

# A Molecular Beam Study of the Oxidative Dehydrogenation of Alcohols on Cu(110)

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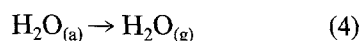
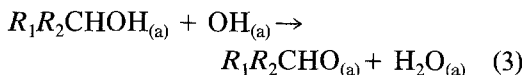
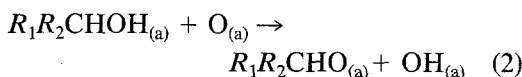
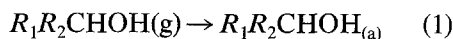
The adsorption and reaction of ethanol, propan-1-ol, and propan-2-ol have been studied on clean and oxygen-covered copper(110) by using a thermal molecular beam. The preadsorption of oxygen greatly enhances the sticking probability of all the alcohols, although a saturation coverage ( $p \times 1$ ) LEED pattern) poisons the oxidative dehydrogenation reaction. The reaction mechanism has been worked out in detail with the help of isotopic labeling experiments and is common to all alcohols examined. There is a change of stoichiometry observed with temperature, at low temperatures (at ambient or just above)  $2R_1R_2CHOH + O_{(a)} \rightarrow 2R_1R_2CO + H_2O + H_2$ , changing to  $R_1R_2CHOH + O_{(a)} \rightarrow R_1R_2CO + H_2O$  at higher temperature, the exact temperature depending on the alcohol involved. The rate of reaction follows the stability of the intermediate alkoxy species except for 2-propoxy which shows a slower rate than expected. This effect and the poisoning observed for saturation coverages of preadsorbed oxygen are due to the stabilization of the alkoxy species by coadsorbed surface hydroxyl groups or oxygen atoms. Overall the reaction rate is limited by the decomposition of the alkoxy species. © 1991 Academic Press, Inc.

## 1. INTRODUCTION

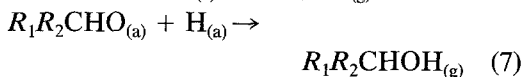
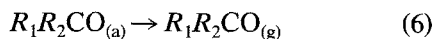
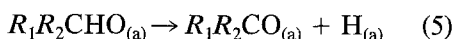
The oxidative dehydrogenation of alcohols on copper and silver has received a great deal of attention in recent years in the surface science literature (1–7). This has included spectroscopic studies to look at the stable species produced on the surface and thermal desorption studies to elucidate the reaction mechanism. These studies have had a great deal of success in showing the presence of stable alkoxy species on the surface as reported originally by Blyholder and Wyatt (8) on supported metal catalysts using transmission infrared spectroscopy. These species have since been observed on a number of single-crystal surfaces by a variety of spectroscopic techniques including EELS (3, 9, 10), RAIRS (11), UPS (4, 12, 2, 13), XPS (2, 13), and NEXAFS (14–16).

Temperature-programmed desorption (TPD) has been able to show the major steps that appear to be important in the reaction mechanism (2, 13), that is:

at low temperature ( $<200$  K)



at higher temperatures



It was also observed that two alcohol molecules were adsorbed per adsorbed oxygen atom. However, TPD is unable to provide any information about the reaction above the decomposition temperature of the al-

koxy species and the reaction is studied in the absence of oxygen since it is lost as water at a low temperature. As was illustrated by our previous work on methanol on this surface (17, 18), thermal molecular beam experiments can give additional and complementary information to TPD on the mechanism and kinetics of a reaction. Beam studies with preadsorbed oxygen showed that methanol reacts in three different temperature regimes. Below 330 K methanol adsorbs to produce two methoxy species on the surface per adsorbed oxygen atom and water is desorbed. Above this temperature methoxy decomposes to give methanal (formaldehyde) and hydrogen in the gas phase. If the methanol is beamed onto the surface at even higher temperature (>450 K) the reaction mechanism changes such that the stoichiometry between methanol uptake and adsorbed atomic oxygen becomes 1:1, producing methanal and water with no hydrogen; this was not and cannot be observed by TPD.

The molecular beam work also showed that the coverage of preadsorbed oxygen affects the reaction. At low coverages oxygen promotes both adsorption and the oxidative dehydrogenation of the methanol. However, at 0.5 monolayer coverage (saturation,  $p(2 \times 1)$  structure) it poisons the reaction causing the overall reaction rate to be greatly reduced, with an induction time before the products are observed in the gas phase (ca. 30 min at 333 K for the beam intensity used). This was thought to be due to the stabilization of methoxy species by coadsorbed hydroxyl or oxygen groups which block the adjacent (110) trough sites where the methoxys were thought to decompose.

