

DECOMPOSITION PATHWAYS OF C₁–C₄ ALCOHOLS ADSORBED ON PLATINUM (111)

B.A. SEXTON, K.D. RENDULIC * and A.E. HUGHES

CSIRO Division of Materials Science, Catalysis and Surface Science Laboratory, University of Melbourne, Parkville, Victoria 3052, Australia

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The adsorption and decomposition of methanol, ethanol, propan-1-ol, propan-2-ol and butan-1-ol has been studied on clean, and oxygen pre-covered Pt(111) surfaces. Temperature Programmed Reaction Spectroscopy (TPRS), Surface Potential Measurements (ΔV), UPS and XPS were used to characterise the adsorbed layer as a function of temperature. Each alcohol adsorbed into two states, a monolayer phase and a multilayer phase which were distinguishable by TPRS and spectroscopy measurements. The monolayer alcohol adsorption heats increased sequentially from methanol to n-butanol (11.5–15 kcal mole⁻¹). On the clean surface, less than 10% of the adsorbed monolayer dissociated, with 90% of the alcohol desorbing intact. Two competing dissociative pathways were observed: complete dissociation to adsorbed CO, H and C, and with propan-1-ol and butan-1-ol, scission of the C–C bond nearest the C–O group to form adsorbed CO, H and ethylidyne and propylidyne species respectively. The latter reaction probability was constant at 30% for n-propanol and n-butanol. In all cases the final desorption products were the parent alcohol, CO and H₂ with carbon remaining on the surface for the higher alcohols. Atomic oxygen removed hydrogen from the alcohols as water but did not change the final reaction products.

1. Introduction

The reactions of alcohols with metal surfaces have been the subject of several previous studies. Most concentrate on methanol, and its adsorption states and decomposition reactions on Cu [1,2], Ag [3], Pd [4], Ni [5], Pt [6], Fe [7], to name a few. Methanol selectively oxidises to formaldehyde on Cu and Ag [1–3], and thermal desorption [1] and EELS data [2] on copper has conclusively shown that a methoxy (CH₃O) intermediate is involved. On metals with high chemisorption heats of CO and H₂, e.g. Pt [6], Ni [5], and Fe [7], methoxy intermediates are less stable and complete decomposition to CO and H has been observed. The interest in surface intermediates obviously stems from the Fischer–Tropsch reaction where the reverse CO + H₂ reaction may synthesize methanol and hydrocarbons over these surfaces (at high pressures).

* Permanent address: Institut für Festkörperphysik, Technische Universität, A-8010 Graz, Austria.

Higher alcohols have not been studied in anywhere near the same detail as methanol. Higher alcohols have carbon-carbon bonds which must break in order to liberate carbon monoxide, and the reaction kinetics are not as simple as methanol. Ethanol has been studied on Cu [2] where it is known to form an ethoxy (C_2H_5O) intermediate by reaction with pre-adsorbed oxygen. The ethoxy intermediate decomposes to acetaldehyde and hydrogen. A recent photoelectron (UPS) study of methanol, ethanol and isopropanol/Cu(110) by Carlson [8] has also proposed the formation of alkoxy intermediates. For the simple alcohols, therefore, the reaction with metals may be divided into two groups. Copper and silver selectively form stable alkoxy intermediates which liberate the corresponding aldehyde as the main product. Metals which have high CO and H_2 chemisorption heats (Pt, Ru, Ni, W, Pd) result in complete dissociation to CO and H.

In this study, we adopt a different approach from previous work and attempt to systematically study the decomposition routes of the 5 smallest alcohols, methanol to n-butanol. Whereas $CH_3OH/Pt(111)$ decomposition has already been studied in detail with EELS and TPRS [6], we extend this previous work to examine the types of bond-breaking reactions that occur as the carbon chains increase in length. In order to completely dissociate larger molecules like n-butanol to CO and H, C-C bonds and C-H bonds must be broken. We would expect to see more of a contribution from alkane-type intermediates as the chain length increases. This work is part of a series of comparative chemistry studies on platinum in which we attempt to examine C-C, C-H and O-H bond breaking probabilities in related molecules.

