak increases sharply at $\theta_O = 0.28$. Except for the low-temperature acrolein peak, the yield of each product reaches a maximum at or slightly above one-quarter of a monolayer and decreases at higher coverages of oxygen (Figures 2 and 3). This behavior is similar to that of methanol[1] and water[9] on preoxidized Cu(110) surfaces. The allyl alcohol desorption peak is fairly symmetric on the clean surface but develops a high-temperature tail at high coverages of $O_{(a)}$. The low-temperature propanal peak (320 K) broadens and shifts to higher temperature as it decreases in size. The high-temperature propanal peak (435 K) increases in height and shifts slightly to lower temperatures with increasing oxygen coverage; it also decreases in size at high coverages of oxygen (0.4 monolayer).

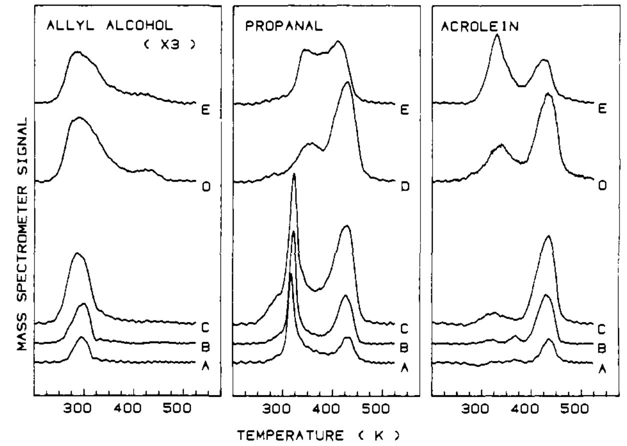

Figure 2. Effect of oxygen coverage on the desorption of allyl alcohol, propanal, and acrolein. The coverage of $O_{(a)}$ before the allyl alcohol dose (monolayer) was (A) 0.0, (B) 0.1, (C) 0.26, (D) 0.28, and (E) 0.4. Allyl alcohol was dosed onto the clean or oxygen-covered surface and then annealed to 245 K before each TPRS experiment (heating rate = 4 K/s).

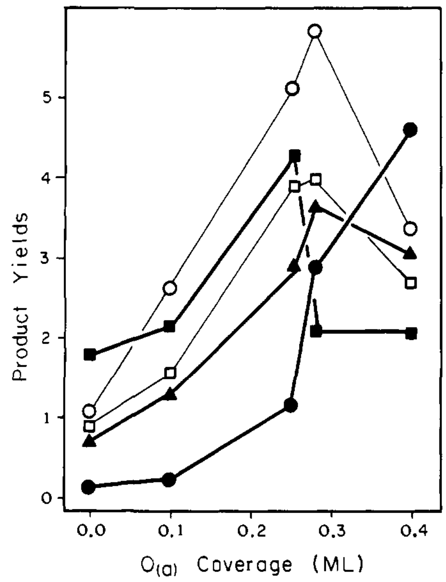

Figure 3. Product yields for the TPRS product peak vs coverage of $O_{(a)}$: propanal (■, □), acrolein (●, ○), and allyl alcohol (▲). Solid figures represent low-temperature peaks; open figures represent high-temperature peaks. Yields were determined from the decomposed spectra and were corrected for relative mass spectrometer sensitivity. The oxygen coverage was calculated from Auger peak heights. The Cu(110) crystal was annealed to 245 K after exposure to allyl alcohol prior to heating.

The low-temperature acrolein peak (Figure 3) is the only peak that continues to increase in magnitude at high oxygen coverages. This peak also shifts to a slightly lower temperature with increasing coverage of oxygen.

Hydrogen-Covered Cu(110). Hydrogen atoms were dosed onto a Cu(110) surface at 120 K by dissociation of molecular hydrogen (1.25 langmuirs) on a platinum filament at 1300 K. Exposure of this surface to allyl alcohol (4 langmuirs) followed by annealing to 245 K yields the reaction spectrum shown in Figure 4. One

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(9) Bange, K.; Grinder, D. E.; Madey, T. E.; Sass, J. K. *Surf. Sci.* **1984**, *136*, 38-64.

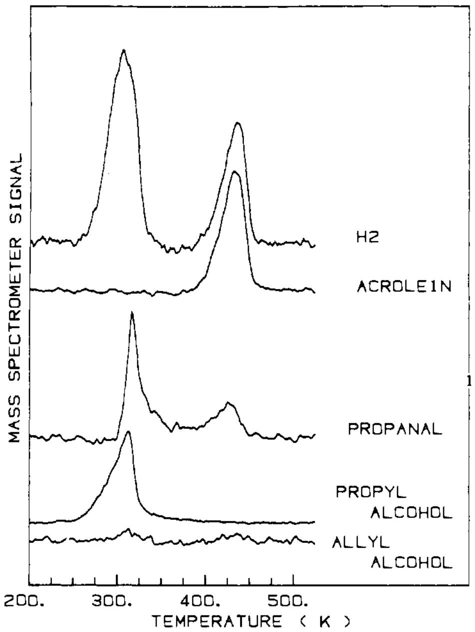

Figure 4. Temperature-programmed reaction spectra for a 0.45-langmuir dose of allyl alcohol on a surface predosed with 1.25 langmuirs H_2 at 120 K.

interesting feature of this spectrum is that no allyl alcohol is produced. Instead, 10 times more propyl alcohol is produced on this surface than from the reaction of allyl alcohol with the clean surface. The propanal and the high-temperature acrolein peaks are about the same size as those observed on the clean surface. No acrolein was produced at 325 K, in sharp contrast to the reaction channel produced with coadsorbed oxygen. Identical results are obtained independent of the order in which allyl alcohol and hydrogen atoms were dosed. The H_2 produced at 325 K is desorption-limited, whereas that appearing at 435 K is reaction-limited. The evolution of propyl alcohol at 300 K and the absence of allyl alcohol desorption is clear evidence of increased hydrogenation of the double bond due to excess hydrogen.