This paper reports the results of an extension of the methanol work to include the higher alcohols, namely ethanol, propan-1-ol, and propan-2-ol. This was carried out in order to determine whether the reaction mechanism and its temperature dependence are a general phenomenon common to the higher alcohols as well as to methanol. Addi-

tionally to ascertain whether the kinetic changes observed with oxygen coverage variations also manifested themselves and if they are related to the relative stability of the intermediate alkoxy species involved.

## 2. EXPERIMENTAL

The apparatus used in this study has been described in detail elsewhere (17) and is only outlined briefly here. It consists of a VSW UHV chamber with a preparation chamber and high pressure cell. Attached to the main vacuum chamber is a VG Micromass 200D quadrupole mass spectrometer for gas analysis from the beaming experiments as well as residual gas analysis, an Omicron rear-view LEED/Auger system and an argon ion gun (VSW AS10). The beam system is attached to the main chamber on a FC 38 flange. The beam system itself consists of two six-way crosses and one four-way cross. The first stage includes the four-way cross and is attached to a gas handling system; this is the source chamber from which the beam is produced through a quartz capillary into the second stage. The capillary is 0.2 mm in diameter and 20 mm in length; it has a platinum heater wire wound round it and a thermocouple attached to the end so that the beam temperature can be varied up to 1000 K. The capillary is attached to a VSW x-y-z manipulator in order that it can be positioned accurately with respect to a conical skimmer (90° cone angle, with a hole at the apex 0.3 mm in diameter) which is the first collimating element. In the final stage the beam enters the chamber through a glass tube (2.5 mm internal diameter, 20 mm long, which defines the beam diameter of 2.85 mm at the crystal, 60 mm from the final collimator). The beam is differentially pumped by two  $50 \text{ l s}^{-1}$  turbomolecular pumps backed by rotary pumps.

The Cu(110) crystal was cleaned by cycles of hot and cold argon ion bombardment followed by annealing to 650 K until no sulphur or carbon contamination (the main initial impurities) could be seen in the Auger spectrum and until the sticking probability for

oxygen was constant at 0.21 ( $\pm 0.01$ ) (18). The surface also gave a sharp ( $1 \times 1$ ) LEED pattern at this stage with low background intensity. The crystal was then cleaned between each experiment by argon bombardment and annealing at 650 K. The base pressure in the chamber was generally  $< 2 \times 10^{-10}$  Torr which consisted mostly of hydrogen. The molecular beam experiments were carried out by filling the source chamber with gas (or vapor in the case of the alcohols) to a pressure that gave the required beam intensity at the sample; this usually meant using a source pressure of 10 Torr. This is carried out with the beam blocker in place (a metal flag on a wobble stick), and the mass spectrometer is then started scanning to record the background signal levels of the gases to be observed. The experiment is begun by moving the blocker out of the beam; when the adsorption of the gas on the surface is complete or the reaction is observed to have finished the blocker is replaced in front of the beam. During the experiments only randomly scattered gases were measured, with direct scattering into the mass spectrometer prevented by a stainless-steel flag placed in front of the ionization chamber. While beaming, the level of background leakage into the chamber was around  $3 \times 10^{-11}$  Torr. The deuterated alcohols were all quoted to be at least 99% pure and were then freeze-thawed several times before use.

### 3. RESULTS

The reactions of all the alcohols have been examined at various oxygen precoverages and on the clean surface, with different substrate temperatures. A detailed study of oxygen adsorption has been carried out previously on this surface and has been reported in detail elsewhere (19). This work showed that above 180 K oxygen adsorption takes place dissociatively with a sticking probability which shows a near linear decrease with coverage until the saturation coverage of 0.5 monolayers, which gives a clear sharp  $p(2 \times 1)$  LEED pattern. This

linear decrease in sticking probability with coverage is due to an island growth mechanism with localized areas of the  $p(2 \times 1)$  half monolayer coverage of oxygen. This was observed by LEED which shows a  $p(2 \times 1)$  pattern at as low a coverage as 0.1 monolayers with streaking in the 110 direction (implying a small domain size or disorder in this direction) but ordered in the orthogonal direction. This is supported by STM which shows oxygen atom chains along the 001 direction at a coverage of 0.01 and above (20). As a result of that work the accurate predosing of various absolute coverages of oxygen was a routine procedure.