2. Experimental

Experiments were conducted in two separate vacuum systems. For the spectroscopy experiments, (UPS, XPS and work function change), a Vacuum Generators ESCALAB 5 system was used, with a base pressure of 1×10^{-10} Torr. The thermal desorption experiments were done in a turbomolecular-pumped 6-way cross (6 inch OD), with a base pressure of 5×10^{-10} Torr.

Two identical platinum (111) crystals were suspended on tantalum heating wires and mounted on liquid-nitrogen cooled sample manipulators. Each crystal could be cooled to 100 K and heated to 1400 K. In the ESCALAB, the Pt(111) crystal was judged to be clean after extensive oxygen treatment at 1200 K and flashing to 1400 K to remove oxide [9]. Auger analysis showed no traces of C or Ca. Prior to an experiment, several oxygen doses were adsorbed at 100 K and the intensities of both the molecular and atomic desorption states checked to ensure a clean surface. The alcohols were high purity reagents degassed in small glass bottles with teflon valves, and connected to a gas dosing manifold by a Cajon fitting. An equilibrium pressure (~ 10 Torr) of the

alcohol was established in a volume behind the leak valve and the vapors were dosed into the vacuum chambers via a micro-capillary array. Exposure times for a monolayer were approximately 10^{-7} Torr s background pressure, indicating an enhancement of about 30 in the incident flux from the doser relative to background. The micro-capillary dosers were essential to coat only the front face of the crystal and resolve the monolayer and multilayer states in the TDS spectra. In both systems, several monolayers (~ 3) of the alcohols were condensed on the clean or oxygen-precovered surface at 100 K. For the TPRS experiments, the temperature was ramped at a rate of 5 K s^{-1} using a linear programmer. A quadrupole mass spectrometer with a mass multiplexer monitored up to four masses simultaneously as the temperature was ramped and the output was stored in a MCA memory (1 K). The data were converted to paper tape output and analysed on a separate computer later.

In the spectroscopy experiments, XPS data were taken with 100 W X-ray power ($\text{MgK}\alpha$) and stored on a Tracor-Northern 1710 MCA system. The spectrometer was operated at 35 eV pass energy (4 mm slits). Multiple scans were taken until the spectral signal-to-noise was satisfactory. UPS (He I and He II) spectra were taken with a VG photon source. Work functions were determined from the secondary cutoff in the UPS spectrum, with a negative 5–10 V bias applied to the crystal. After the initial adsorption at 100 K, the temperature was stepped sequentially up to 600 K and the appropriate spectroscopic measurement taken.

With the higher alcohols (C_3 , C_4), noticeable carbon deposition was observed after the decomposition reaction had occurred at 600 K. This carbon was always removed by oxygen cleaning prior to a new run.

3. Results

The experimental results are separated into three groups, TPRS and ΔV measurements, XPS and UPS. Since the majority of mechanistic evidence was derived from the TPRS results, these are discussed first.

3.1. Temperature programmed reaction spectroscopy (TPRS) and surface potential (ΔV) measurements

Each alcohol (methanol, ethanol, n-propanol, iso-propanol and n-butanol) was condensed on the clean Pt(111) surface at 100 K to form a multilayer film approximately 3 layers thick. Doses of approximately 5×10^{-9} Torr background with the multichannel array for 20–30 s were sufficient to form a multilayer film. The TPRS results are shown in figs. 1 and 2, and superimposed on these figures (lower section) are the surface potential (ΔV) results as determined from the secondary electron cutoffs in the UPS spectra. Data for