Reaction of Allyl Alcohol-d_1 ($CH_2{=}CHCH_2OD$) on Clean Cu(110). The results presented to this point suggest that allyl alcohol reacts on clean Cu(110) surfaces to cleave the O–H bond and the C–H bond α to oxygen and to hydrogenate the olefin functionality to form propanal. The mass balance indicates that aside from the H_2 produced at 435 K, all of the hydrogen released during the cleavage of the O–H and α-C–H bonds is transferred to the olefinic carbons. We studied the reaction of allyl alcohol-d_1 ($CH_2{=}CHCH_2OD$) on this surface to verify these hydrogen-transfer reactions.

Allyl alcohol-d_1 (3 langmuirs, 80% d_1, 20% d_0) was dosed onto a clean Cu(110) surface, and the surface was annealed to 245 K. This surface produced the TPRS spectra shown in Figure 5. Despite the complications concerning the deconvolution of these spectra discussed in the Experimental Section, several useful conclusions can be made. The sharp 320 K propanal peak is largely d_1 ($m/q = 59$). This fact is established by the sharp peak shape for $m/q = 59$, the peak temperature (see Figure 1), and the magnitude of the $m/q = 59$ peak relative to m/q 60–62. Further, the *maximum* possible yield of propanal-d_2 is obtained by assuming that the $m/q = 60$ peak is all due to propanal-d_2; the yield of d_2 is then only 6% of that of propanal-d_1. This value is only an upper limit for the amount of propanal-d_2 produced, since part of this peak is probably also due to propyl alcohol-d_0. Further, the amount of propanal-d_0 produced also appears to be small, as no 320 K peak or shoulder appears on the $m/q = 58$ curve before or after the computer reduction of the curves. The high-temperature propanal peak contains propanal-d_0 and propanal-d_1; the estimated percentages are 77% d_0 and 23% d_1. A substantial amount of the propyl alcohol formed appears to be deuterated. Assuming that all of the $m/q = 60$ curve is due to propyl alcohol-d_0, the ratio of propyl alcohol-d_0, -d_1, and -d_2 is 1:2.5:1.

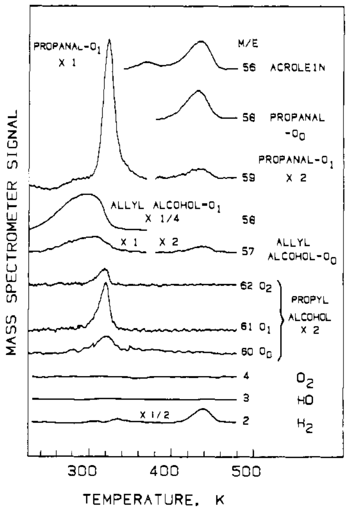

Figure 5. TPRS spectra resulting from the reaction of allyl alcohol-d_1 with a clean Cu(110) surface. Masses used to represent each compound are indicated in the figure. Deconvolution procedure described in text.

Table III. Product Integrals for the Reaction of Alcohol-d_1 with Cu(110)

product	peak temp, K			sum of integrals
	290–320	370	435	
allyl alcohol-d_0	11		1.3	
propanal-d_0			10	
propyl alcohol-d_0	2.4			34.7-d_0
H_2			10	
acrolein[a]		1.1	11	
allyl alcohol-d_1	100			
propanal-d_1	37		3.1	146.1-d_1
propyl alcohol-d_1	6			
propyl alcohol-d_2				2.6-d_2 81% d_1, 19% d_0

[a] Acrolein is not counted as one of the d_0 products since the combination of acrolein and H_2 produce propanal, and H_2 is already counted.

At first glance deuterium does not appear to be conserved. No HD or D_2 desorbs; only a small amount of propanal-d_1 is produced at high temperatures; there are no other high-temperature products containing deuterium. Careful examination of the product yields (Table III), however, reveals that the allyl alcohol desorbing at 290 K actually has a higher isotopic purity (90% d_1) than the starting material (80% d_1-allyl alcohol). (Note the isotopic purities are compared on the same basis: by comparing m/q 57 vs 58 for both the multilayer and the 290 peak.) A comparison between the *total* amount of deuterated and nondeuterated compounds produced in this reaction (including allyl alcohol-d_1 and -d_0) indicates that the desorbing material is about 81% d_1, which agrees with the isotopic purity of the starting material. However, if one makes the same comparison excluding d_1- and d_0-allyl alcohol, the products are only 68% d_1. In other words, the 80% pure starting material in which D:H is 4:1 forms products in which the D:H ratio is less. Clearly there is a kinetic or equilibrium isotope effect involved in the initial transfer of hydrogen (deuterium) from the hydroxyl group in allyl alcohol to the Cu(110) surface which skews the isotopic distribution among the products.

Arrhenius Activation Parameters. Figure 6 shows an Arrhenius plot of the desorption of propanal during its low-temperature and high-temperature reaction determined by using the method of heating rate variation over the range 0.2–11 K/s.[10] The activation parameters for these two reactions are $E_a = 19.1$ kcal/mol, log $A = 12.9$ and $E_a = 27.3$ kcal/mol, log $A = 13.2$, respectively. The

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[10] Falconer, J. L.; Madix, R. J. *Surf. Sci.* **1975**, *48*, 393–405.

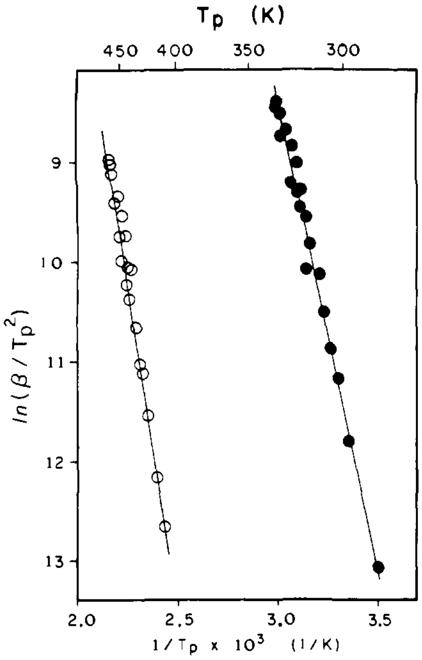

Figure 6. Arrhenius plot used to determine the activation parameters for the low-temperature (●) and the high-temperature (○) propanal producing reactions.

activation energy for the low-temperature reaction (19 kcal/mol) is about the same as that expected for the decomposition of primary alkoxides (21 kcal/mol) on the Cu(110) surface.[2,11] The activation energy of 27 kcal/mol for the high-temperature reaction is quite large and clearly arises from the decomposition of an intermediate that is substantially more stable than acyclic, primary alkoxides on this surface.