The beaming of the alcohols onto the clean surface showed little sticking or reaction at the substrate temperatures under which they were observed to react with the oxygen-precovered surface. The results for adsorption of the parent alcohols are presented as sticking probability versus uptake curves; this method has been described previously (18). It simply entails measuring the ratio of the number of molecules sticking on the surface and then dividing by the total number impinging on the surface, measured as the amount reflecting from the surface when it is not adsorbing at the end of the experiment to give the sticking probability,  $S$ . The coverage or uptake at a given time during the reaction is given by

$$N(t) = F \int S(t) dt,$$

where  $N(t)$  is the uptake at time  $t$  and  $F$  is the beam flux.

#### 3.1 ETHANOL

The reactions of a beam of three different isotopically labeled ethanol molecules were studied in order to elucidate the reaction mechanism in detail. When oxygen is preadsorbed on the surface ethanol is observed to stick on the surface with an enhanced sticking probability as compared to the clean surface and the desorbed products of

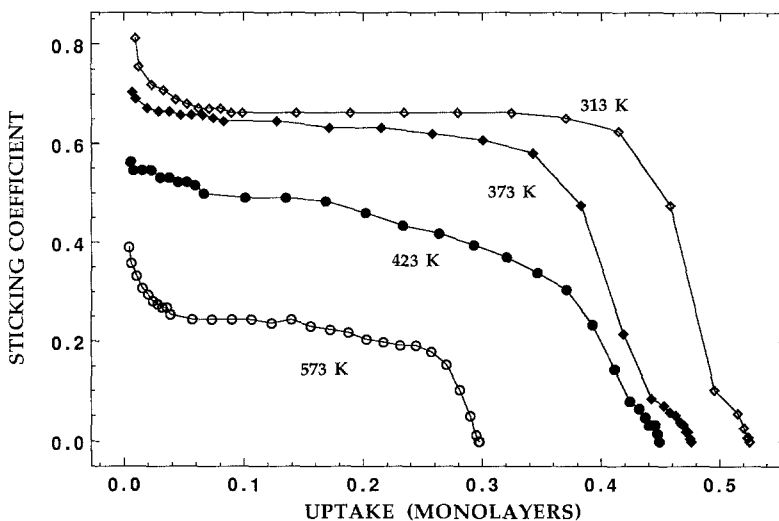


FIG. 1. The sticking probability of ethanol versus the uptake of ethanol with 0.25 monolayers of preadsorbed oxygen atoms at various substrate temperatures.

the surface reaction are then measured in the gas phase.

### 3.1.1 $CH_3CH_2OH$ Reaction with 0.25 Monolayers of Adsorbed O Atoms

Figure 1 shows the results obtained from the raw data displayed as a graph of sticking probability of ethanol versus ethanol uptake in monolayers. It can be seen from this figure that as the substrate temperature is increased the uptake of ethanol decreases as does the sticking probability. However, for each substrate temperature examined the sticking probability remains constant through the majority of the reaction. The time for the reaction to complete increases with temperature (68 s at 303 K to 145 s at 573 K). The product evolution is shown in Fig. 2; water is evolved at a constant rate throughout the reaction at all temperatures. Ethanal production increases as the reaction proceeds at low temperature, with this effect diminishing with increasing substrate temperature. Hydrogen production could not be monitored due to the background level but was observed in the isotopically labeled experiments (see later).

### 3.1.2. $CH_3CH_2OH$ Reaction with 0.5 Monolayers of Adsorbed O Atoms

The details of the reaction of ethanol with a saturation coverage of oxygen atoms are different from that observed for the 0.25-ml coverage. Although the same products and the same decrease in uptake of ethanol with increasing substrate temperature are observed, the rate of uptake, the sticking probability of ethanol, and the evolution of products have a much more complex pattern, as shown in Figs. 3 and 4. Initially ethanol has a high sticking probability which is coincident with the production of a small burst of water, and the sticking probability is then markedly reduced. As the reaction proceeds ethanol and more water are evolved with the amount increasing with time, and the sticking probability of ethanol increasing simultaneously. This continues until the water production and the ethanol sticking probability reach a coincident maximum and then decrease again. The evolution of ethanal also follows this general pattern except that its maximum production occurs slightly after that of water evolution and ethanol sticking probability. This effect becomes less pronounced as the substrate tempera-