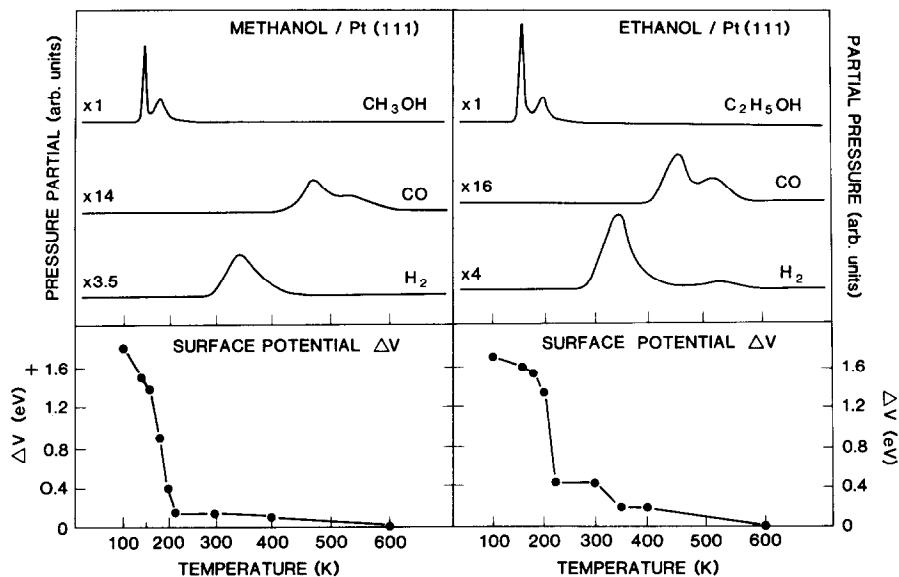


Fig. 1. Thermal desorption of methanol (CH₃OH) and ethanol (CH₃-CH₂OH) adsorbed on Pt(111) at 100 K. The surface potential was measured at 100 K after annealing to the specified temperature.

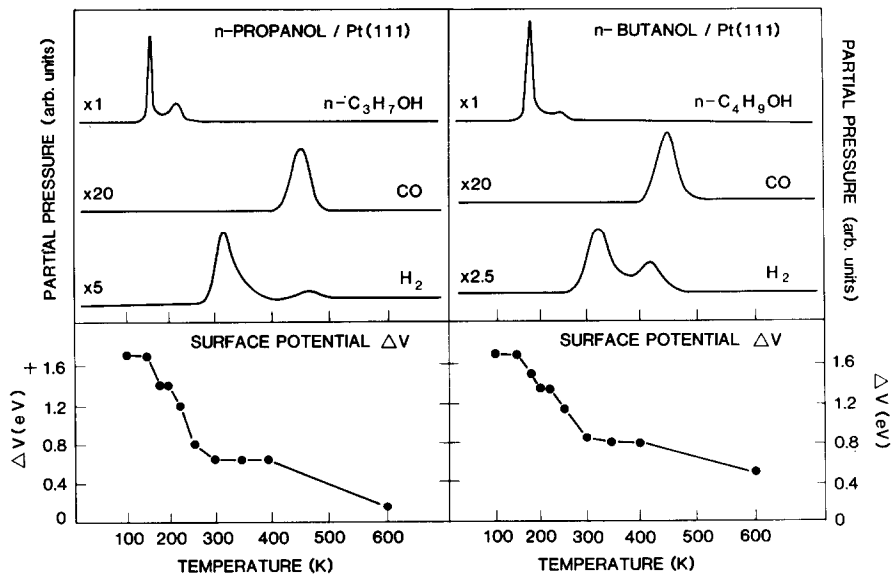


Fig. 2. Thermal desorption of n-propanol (CH₃-CH₂-CH₂OH) and n-butanol (CH₃-CH₂-CH₂-CH₂OH) adsorbed on Pt(111) at 100 K. The surface potential was measured at 100 K after annealing to the specified temperature.

Table 1
Desorption temperatures (K) for alcohols adsorbed on Pt(111)

Alcohol	Boiling point	Multilayer desorption	Monolayer desorption	CO desorption	H ₂ desorption
CH ₃ OH	338	145	190	470, 520	350
C ₂ H ₅ OH	352	150	200	450, 510	350
n-C ₃ H ₇ OH	370	160	230	450	320, 450
iso-C ₃ H ₇ OH	355	165	210	480	320
n-C ₄ H ₉ OH	390	180	245	440	310, 410
H ₂ O	373	160	170	-	-

iso-propanol have been omitted but are included in table 1. The surface potential (ΔV) has been defined as:

$$\Delta V = -\Delta\phi = \phi_c - \phi_a,$$

where $\Delta\phi$ = work function change, ϕ_c = clean Pt(111) work function, and ϕ_a = adsorbate covered Pt(111) work function.