Oxidation of *n*-Propyl Alcohol on Cu(110) Surfaces. *n*-Propyl alcohol reacts with clean or oxygen-covered Cu(110) surfaces producing propanal, dihydrogen, and *n*-propyl alcohol via a propoxide intermediate. The preoxidized Cu(110) surface gives higher yields of these products, as previously described.[2] The TPRS curves for the reaction of *n*-propyl alcohol with the oxidized surface and for the reaction of allyl alcohol on the clean surface are compared in Figure 7. The propanal reaction curve produced during the reaction of *n*-propyl alcohol is 4 times wider (at half maximum) than the propanal peak produced during the reaction of allyl alcohol. Although both reaction peaks begin at nearly the same temperature, the rate of evolution of the propanal produced from allyl alcohol increases rapidly, reaches its maximum, then decreases rapidly. Thus, the temperature of this peak maximum is 30 K lower than that from propyl alcohol. Large quantities of H_2 are produced from the decomposition of propyl alcohol; no H_2 is produced during the low-temperature reaction pathway of allyl alcohol.

Mechanistic studies of the decomposition of *n*-propyl alcohol and other alcohols[1,2] on Cu(110) surfaces indicate that the rate-limiting step for the oxidation of *n*-propyl alcohol on this surface is the cleavage of a C–H bond α to oxygen in *n*-propoxide ($CH_3CH_2CH_2O_{(a)}$), yielding propanal and $H_{(a)}$ (eq 2). Hydrogen atoms recombine to yield H_2 at a slightly higher temperature than the propanal peak.

$$\underset{3}{CH_3CH_2CH_2O_{(a)}} \rightarrow CH_3CH_2CHO + H_{(a)} \quad (2)$$

Clearly, the reaction yielding propanal from allyl alcohol is mechanistically different from that from propyl alcohol. Oxametallacycle **2b** could form propanal by a 1,2 hydrogen shift. This mechanism is consistent with the dominance of propanal-d_1 formed from d_1 (OD) allyl alcohol and the absence of any effect of excess coadsorbed hydrogen atoms on the kinetics of propanal formation. However, this reaction has no precedent in organometallic chemistry. Furthermore, a reaction of this type should show a peak shape indicative of simple first-order kinetics, which is not exhibited by the propanal product peak at 320 K. Propanal might also be formed from the surface-bound aldehyde $-CH_2CH_2CHO_{(a)}$ (**4**, eq 3). However, this reaction can be ruled out by using the

$$\mathbf{2a} \rightarrow \underset{\mathbf{4}}{-CH_2CH_2CHO_{(a)}} + H_{(a)} \rightarrow CH_3CH_2CHO \quad (3)$$

following arguments. Species **4** and $H_{(a)}$ would have to be formed from β-hydride elimination of oxametallacycle **2a** (eq 3), yet no H_2 is formed below 435 K. Further, metallacycles are more stable in coordination compounds toward β-hydride elimination than are their acyclic analogues (vide infra). This generalization also seems to be true on surfaces. For example, on Ag(110) the cyclic dialkoxide of ethylene glycol is 6 kcal/mol more stable than the ethoxide.[12] Thus **2a** would not be expected to decompose below the temperature at which $CH_3CH_2CH_2O_{(a)}$ decomposes.

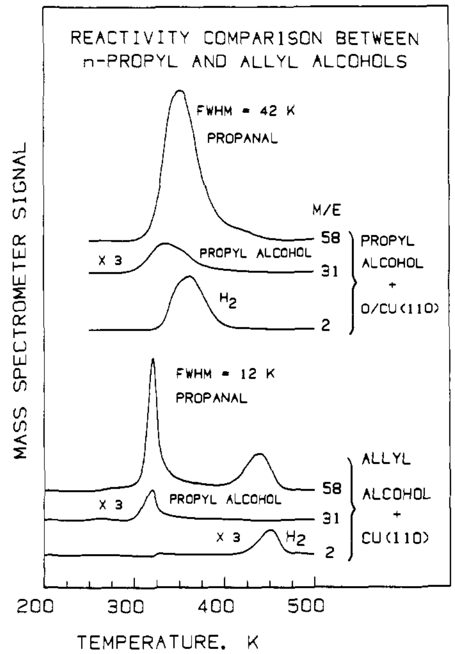

Figure 7. Comparison of the reactivity of *n*-propyl alcohol and allyl alcohol on the Cu(110) surface (β = 10 K/s).

Though the kinetics of formation of propanal differ considerably for allyl and propyl alcohol, both reactions may involve the same intermediate, *n*-propoxide. There is a critical difference in the two reactions. In the conversion of *propyl alcohol to propanal*, *n*-propoxide (**3**) is only consumed, and the reaction kinetics are dictated solely by the rate constant for its dehydrogenation. On the other hand, in the conversion of *allyl alcohol to propanal*, *n*-propoxide (**3**) may be *both generated* by olefin hydrogenation *and consumed* by β-hydride elimination (eq 4). Thus, in the

$$CH_2{=}CHCH_2OH_{(a)} \rightarrow \rightarrow \mathbf{2a} \text{ or } \mathbf{2b} \xrightarrow{+H_{(a)}}$$
$$\underset{\mathbf{3}}{CH_3CH_2CH_2O_{(a)}} \xrightarrow{-H_{(a)}} CH_3CH_2CHO \quad (4)$$

reaction of propyl alcohol to propanal, *n*-propoxide (**3**) is the *starting material*, and its surface concentration is determined solely by its first-order decomposition. In the reaction of allyl alcohol to propanal, *n*-propoxide (**3**) is a *reaction intermediate*, and its surface concentration is dependent upon its rate of formation, its rate of decomposition, the concentrations of allyl oxide, **2a**, **2b**, propoxide, and $H_{(a)}$, and the rates of all reactions that compete for $H_{(a)}$.