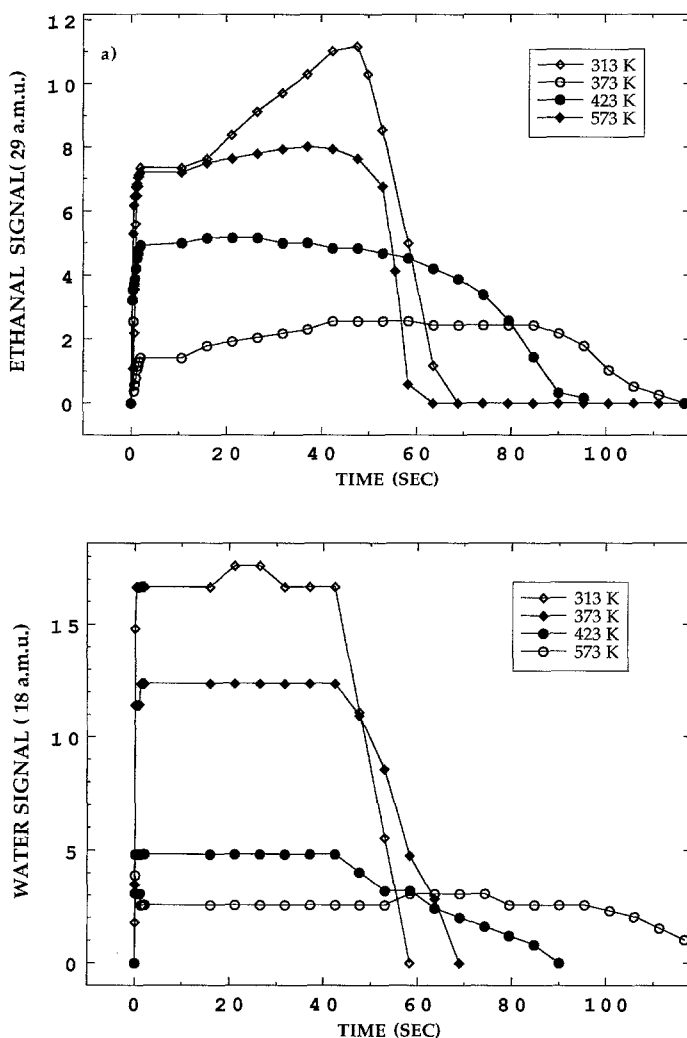


FIG. 2. The evolution of (a) ethanal (b) water during the reaction of ethanol with 0.25 monolayers of oxygen atoms at various substrate temperatures.

ture increases, where a more constant level of production and sticking probability of ethanol are observed.

### 3.1.3. Isotopic Labelling Experiments

$CH_3CH_2OD$ . Experiments were carried out with both 0.25 and 0.5 monolayers of preadsorbed oxygen. The uptake of the reactant, its sticking probability, and ethanal production follow that of the undeuterated ethanol; however, the time for the reaction to go to completion does increase (see Table

1). Under all conditions no  $D_2$  or HD are observed, so any hydrogen evolved is exclusively  $H_2$ . At low substrate temperatures water is evolved mostly as  $D_2O$  with a small amount of HDO (20%); at higher substrate temperatures the proportion of HDO increases to 80% with no  $H_2O$  observable.

$CD_3CD_2OD$ . The reaction of totally deuterated ethanol with predosed oxygen was significantly slower than for undeuterated ethanol, showing a kinetic isotope effect similar to that observed for methanol (18).

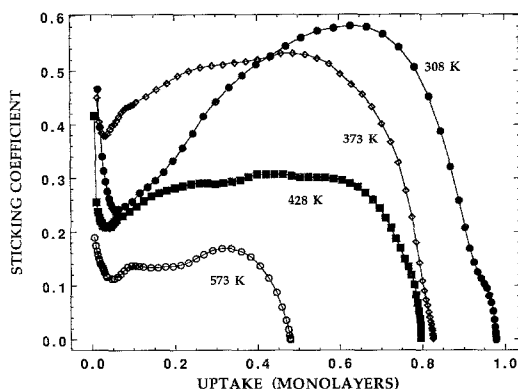


FIG. 3. The sticking probability versus the uptake of ethanol with 0.5 monolayers of preadsorbed oxygen atoms at various substrate temperatures.

It is particularly noticeable for the reaction with 0.5 ml of preadsorbed oxygen, where, for example at 308 K substrate temperature, the reaction goes to completion in 5 min with ethanol but takes 23 min with the fully deuterated form (see Table I). However, the reaction that takes place with the deuterated ethanol is similar to that of unlabeled ethanol except that it is displaced to higher temperature by approximately 40 to 50 K to produce a similar rate. Labeling allows us to follow the deuterium evolution from which we can make deductions about the unlabeled system.