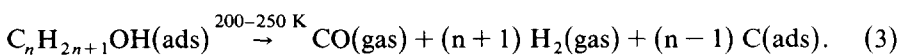
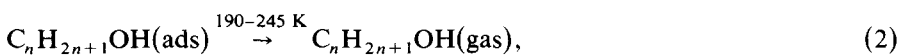
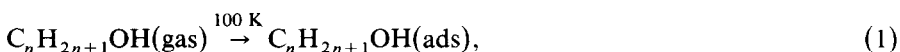
For each alcohol in figs. 1 and 2, a separate, resolved monolayer and multilayer state was observed in the desorption curves for the parent alcohol fragment. Although no coverage dependence data are shown, the low temperature multilayer peak (150–180 K, see table 1) was found to increase in intensity only after the high temperature monolayer peak (190–245 K, table 1) was saturated. Furthermore, the multilayer states in figs. 1 and 2 continued to grow in intensity with increasing exposure at 100 K, whereas the monolayer peak remained saturated. It is sufficient at this stage to establish the existence of the adsorbed monolayer and multilayer states, and to observe that the monolayer desorption temperatures (table 1) are a function of the molecular weight of the alcohol.

Above 250 K in figs. 1 and 2, both CO and H₂ are desorbed from the surface. Peak desorption temperatures are listed in table 1. For the lower alcohols (C₁, C₂), hydrogen was desorbed in a main peak near 350 K. For the higher alcohols, a second smaller peak of hydrogen was observed near 450 K in the n-propanol spectrum and a very pronounced peak at 410 K for n-butanol. CO desorption also showed differences between the four alcohols. Methanol and ethanol both had a main peak near 450 K and a tail, or secondary peak, near 510–520 K. This high temperature CO state was not seen in the higher alcohol desorption curves however (fig. 2). With n-propanol and n-butanol, a single CO desorption state near 440–480 K was observed. As will be discussed later, calibrations of the XPS and CO and H₂ desorptions show that the reaction probability for dissociation of the adsorbed monolayer is less than 10%. Approximately 90% of the adsorbed alcohol molecules desorb in the

monolayer peak of figs. 1 and 2. The coverage of adsorbed complexes on the Pt(111) surface above 250 K is therefore quite low under the conditions of an experiment.

Further evidence for the adsorbed alcohol states desorbing and dissociating can be seen in the ΔV results of figs. 1 and 2. All of the surface potentials measured were positive, indicating a reduction in the Pt(111) work function at all stages of the reaction. Multilayer states of the alcohols produced positive surface potentials of +1.6 to +1.8 V as shown in figs. 1 and 2. After desorption of the multilayers, the monolayer surface potentials were all $+1.5 \pm 0.1$ V. These values are similar to those reported by Christmann [10] ($\Delta\phi = -1.6$ eV for $\text{CH}_3\text{OH}/\text{Pd}(100)$ and Rubloff and Demuth [11], $\Delta\phi = -1.6$ eV for $\text{CH}_3\text{OH}/\text{Ni}(111)$). Since the permanent dipole moments of the alcohols are all very similar [12], the constancy of the monolayer surface potential is not surprising. Orientation of the alcohols with the oxygen (negative) end bonding to the surface and the hydrocarbon tail (positive) pointing away from the surface is necessary to explain the reduction in clean surface work function [10,11]. When the monolayer states desorbed near 190–245 K in figs. 1 and 2 a large reduction in ΔV was observed. Between 250–300 K, however, before any desorption products were observed, the value of ΔV increased in the sequence methanol to *n*-butanol (0.15 to 0.8 V). After the desorption of H_2 and CO had ceased, residual ΔV values of +0.2 and +0.5 V were observed for *n*-propanol and *n*-butanol at 600 K. As will be discussed later, these values are attributed to surface carbon deposition on Pt(111) during the dissociation reaction. After burning off the excess carbon with oxygen at 1200 K, the work function of the Pt(111) surface returned to its normal value ($5.9 \text{ eV} \pm 0.1$).

From the preceding results, the following reactions have been established on the clean surface.



Since no other desorption pathways were observed, the stoichiometry of reaction (3) is correct, irrespective of any other surface intermediates involved prior to CO and H_2 desorption. Surface carbon must be produced in the reaction for molecules larger than methanol.