Basically, the sharp falloff of the propanal product peak appears to be the result of a competitive hydrogen scavenging reaction

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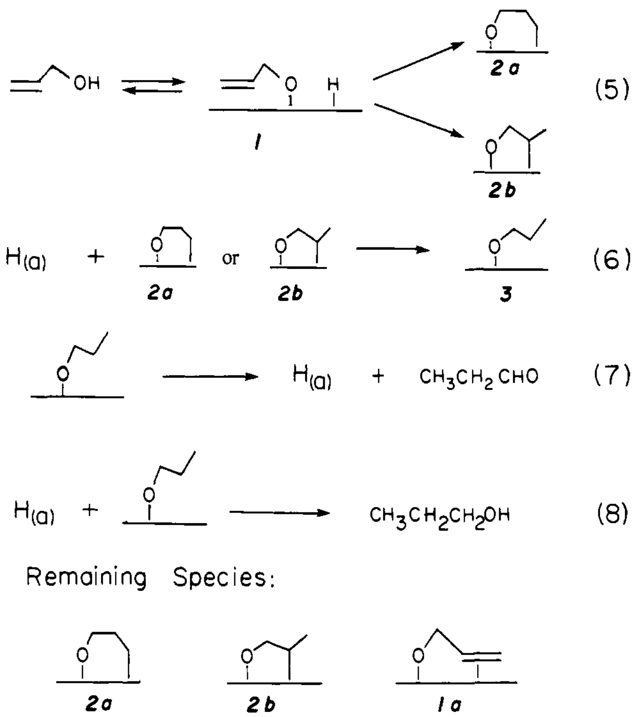
[11] Capote, A. J.; Madix, R. J., in progress.

[12] Brainard, R. L.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 8082–8083.

Scheme I. Proposed Mechanisms for Reactions Occurring between 290 and 320



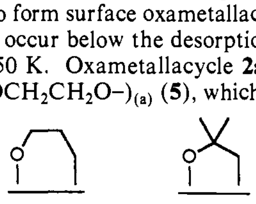
at 320 K. This reaction removes reactive hydrogen atoms from the surface, causing this sharp decrease in the rate of propanal formation and precluding the hydrogen recombination reactions near 350 K. The most likely hydrogen scavenger is the propoxide intermediate which leads to propanol formation. Clearly, little adsorbed hydrogen is needed to carry the chain of reactions (4) producing propanal. The large ratio of propanal to propanol formed supports this reaction scheme. Indeed, coadsorption of H atoms leads to greater production of propanol, consistent with a greater rate of termination reactions over chain-carrying reactions. For reasons not currently understood, however, **2a** and **2b** are *not* fully hydrogenated to propoxide with excess coadsorbed H atoms. The origin of this effect may rest in the competitive desorption of H_2, which occurs in the same temperature range.

Attempted Hydrogenation of Propylene. A Cu(110) surface covered with $H_{(a)}$ was prepared by exposure of a clean Cu(110) surface at 120 K that was 1.5 cm from a hot mass spectrometer filament to 18 langmuirs of dihydrogen. This surface was then exposed to 0.03 langmuir of propylene. Thermal desorption of this surface produced hydrogen (52%), propylene (100%), and propane (0.5%). Thermal desorption of propylene from the clean Cu(110) surface in the absence of coadsorbed hydrogen indicated that the propylene was contaminated with 0.5% propane. Thus, propylene is not hydrogenated by the Cu(110) surface under UHV conditions.

Discussion

The reaction of allyl alcohol with the Cu(110) surface is much more complicated than that observed for the reactions of monofunctional alcohols or olefins on this same surface or of allyl alcohol with the Ag(110) surface. The alkoxide linkage leads to retention of the double bond near the surface at temperatures significantly above those characteristic of olefin desorption and allows the formation of oxametallacycle species. As shown above, the product distribution is very sensitive to the coadsorption of hydrogen and oxygen in a way that clearly shows the importance of partial self-hydrogenation. Below we discuss the mechanisms for the reaction of allyl alcohol with the clean Cu(110) surface that give rise to products between 290 and 320 K, to the low-temperature acrolein peak (370 K), to the propene peak (390 K), and to the high-temperature reaction products (435 K).

Reactions Occurring between 290 and 320 K. Scheme I shows the most likely mechanisms for the reactions that occur between 290 and 320 K. First, adsorbed allyl alcohol either desorbs or undergoes reversible O–H bond cleavage to form allyl oxide (**1**) and $H_{(a)}$. These two species then react via partial hydrogenation of the double bond to form surface oxametallacycles **2a** or **2b** (eq 5). These reactions occur below the desorption temperature of H_2, which is 320–350 K. Oxametallacycle **2a** is similar to the oxametallacycle $(-OCH_2CH_2O-)_{(a)}$ (**5**), which is formed during the reaction of ethylene glycol with preoxidized Ag(110) surfaces.[11] Oxametallacycle **2b** is similar to the oxametallacycle $(-CH_2C(CH_3)_2O-)_{(a)}$ (**6**), believed to be a transient intermediate in the decomposition of t-$BuO_{(a)}$ on Ag(110)[13] and Cu(110)[14] surfaces near 600 K. Oxametallacycles **2a** or **2b** can also react with $H_{(a)}$ forming *n*-propoxide ($CH_3CH_2CH_2O_{(a)}$, **3**), though this reaction does not occur readily at the dosing temperature since little propanal-d_2 is formed by reaction of the allyl oxide with deuterium atoms liberated by allyl alcohol-d_1 (OD).