TABLE I

Time for the Reaction of Ethanol and Its Various Isotopes to Go to Completion

Temperature	Time in seconds		
	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CH <sub>2</sub> OD	CD <sub>3</sub> CD <sub>2</sub> OD
	0.5 Monolayers		
308 K	282	400	1380
423 K	340	360	480
573 K	410	403	590
	0.25 Monolayers		
308 K	70	100	132
423 K	114	100	155
573 K	145	177	183

Deuterium is evolved from the surface during the reaction at ambient temperatures up to approximately 490 K; above this temperature only trace amounts are observed to desorb. Figure 5 shows the reaction of deuterated ethanol with 0.5 monolayers of oxygen at 308 K. The initial introduction of ethanol shows some adsorption with the evolution of a small amount of D<sub>2</sub>O but no D<sub>2</sub>, but as beaming continues the sticking probability of ethanol decreases and reaches a minimum after 4 min; after this the ethanol and D<sub>2</sub>O evolution gradually increases. The sticking probability of ethanol reaches a maximum after approximately 14 min with a coincidental maximum in D<sub>2</sub>O production. Deuterium evolution begins just before this maximum with its peak lagging 5 min behind that of maximum ethanol sticking. As the substrate temperature is increased the reaction rate increases and no lag is observed between the maximum in the ethanol sticking probability and the peak in the evolution of the three products. Reactions above a substrate temperature of 425 K show a sharp decrease in the amount of deuterium being evolved with none being observed above the noise levels above 490 K.

### 3.2 PROPAN-1-OL

The reaction of propan-1-ol was measured at two precoverages of oxygen, 0.25 and 0.5 ml, and at various substrate temperatures. The sticking curves for 0.5 ml precoverage of oxygen are shown in Fig. 6; the 0.25 coverage data are not shown, but are very similar to that of ethanol. It is immediately evident from these curves that the same trend of alcohol uptake with increasing substrate temperature is present, with halved uptake at higher temperature. The sticking probability during the reaction with the 0.5 ml precoverage is higher with the drop of sticking probability after the initial adsorption not as pronounced as it is with ethanol or methanol (18). The evolution of the product molecules from the surface also followed the

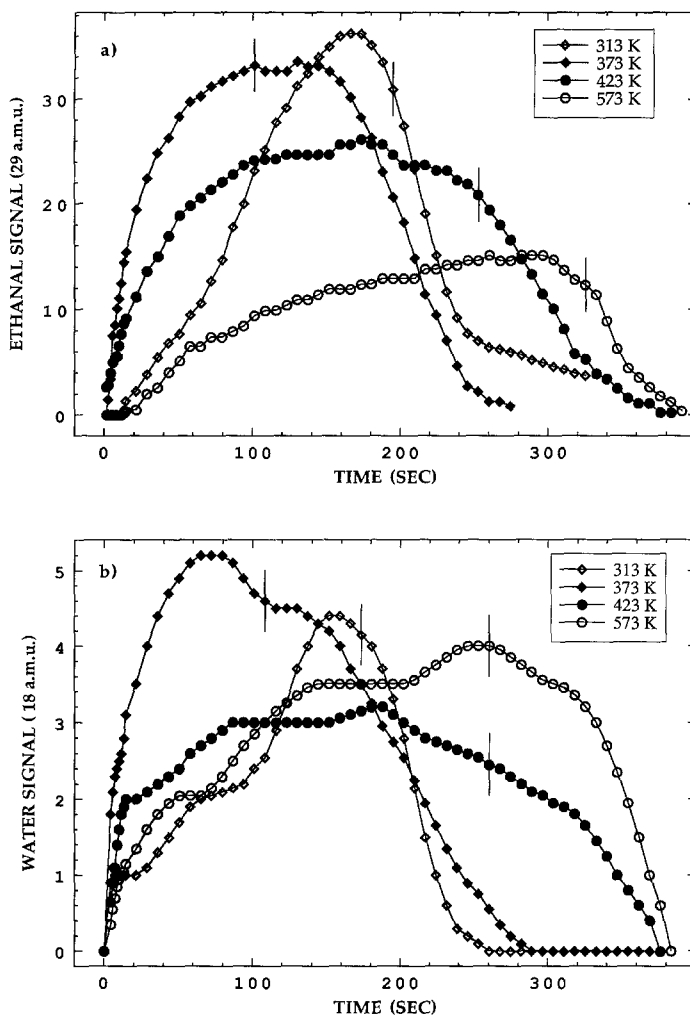


FIG. 4. The evolution of (a) ethanol (b) water during the reaction of ethanol with 0.5 monolayers of oxygen atoms at various substrate temperatures.

same trends observed for ethanol, and so are not shown here.