In fig. 3 we have correlated the desorption peak temperatures of the five alcohols in a saturated monolayer with their boiling points. A surprising correlation is observed. The graph is quite linear showing that

$$T_{\text{des}} \approx T_{\text{B}} - 150 \text{ K}. \quad (4)$$

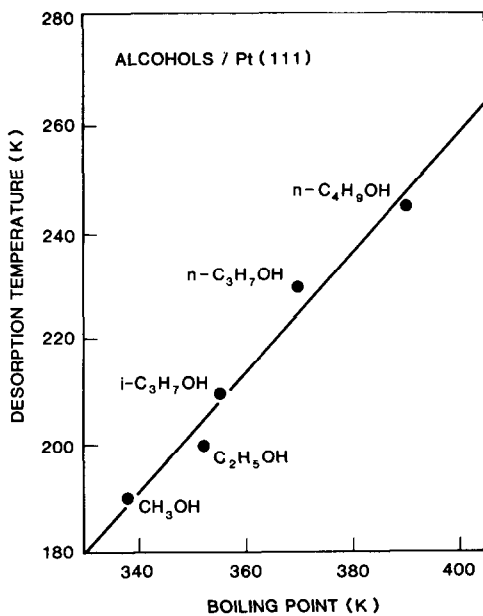


Fig. 3. The peak desorption temperature for a saturated alcohol monolayer versus the alcohol boiling point.

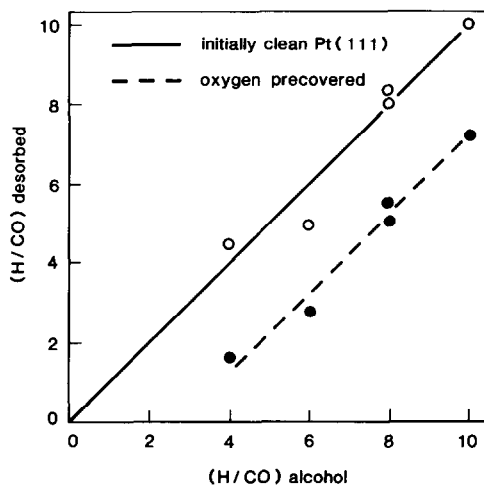


Fig. 4. The (H/CO) ratio desorbed from Pt(111) versus the (H/CO) ratio for the parent alcohol on the clean and atomic oxygen covered surfaces. The data have been normalized to a value of 10 for n-butanol.

Since the peak desorption temperature for first order desorption is proportional to the activation energy for desorption (\approx heat of adsorption) [13], there is obviously a correlation between the adsorption heat and the heat of vapourization. This is surprising since the intermolecular forces in the monolayer would be expected to be weaker than the surface bond (lone pair oxygen orbital interaction with Pt). An estimate of the heat of adsorption from the peak temperatures in fig. 3 give ~ 11 kcal mole $^{-1}$ for methanol up to ~ 15 kcal mole $^{-1}$ for n-butanol, assuming a frequency factor of 10^{13} - 10^{14} s $^{-1}$.

3.1.1. Reaction of the alcohols with pre-adsorbed atomic oxygen

Atomic oxygen was pre-adsorbed on the Pt(111) surface and the experiments of figs. 1 and 2 were repeated. The results showed a new desorption product, water (H_2O) and the ratio of H_2 to CO was reduced relative to the clean surface values. For all of the alcohols, a water desorption peak near 170 K was observed. We also measured quantitatively the H/CO desorbed ratio and compared this with the initially clean surface desorption ratio. It should be noted that only the first H_2 peak (310-350 K) was attenuated by pre-adsorbed oxygen.

In fig. 4 we have plotted the H/CO ratio as measured from the desorption curves and compared the clean and oxygen-covered surfaces. The measured H/CO ratio is compared with the H/CO ratio of the gaseous alcohol ($2n + 2$, where n = carbon number). The measured H/CO ratio depends on the relative pumping speeds and gauge sensitivity factors for the two gases. The data in fig. 4 are the measured H/CO area ratios of the desorption curves normalized to a value of 10 for n-butanol. We also calibrated the H_2 and CO desorption peaks with saturated layers of H_2 and CO on Pt(111) and obtained absolute values of the ratios within $\pm 20\%$ of the values in fig. 4. The main point is that the line of best fit to the H/CO ratio as measured from the areas agrees well with the H/CO ratio of the parent alcohol. Thus eq. (1) is correct; the H/CO desorbed is completely accounted for by the dissociation of individual alcohol molecules. On the oxygen precovered surface, however, the desorbed H/CO ratio is considerably reduced, but again a linear best fit is observed in fig. 4. To account for the oxygenated surface data in fig. 4, a mechanism may be proposed. At this stage we can ignore any surface complexes other than the adsorbed alcohol and the dissociation products CO and H. If we assume there are θ_o adsorbed oxygen atoms initially and θ_a adsorbed alcohols molecules which dissociate, then a simple analysis gives the H/CO ratio desorbed from the surface (assuming oxygen acts as a scavenger for H atoms and desorbs as H_2O)