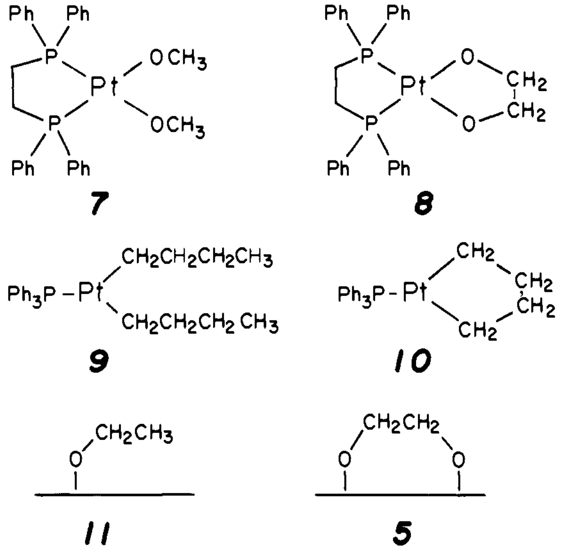


5 **6**

At 320 K *n*-propoxide (**3**) can undergo β-hydride elimination to form propanal and $H_{(a)}$. At this temperature some surface hydrogen may react with metallacycle **2a** or **2b** to form more propoxide. Thus, a cyclic reaction mechanism in which $H_{(a)}$ is conserved converts metallacycles **2a** and **2b** into propanal. However, this cycle is not autocatalytic in nature and cannot proceed faster than propoxide decomposition. Thus even in the presence of excess $H_{(a)}$, propanal cannot be created from this reaction any faster than it is from pure *n*-propoxide from propyl alcohol. Propanol is formed by a chain-terminating step between the propoxide and adsorbed H atoms.

One concept that is central to the understanding of the reaction of allyl alcohol on the clean Cu(110) surface is the fact that metallacycles are often significantly more stable toward β-hydride elimination than their acyclic counterparts.[11,16-18] For instance, $(DPPE)Pt(OCH_3)_2$ (**7**, Scheme II) decomposes at 393 K at a rate that is at least 10^7 times faster than at which $(DPPE)Pt(OCH_2)_2$

Scheme II. Comparison between Cyclic and Acyclic Ligands



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(13) Brainard, R. L.; Madix, R. J. *Surf. Sci.*, in press (t-BuOH/Cu(110)).

(14) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, P. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805–4831.

(15) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

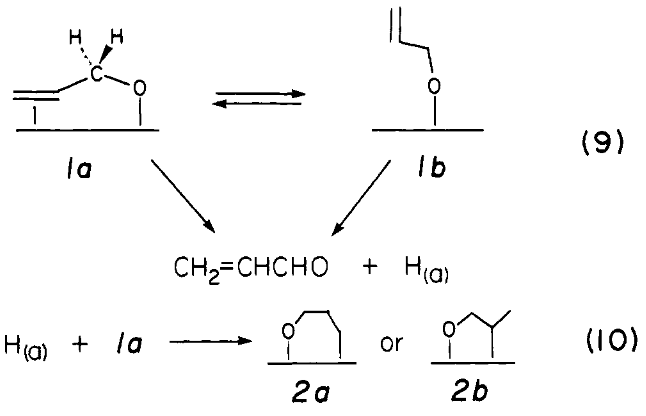
(16) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536.

(17) Miller, T. M.; Whitesides, G. M. *Organometallics* **1986**, *5*, 1473–1480.

(18) Thorn, D. L.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.

(19) If each pair of reactions is assumed to have the same preexponential (A), then the difference in activation energies (cyclic vs acyclic) are 12 and 9 kcal/mol for the alkoxide and the alkyl systems, respectively.

Scheme III. Proposed Mechanism of Formation of the Low-Temperature Acrolein Product (370 K)



(**8**) decomposes.[14] Similarly, (Ph$_3$P)PtBu$_2$ (**9**) decomposes at 393 K at a rate that is 10^5 times faster than that at which (Ph$_3$P)Pt(CH$_2$)$_4$ (**10**) decomposes,[16] corresponding to a difference in activation energies of 9 and 5 kcal/mol, respectively.[20] This large stability difference is believed to stem from the torsional strain that metallacycles must overcome to achieve the 0° M–C–C–H dihedral angle considered to be necessary for β-hydride elimination.[16-19] Surface metallacycles show similar stabilities. The surface metallacycle (–OCH$_2$CH$_2$O–)$_{(a)}$ (**5**) decomposes on Ag(110) surfaces to yield (CHO)$_2$ and H$_2$ at a temperature 100 K higher[12] (375 K) than the peak temperature for the decomposition of acyclic EtO$_{(a)}$ (**11**) on the same surface.[21,22]

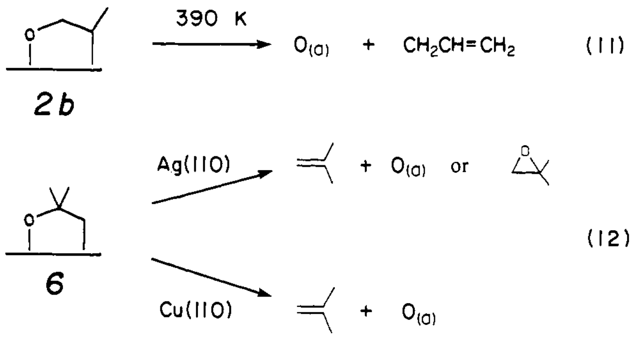
Thus, oxametallacycles **2a** or **2b** are expected to be 5–9 kcal/mol more stable toward β-hydride elimination than *n*-propoxide. Further, these metallacycles *must* react with H$_{(a)}$ to form the acyclic *n*-propoxide before β-hydride elimination to give propanal could occur at 320 K.