### 3.3 PROPAN-2-OL

As with the previous alcohols examined, the reaction of propan-2-ol was observed on the oxygen-covered surface and like the other alcohols the main products are the dehydrogenated reactant molecule (in this case acetone), water, and hydrogen. The sticking probability versus uptake curves again show the change in stoichiometry go-

ing from low to high substrate temperatures, as shown in Fig. 7. The shape of these curves shows an early minimum similar to that seen with ethanol rather than the flatter profile of propan-1-ol. The product evolution follows a similar pattern to that seen for the other alcohols with one significant difference being that an increase in acetone evolution occurs at the end of the reaction when water evolution has ceased and the propan-2-ol sticking is decreasing; an example being shown in Fig. 8. This is observed

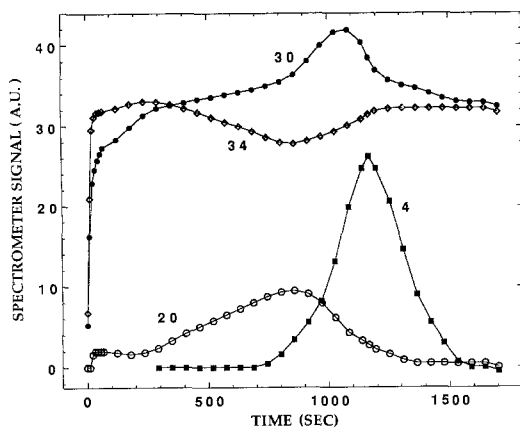


FIG. 5. The reaction of totally deuterated ethanol with 0.5 monolayers of oxygen at 308 K. 34 = ethanol, 30 = ethanal + 25% of the ethanol signal, 20 = water signal  $\times$  3, 4 = deuterium signal  $\times$  10.

at all precoverages of oxygen but is more pronounced at lower substrate temperatures.

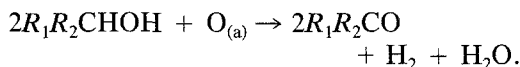
The initial sticking probability ( $S_0$ ) of propan-2-ol was also determined for several different precoverages of oxygen. The coverage of oxygen was reduced to as low as 0.008 of a monolayer (1.5% of the oxygen saturation coverage). All these precoverages result in the same  $S_0$  for propan-2-ol, showing clearly that propan-2-ol exists in a precursor state which has considerable mobility, enabling it to diffuse to the dilute oxygen atom sites; this effect is illustrated and discussed in detail in a separate paper (21).

#### 4. DISCUSSION

Despite the seemingly complex nature and variety of the results presented here, a number of common features for all of the different alcohols is apparent. The most notable effect is that the sticking probability of all the alcohols is greatly enhanced by the presence of oxygen on the surface. This is the case even at very low oxygen precoverages. This then highlights two important points; first it shows how trace amounts of a substance on the surface can dramatically

affect its reactivity and second it illustrates that precursor states can have an important effect in surface and catalytic chemistry (21).

Another general feature of the reactions of all the alcohols was shown in the sticking probability versus uptake curves. These showed that there is a change in the reaction stoichiometry above the decomposition temperature of the alkoxy species. At low temperatures (ambient and just above) two alcohol molecules are adsorbed per pre-dosed oxygen atom, but this changes to a one-to-one ratio at higher temperatures. As the product evolution was monitored simultaneously during the experiments the overall reaction mechanism can be readily reduced. The main product in all cases was the dehydrogenated alcohol, that is an aldehyde or ketone, and water; from isotopic labeling experiments it could also be deduced that at low temperatures hydrogen is evolved, so overall we have



However, at higher temperatures no hydrogen is evolved, half as much alcohol is reacted, and hence

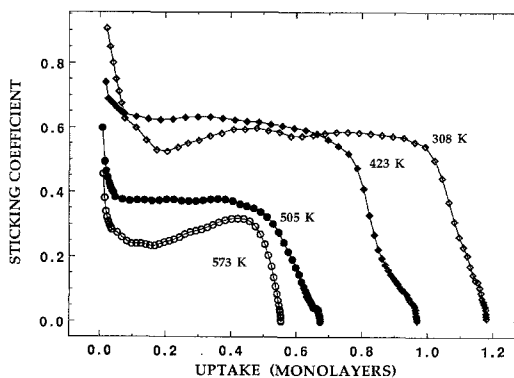
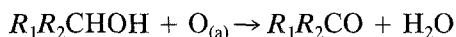


FIG. 6. The sticking probability versus uptake of propan-1-ol with 0.5 monolayers of preadsorbed oxygen atoms at various substrate temperatures.