$$\therefore (H/CO)(\text{desorbed}) = 2(n + 1) - 2\theta_o/\theta_a. \quad (5)$$

From the data in fig. 4, the value of $2\theta_o/\theta_a$ must be constant to obtain a linear plot and we calculate $\theta_o \approx 1.3\theta_a$ for all of the alcohols. Therefore there is

approximately one atomic oxygen reacting with each alcohol molecule to produce the H/CO ratio reductions on the oxygenated surface of fig. 4. Oxygen does not play an important role in alcohol dissociation on Pt(111) except to scavenge hydrogen and desorb as H₂O. The water produced, however, must be formed from at least two hydrogen atoms per alcohol molecule, on the average.

3.2. XPS results

In fig. 5 is shown the O 1s region for CH₃OH adsorbed on Pt(111). The binding energy scale increases from left to right in all of the diagrams. A major feature in the spectrum is the Pt 4p^{3/2} peak at 519.4 eV with the O 1s peak near 532 eV. For the methanol multilayer, a value of 532.7 eV was obtained, corresponding to 3 layers of adsorbed CH₃OH. A shift to 532.1 eV was

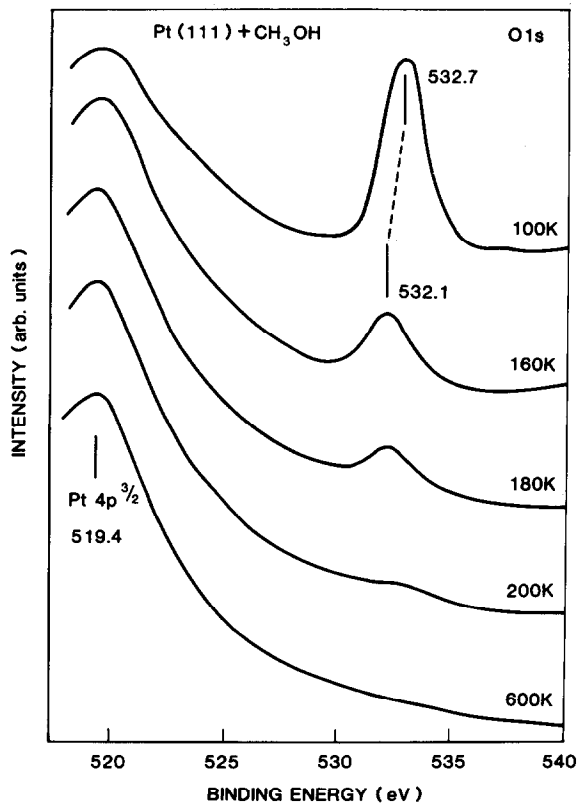


Fig. 5. O 1s XPS results for CH₃OH adsorbed on Pt(111) at 100 K and annealed to the temperatures specified.

observed in the monolayer at 160 K in fig. 5. After annealing above 100 K the O 1s feature attenuated significantly and finally disappeared at 600 K. The value of 532.1 eV is consistent with molecularly adsorbed methanol. For water adsorbed on Pt(111), Fisher et al. [14] obtained a binding energy of 532.0 eV. We see no evidence in the XPS for new O 1s features indicative of new surface complexes. The two main results are the binding energy value of the monolayer, with its subsequent shift to higher binding energy in the multilayer (caused by extra atomic relaxation), and the estimate of the dissociation probability based on the attenuation of the monolayer O 1s peak after annealing to ~ 200 K. For all of the alcohols we estimate that $< 10\%$ of the adsorbed monolayer is dissociated after annealing to > 200 K.