Low-Temperature Acrolein Peak. One unexpected result in this study was the observation that the lowest temperature reaction that forms acrolein on clean Cu(110) occurs at a significantly *higher* temperature than that of the dehydrogenation of *n*-alkoxides forming aldehydes on this surface.[1-3] This is surprising because, in general, the temperatures at which alkoxides decompose on Cu(110) surfaces decrease with decreasing strength of the C–H bonds α to oxygen.[2] In this case, the C–H bond α to oxygen in allyl alcohol is 12 kcal/mol *weaker* than the analogous C–H bond in propyl alcohol (80 and 92 kcal/mol, respectively).[23] On *Ag(110)* surfaces, allyl oxide does indeed decompose to acrolein at a lower temperature than *n*-propoxide decomposes to form propanal, as expected on this basis.[5]

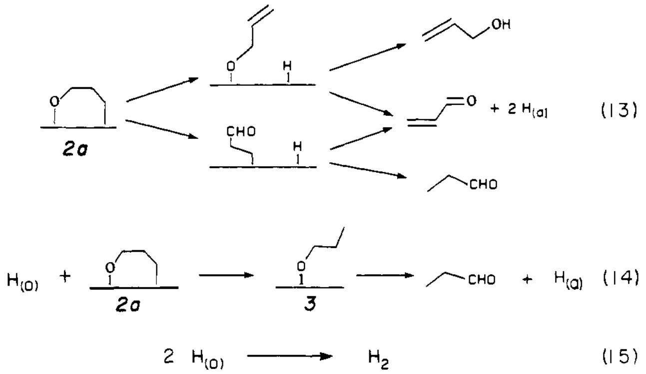
We rationalize the unexpectedly higher stability of this intermediate to acrolein using the following arguments. The carbon–carbon double bond in allyl alcohol (or in the surface allyl oxide) obviously interacts with the surface strongly enough to be hydrogenated, as shown by the increased formation of propyl alcohol in the hydrogen coadsorption experiments. Thus, the double bond in allyl oxide probably also interacts strongly with the surface (**1a**, Scheme III). We assert that this species (**1a**) either undergoes β-hydride elimination by first breaking the olefin–surface bond, which adds to the activation energy, or it reacts directly via β-hydride elimination; because **1a** is cyclic, torsional strain increases the activation barrier.

Another important aspect of this reaction is that the conversion of allyl oxide (**1a**) is acrolein produces H$_{(a)}$, yet no significant amounts of H$_2$ or allyl alcohol are produced. We propose that the H$_{(a)}$ reacts with a second allyl oxide to form oxametallacycles **2a** or **2b**. In fact, the mass balance establishes that only oxametallacycles **2a** or **2b** should remain on the surface after this reaction, consistent with this proposal.

Scheme IV. Comparison between the Proposed Mechanism of Decomposition of Metallacycle **2b** and That of Metallacycle **6** on Cu(110) and Ag(110) Surfaces



Scheme V. Proposed Mechanisms for the High-Temperature Reaction Occurring at 435 K



Desorption of Propylene at 390 K. The small, reaction-limited propylene peak occurring at 390 K may result from the unimolecular decomposition of residual amounts of oxametallacycle **2b** in which C–O and C–surface bonds are broken simultaneously (Scheme IV). There appears to be significantly less **2b** than **2a** that survives the reactions at 320 K. This feature may be related to selectivities in both reactions 5 and 6 (Scheme I). Oxametallacycle **2b** is quite similar to oxametallacycle **6**, which is believed to yield isobutylene and O$_{(a)}$ on both Ag(110)[13] and Cu(110)[14] surfaces. In these studies formation of oxametallacycle **6** is rate-limiting, and its subsequent decomposition at 440 K on Ag(110) and at 550 K on Cu(110) is fast.

High-Temperature Reaction Pathway (435 K). The most likely high-temperature reaction pathway is shown in Scheme V. Initially there are two surface species prior to the onset of reaction, oxametallacycle **2a** and a small amount of O$_{(a)}$ as established by analysis of mass balance. Since initially there is no H$_{(a)}$ available for reaction, **2a** probably undergoes rate-limiting β-hydride elimination forming either allyl oxide **1** or CH$_2$CH$_2$CHO$_{(a)}$ (**4**). These acyclic products (**1** and **4**) could then undergo a second β-hydride elimination reaction that should be faster than the first because of their acyclic structures. All of these β-hydride reactions produce H$_{(a)}$. Thus, surface hydrogen can react with either **1** or **4**, producing allyl alcohol or propanal. Similarly, H$_{(a)}$ could react with oxametallacycle **2a**, forming *n*-propoxide **3**, which in turn could produce propanal and more H$_{(a)}$. Surface hydrogen can also undergo recombination to form H$_2$.

The activation energy for this reaction (27 kcal/mol) is 8 kcal/mol higher than that of the propanal-producing reaction occurring at 320 K. This stability of oxametallacycle **2a** toward decomposition via β-hydride elimination is in keeping with that (5–9 kcal/mol) expected of organometallic metallacycles and surface metallacycles relative to their acyclic analogues (vide supra, Scheme II).

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[20] This difference in temperature corresponds to approximately 6 kcal/mol difference in activation energy if one assumes that these reactions both have preexponentials of 10^{13}.

[21] Wachs, I. E.; Madix, R. J. *Appl. Surf. Sci.* **1978**, *1*, 303.

[22] Carbon–hydrogen bond strengths were calculated by using methods described in: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp. 72–77, 272–275.

[23] Ko, E. I.; Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *62*, 264.

Table IV. Correction Factors

compound	m/q of monitored mass	correction
H_2	2	0.96
H_2O	18	1.0
CO	28	1.0
propanal	58	4.56
acrolein	56	3.46
propyl alcohol	31	0.51
propyl alcohol	60	11.2
allyl alcohol	57	3.72
propylene	41	1.43

The product distribution observed with coadsorbed hydrogen can also be explained on the basis of these reaction intermediates (Figure 4). First, the recombinative desorption of the H_2 at 320 K indicates that $H_{(a)}$ was present in excess. The absence of allyl alcohol and acrolein at 370 K among the products clearly shows that all of the allyl oxide intermediates (**1a** and **1b**, Scheme III) are hydrogenated. The oxametallacycle **2a**, however, is not *completely* hydrogenated to propoxide and, therefore, acrolein formation at 435 K is observed.