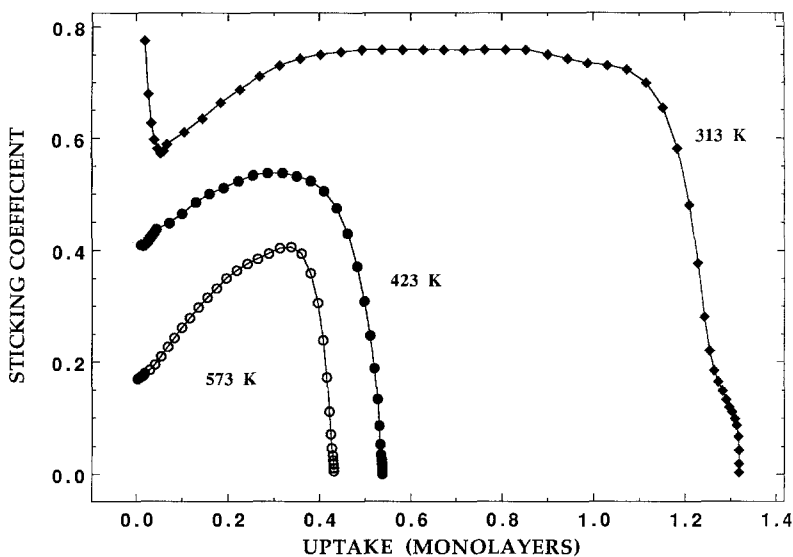
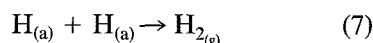
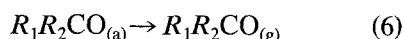
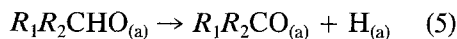
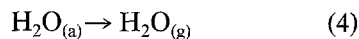
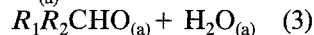
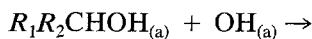
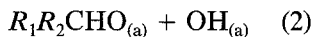
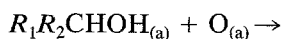
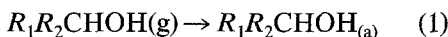


FIG. 7. The sticking probability versus uptake of propan-2-ol with 0.5 monolayers of preadsorbed oxygen atoms.

The experiments with deuterium-labeled ethanol allow a more detailed analysis of the reaction mechanism to be made. The experiments with  $\text{CH}_3\text{CH}_2\text{OD}$  showed that no  $\text{D}_2$  or  $\text{HD}$  is evolved during the reaction, indicating that the alcoholic hydrogen goes exclusively to form water. At low temperatures the water observed is almost exclusively as  $\text{D}_2\text{O}$ , and hence the hydrogen from the decomposed ethoxy species is evolved as  $\text{H}_2$  only. This is supported by the results of  $\text{CD}_3\text{CD}_2\text{OD}$  at low temperatures where the reaction is very slow. Initially upon adsorption of  $\text{CD}_3\text{CD}_2\text{OD}$  only  $\text{D}_2\text{O}$  evolved, with no  $\text{D}_2$ , its evolution being much later in the reaction near to the maximum aldehyde evolution, supporting the conclusion that the alcoholic hydrogen goes into water production. Hence at low temperatures the detailed mechanism is



At higher substrate temperatures  $\text{CH}_3\text{CH}_2\text{OD}$  gives  $\text{HDO}$  as a product as well

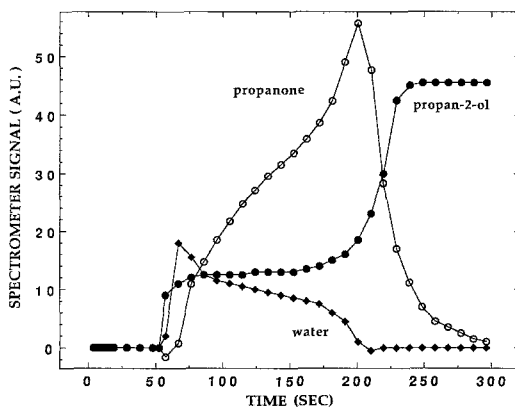


FIG. 8. The reaction of propan-2-ol with 0.25 monolayers of preadsorbed oxygen atoms at 308 K, showing the product evolution and propan-2-ol pressure profile.

as D<sub>2</sub>O and no D<sub>2</sub> gas is seen from the reaction of CD<sub>3</sub>CD<sub>2</sub>OD. This shows that the hydrogen coming from the ethoxy group now forms water exclusively, instead of combining with a second adsorbed hydrogen atom to desorb as H<sub>2</sub>, as is seen at low temperatures. Hence another step needs to be added to the reaction mechanism:



with step (7) in the reaction ceasing to be an important pathway. This is a similar mechanism to that observed with methanol (18) and applies to all alcohols examined in this study.