Fig. 6 is a comparison of the monolayer and multilayer intensities, and binding energies. The binding energy shift of $+0.4$ to $+0.7$ eV between the monolayer and multilayer states is attributed to decreased extra-atomic relaxation in the condensed alcohol. Obviously this shift will be a function of the thickness of the layer. All of the alcohols have a monolayer binding energy of 532.0 ± 0.1 eV, which is consistent with molecular adsorption of the alcohol. From the relative intensities of the monolayer O 1s peaks in fig. 6, one can see that the surface coverages (molecules per unit area) decrease with increasing size of the alcohol. The coverage of n-butanol at monolayer saturation is

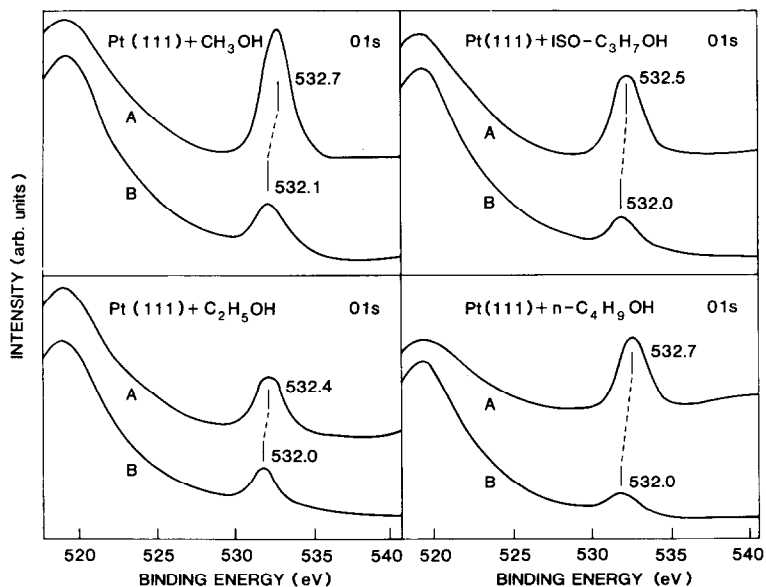


Fig. 6. Comparison of the multilayer and monolayer O 1s spectra for four alcohols adsorbed on Pt(111): (A) multilayer film; (B) monolayer.

estimated to be only $\sim 50\%$ of the saturation methanol coverage for a monolayer.

The XPS results support the model of molecular adsorption of the alcohols at low temperature followed by a small dissociation probability ($\sim 10\%$) at higher temperatures. In addition to the clean surface data of figs. 5 and 6 we also took O 1s data for the reaction of the alcohols with atomic oxygen on Pt(111). The O 1s peak was observed near 529.6 eV, quite distinct from the alcohol O 1s at 532.0 eV. Between 160 and 180 K the O 1s peak disappeared, leaving the original alcohol peak at 532.0 eV. Such behaviour correlates with the appearance of a water desorption peak in the TPRS spectra near 170 K. The binding energy of $H_2O/Pt(111)$ (532.0 eV) is identical to the adsorbed alcohols and the two cannot be distinguished if they are co-adsorbed.

3.3. UPS results

The UPS data were less informative in following the details of the dissociation process. We were able to measure good He II spectra for the multilayers, however, and observe the characteristic features of traces of CO adsorbed on the surface above room temperature.

In fig. 7, a reaction sequence is followed with He II (40.8 eV) radiation. At 100 K for the multilayer spectrum, the four characteristic orbitals of methanol were observed, at 4.5–12 eV below the Fermi edge. Orbital A is the $2A''$ (the