Mechanistic Interpretations for the Reaction of Allyl Alcohol on Oxygen-Covered Cu(110). In general, the effect of preadsorbed oxygen tends to increase the size of the TPRS desorption curves up to a coverage of 0.25 monolayer (Figures 2 and 3). This effect is probably largely due to the ability of surface oxygen to facilitate the cleavage of O–H bonds and, perhaps, to increase the two-dimensional ordering (packing) of the allyl oxide. Thus, $O_{(a)}$ helps to convert allyl alcohol to allyl oxide (**1**). Since all of the reaction products are ultimately derived from **1**, increasing coverages of $O_{(a)}$ should increase the yields of all products. Due to competition between adsorbed alkoxide groups and $O_{(a)}$ for binding sites, however, coverages of $O_{(a)}$ that are greater than 0.25 monolayer decrease the conversion of allyl alcohol to allyl oxide and thus, in general, decrease the yields of products. This steric effect has been observed before for the reaction of methanol and water on this surface.[1,9]

The other major effect of preadsorbed oxygen is the low-temperature reaction pathway to acrolein (Figures 2 and 3). The yield of this peak increases continuously with increasing coverage of $O_{(a)}$, in contrast to the other peaks, which decrease at high $O_{(a)}$. The appearance of this peak is due to the scavenging of hydrogen atoms released in alkoxide formation by adsorbed oxygen atoms. This acrolein peak also shifts to lower temperatures with increasing yield and increasing coverage of $O_{(a)}$. We propose that at low coverages of oxygen, the olefin-bound allyl oxide species (**1a**) is formed, but at high coverages of $O_{(a)}$, the coverage of allyl oxide is sufficiently large that the π-bound species cannot form and **1b** is the predominate surface species. This acyclic species should then decompose at a lower temperature than the π-bound species, since it is not stabilized by π interaction with the surface.

Conclusions

Allyl alcohol reacts with clean and oxidized Cu(110) surfaces by a variety of reaction pathways involving its hydroxyl and its olefin functionalities. The hydroxyl group exhibits chemistry expected of hydroxyls in other alcohols: cleavage of the O–H bond and cleavage of the C–H bond α to oxygen. In addition, these functional groups act together to give reaction pathways not expected of the functional groups alone. For instance, cleavage of the O–H bond serves to covalently bind the molecule to the surface such that the olefin is partially or completely hydrogenated. Although hydrogenation of olefins by copper catalysts is known under atmospheric conditions, hydrogenation of monofunctional olefins has not been observed under UHV conditions.

The olefin functionality also produces some unexpected reactivity in the hydroxyl functionality. The π-bound allyl oxide ($CH_2{=}CHCH_2O_{(a)}$, **1a**) is less reactive toward β-hydride elimination than its saturated analogue ($CH_3CH_2CH_2O_{(a)}$, **3**) even though the C–H bond β to the surface in **1a** is 12 kcal/mol weaker than that in **3**. This unexpected stability in **1a** is attributed to its π-bond to the surface. This bond restricts the approach of the β-hydrogens to within bonding distance of the surface.

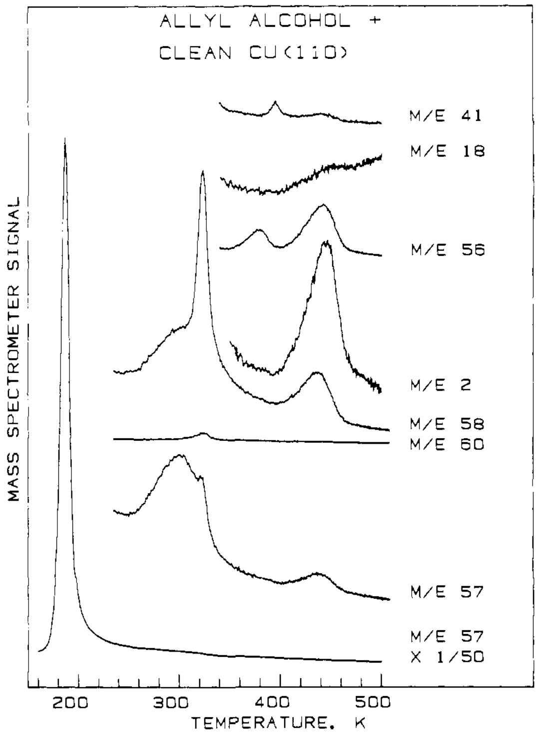

Figure 8. Raw multiplexed mass spectrometer data of Figure 1 uncorrected for cracking fractions.

The partial hydrogenation of the olefin in allyl oxide **1** forms oxametallacycles **2a** and **2b**. Both compounds are more stable toward β-hydride elimination than are acyclic alkoxides. Oxametallacycle **2a** decomposes via β-hydride elimination at 435 K and metallacycle **2b** decomposes via C–O and C–surface cleavage forming propene and $O_{(a)}$ at 390 K.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of R.L.B. during this research work. Partial support of the National Science Foundation (NSF CHE 86 15910) is also gratefully acknowledged.

Appendix: Data Analysis

In temperature-programmed reaction spectroscopy (TPRS), the formation of products is detected by measuring the mass spectrometer signal corresponding to each product. In certain cases, a single m/q value can be found that will uniquely identify each product. In this study, however, the chemical structures of the products are quite similar and, thus, have similar cracking patterns. To determine the desorption rate for each product, it is necessary to separate the contribution that each product makes to the total signal at each m/q value, as described below.

First, a m/q value is chosen to represent each product, such that one m/q signal will contain information primarily about one product with smaller contributions to its intensity from the other products present. The experimental data used for detecting allyl alcohol, propanal, acrolein, and propyl alcohol were the desorption traces for m/q 57, 58, 56, and 60.