The overall reaction kinetics, as observed by the sticking probability versus uptake plots and the product evolution, are less easily compared and explained, especially with 0.5 ml of preadsorbed oxygen. For coverages below saturation of preadsorbed oxygen the situation appears relatively simple. After a short period of initial high sticking probability and hence high rate of adsorption, the rate then attains a relatively constant level until the reaction ceases (or reaches a very low constant steady-state level on the clean surface) due to the removal of all the preadsorbed oxygen. At low temperatures with 0.5 ml of oxygen preadsorbed, after initial adsorption the sticking probability reduces to a relatively low level for a period. The sticking probability of the alcohol then increases again with a subsequent increase in both the amount adsorbed and product evolution; the reaction then continues until all the oxygen is used up. This was also the pattern observed with methanol adsorption. It was speculated that the inert period of low sticking was due to the stabilization of the methoxy species by coadsorbed hydroxyl groups, the methoxy decomposing much faster when next to a bare metal site. If this effect is prevalent with the higher alcohols the magnitude of the effect observed would be expected to follow that of the stability of the intermediate alkoxy species produced.

The stability of the alkoxy intermediates can be taken from a previous TPD study (13); on the clean surface the ethoxy and 2-propoxy are less stable than 1-propoxy. However, with 0.25 ml of preadsorbed oxygen all are stabilized compared to the clean surface with the relative stability being methoxy > ethoxy > 1-propoxy > 2-propoxy. In these TPD experiments there are no coadsorbed hydroxyl groups or oxygen atoms present on the surface as these are desorbed as water at a much lower temperature. The difference between the two surfaces in these experiments is solely the coverage of the adsorbed alkoxy groups, with it being much greater for the surface which had oxygen preadsorbed upon it. The increased stability observed is thus probably due to increased intermolecular interactions between the alkoxy groups, as they are now in closer proximity to each other. The relative stability of the surface species in the beaming experiments appears to be a little different. Whether judged by the total length of the reaction or the observation of the "inert" period the relative order is methoxy > ethoxy > 2-propoxy > 1-propoxy.

This change in relative order seems most likely to be due to the enhanced stability of the 2-propoxy species. The reasons for this are difficult to elucidate as the situation on the surface is quite complicated, the alkoxy groups being coadsorbed with both hydroxyl groups and oxygen atoms. If the same process is happening as proposed previously for the methoxy case, then this may be explained by the fact that 2-propoxy has two methyl groups as opposed to one alkyl chain with 1-propoxy. This extra group would possibly allow a second interaction with the surface further increasing the stability. However, the greater coverage on the surface may also have led to a greater stabilization of 2-propoxy due to its bulkier size and hence the intermolecular interactions may increase more as the coverage increases than for the 1-propoxy case. The hypothesis that the hydroxyl

groups and/or the oxygen atoms are involved is supported further by the behavior of propan-2-ol at the end of the reaction, where the peak in acetone evolution appears after all the water has been desorbed (see Fig. 8), that is after any stabilizing effect has been removed.

### 5. CONCLUSIONS

The adsorption and reaction of ethanol, propan-1-ol and propan-2-ol on copper(110) has been studied in detail. The pre dosing of oxygen on the surface is shown to greatly enhance the absolute sticking probability of all the alcohols. The reaction of the alcohols is shown to follow similar pathways giving the oxidatively dehydrogenated alcohol (an aldehyde or ketone), water, and under some conditions hydrogen into the gas phase. A stoichiometry change in the reaction is observed with increasing substrate temperature. Two alcohol molecules react with one adsorbed oxygen atom at room temperature giving two molecules of aldehyde (or ketone), water, and hydrogen. At higher temperatures the ratio of alcohol molecules to preadsorbed oxygen atoms drops to 1:1, with hydrogen no longer observed as a product.

The reaction of the alcohols with a saturated layer of preadsorbed oxygen produces a relatively unreactive surface which gives rise to an induction period for the reaction. This effect is explained by the intermediate alkoxy species being stabilized by coadsorbed oxygen and surface hydroxyl groups either by blocking the bare metal sites next to the alkoxy groups or by some more direct interaction. The magnitude of this effect varies from alcohol to alcohol with the order of the stability of the alkoxy groups being methoxy > ethoxy > 2-propoxy > 1-propoxy. This showed the ex-

pected order of 1- and 2-propoxy reversed from what would be expected from TPD studies (13), and this is explained as being due to additional stabilization of the 2-propoxy on the surface by the coadsorbates.

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