Second, a series of linear equations is written in which the total intensity of a given signal is set equal to the sum of the contributions from each product. By using the same number of experimental signals as products, a system of linear equations is obtained (eq 16–19), where s_x is the experimentally determined

$$(f_{1A})(S_A) + (f_{1B})(S_B) + (f_{1C})(S_C) + (f_{1D})(S_D) = s_1 \tag{16}$$

$$(f_{2A})(S_A) + (f_{2B})(S_B) + (f_{2C})(S_C) + (f_{2D})(S_D) = s_2 \tag{17}$$

$$(f_{3A})(S_A) + (f_{3B})(S_B) + (f_{3C})(S_C) + (f_{3D})(S_D) = s_3 \tag{18}$$

$$(f_{4A})(S_A) + (f_{4B})(S_B) + (f_{4C})(S_C) + (f_{4D})(S_D) = s_4 \tag{19}$$

signal intensity measured at a given mass-to-charge ratio (m/q

$= x$), S_A is the signal intensity due to product A at the m/q value chosen to represent product A, and f_{xA} is the cracking fraction at $m/q = x$ due to product A.

These equations may also be written in matrix form:

$$\left[\begin{array}{cccc} f_{1A} & f_{1B} & f_{1C} & f_{1D} \\ \hline f_{2A} & f_{2B} & f_{2C} & f_{2D} \\ \hline f_{3A} & f_{3B} & f_{3C} & f_{3D} \\ \hline f_{4A} & f_{4B} & f_{4C} & f_{4D} \end{array}\right] \cdot \left[\begin{array}{c} S_A \\ \hline S_A \\ \hline S_A \\ \hline S_A \end{array}\right] = \left[\begin{array}{c} s_1 \\ \hline s_2 \\ \hline s_3 \\ \hline s_4 \end{array}\right] \tag{20}$$

The 4 × 4 matrix contains the cracking fractions determined experimentally by desorbing multilayers of authentic compounds into the same mass spectrometer used for the TPRS experiments. By multiplying both sides of eq 20 by the inverted matrix, we obtain a set of equations for the signals of interest. Solving these equations gives signal intensities for four individual products.

The experimental TPRS data consists of a series of measurements of signal intensities vs time. The experimental curves are decomposed into product desorption curves by solving the $N \times N$ set of equations for each point in time. These curves are then multiplied by a correction factor (Table IV) so that the relative peak heights of the TPRS spectra represent the relative yields of products. Correction factors were determined based on the masses chosen to represent each compound as previously described.[12,23,24] Figure 8 shows the raw data of Figure 1 prior to the corrections for the cracking functions. It can be seen that the major effects are to reduce the H_2 peak and eliminate the sharp feature on m/q 57 due to the propanal (m/q 58).

Registry No. $CH_2{=}CHCH_2OH$, 107-18-6; Cu, 7440-50-8.

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(24) UTI 100C Precision Mass Analyzer Operating and Service Manual, Appendix B.

Oxidative Addition of the Carbon–Hydrogen Bond Is Not the Rate-Determining Step in the Remote Functionalization of Nitriles by Bare Fe(I) Ions†

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Abstract: The study of D-labeled 5-cyanononane isotopomers in the gas phase provides evidence that the Fe^+-mediated remote functionalization of nitriles, resulting in the regiospecific generation of H_2 and C_2H_4 from the ω and ($\omega - 1$) positions of the alkyl chain, can be described as follows: (i) Oxidative addition of a methyl C–H bond is not rate limiting. For the generation of $C_2H_{4-x}D_x$ it is the elimination of the olefin which is associated with kinetic isotope effects comparable to the ones reported earlier for other systems. (ii) The generation of $H_{2-x}D_x$ is affected by two isotope effects. One concerns the β-hydrogen transfer ($k_H/k_D = 1.59$) and the other the reductive elimination of hydrogen ($k_{H_2}/k_{HD} = 1.70$ and $k_{HD}/k_{D_2} = 1.44$).

The selective functionalization of C–H bonds remains one of the major focuses of catalytic and organic chemistry. High selectivity is often achieved by the presence of activating groups which induce the reactivity of the neighboring C–H bonds. The functionalization of *remote* C–H bonds, i.e., several carbon atoms away from the activating group, represents a great challenge. While such reactions are common to enzymes which coordinate a functional group and *geometrically* select a specific site of the substrate, only a few cases in solution chemistry are reported[1] where a similar principle seems to be operative. Breslow[1c] has coined the term "remote functionalization" for this kind of coordination of a functional group followed by selective reactions at sites away from the complexed functionality. We have recently demonstrated that a similar system exists in the gas phase.[2] The chemistry of the Fe^+ complexes of aliphatic, unbranched, saturated nitriles is very unique, in that selective C–H activation occurs only at positions remote from the cyanide functionality. This unprecedented behavior contrasts with that of other unsaturated systems, such as alkenes[3] and alkynes,[4] where allylic and propargylic activations, respectively, of the C–C and/or C–H bonds are reported to be the major modes of reaction. The primary reason for the unique behavior of nitriles is due to the initial interaction of the cyanide group with Fe^+. The preferred coordination leads to an "end-on" complex **1** characterized by a "linear"[5] $—CH_2—C{\equiv}N—M^+$ entity (M = transition-metal atom). The linear fragment in turn constrains the remainder of the molecule such that Fe^+ activates C–H bonds while trying to

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† Dedicated to Dr. Günther Ohloff on the occasion of his 65th birthday.

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(5) In the present context we use the term "linear" very loosely, as we know little about the energetics and electronics of this coordination. No doubt that depending on the nature of the transition-metal ion M^+ and on the internal energy of **1**, deviation from linearity of the $—CH_2—C{\equiv}N—M^+$ unit must occur (see ref 2c for a comparison of Fe^+, Co^+, and Ni^+), which may even result in the formation of a "side-on" complex for $M = Cu^+$ (Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450). A quite interesting case has been reported recently for *unsaturated* aliphatic nitriles (Püsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 2857) of the general structure $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$. Data were reported that strongly suggest that depending on the length of the methylene chain $-(CH_2)_m-$ the bidentate Fe^+ complexes may contain an "end-on" or a "side-on" complexed nitrile function.

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