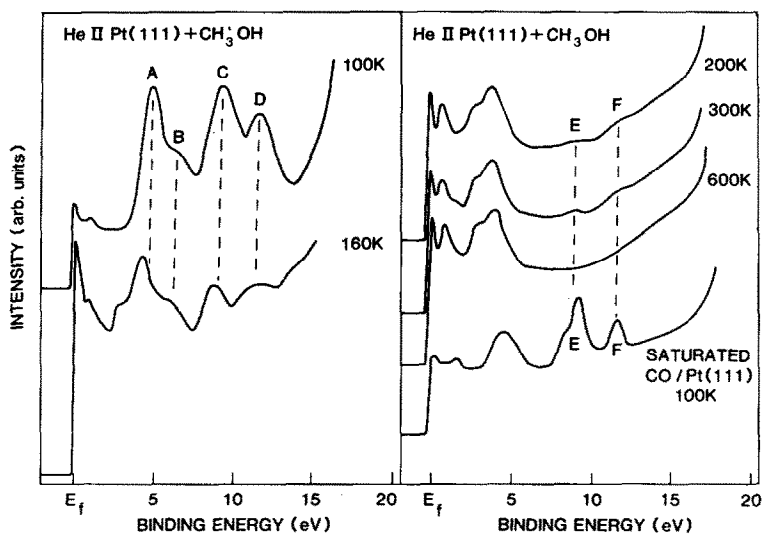


Fig. 7. UPS (He II) spectra of methanol adsorbed on Pt(111) at 100 K and heated to the specified temperatures. A–D are methanol orbitals. E and F are CO orbitals.

out-of-plane lone pair) and the others are the $7A'(B)$, $6A'$ and $1A''(C)$ and $5A'(D)$. After annealing to 160 K, where only the monolayer is adsorbed, all of the orbitals decrease in intensity and shift slightly towards the Fermi edge. The d-band features of Pt(111) have now increased in intensity and the $2A''$ and $7A'$ orbitals are superimposed on a broad emission from Pt(111) centred at 5 eV. The other methanol orbitals (C, D) are clearly seen however. With further heating to 200 K and above, a pair of weak orbitals E and F appear at approximately 8.5 and 11.5 eV below E_F . These can be attributed to adsorbed CO (< 10% of a monolayer) based on the comparison with the saturated CO/Pt(111) spectrum in the lower curve of fig. 7.

Normally, difference spectra are presented to more clearly show the adsorbate features and subtract the emission from the metal. We have not presented this data due to the complicated overlap of the $2A''$ orbital with the large emission from the Pt d-band near 5 eV. We would like to have compared the energy of the $2A''$ orbital with the other methanol orbitals to measure the extent (if any) of the bonding of the $2A''$ orbital to the Pt surface. Whereas Christmann [10] saw no differential shift of the $2A''$ orbital of $CH_3OH/Pd(100)$ relative to deeper-lying orbitals, Lüth et al. [4] have reported a chemical bonding shift ΔE_c for CH_3OH/Pd film. We cannot comment on any bonding shifts of the highest occupied molecular orbitals of any of the alcohols because of the overlap problem with the Pt(111) d-band.

In addition to observing the formation of CO from the adsorbed alcohols, we measured He I and He II spectra of all five alcohols in the condensed (multilayer) phases. In fig. 8 we show spectra for the condensed phases (~ 3 monolayers) of methanol up to n-butanol. He I spectra show the four methanol orbitals clearly, but in the higher alcohol He I spectra only the oxygen lone pair orbital near 4.5 eV is easily distinguished. He II spectra in fig. 8 are much better resolved, however. We have marked the highest-lying oxygen lone-pair orbital as "A" near 4.5 eV and simplified the spectral regions into three. Each alcohol may be recognised and distinguished from the others by the lone-pair oxygen orbital "A", the region 1 from 4.5–12.5 eV and region 2 from 12.5–18 eV below the Fermi level. Gas phase photoelectron spectra of all five alcohols have been measured previously with He I and He II radiation. The spectra in fig. 8 may be compared directly with the He I spectra of Peel and Willett [16] or Robin and Kuebler [17], and the He II spectra of Potts, Williams and Price [18]. The agreement between the photoelectron features of fig. 8 (He II) and the gas phase spectra of refs. [16–18] is excellent, once the lone-pair orbital A has been aligned with the equivalent orbital in the gas phase spectrum. Spectral region 2 in fig. 8 is composed of "s" type bands, which are in-phase and out-of-phase combinations of C 2s orbitals as mentioned by Potts et al. [18] in their paper. Carbon 2s derived orbitals normally fall at binding energies > 16–17 eV in the gas phase, or > 12.5 eV in the condensed alcohols on Pt(111) in fig. 8. From 4.5–12.5 eV in fig. 8 is region 1 which is composed of

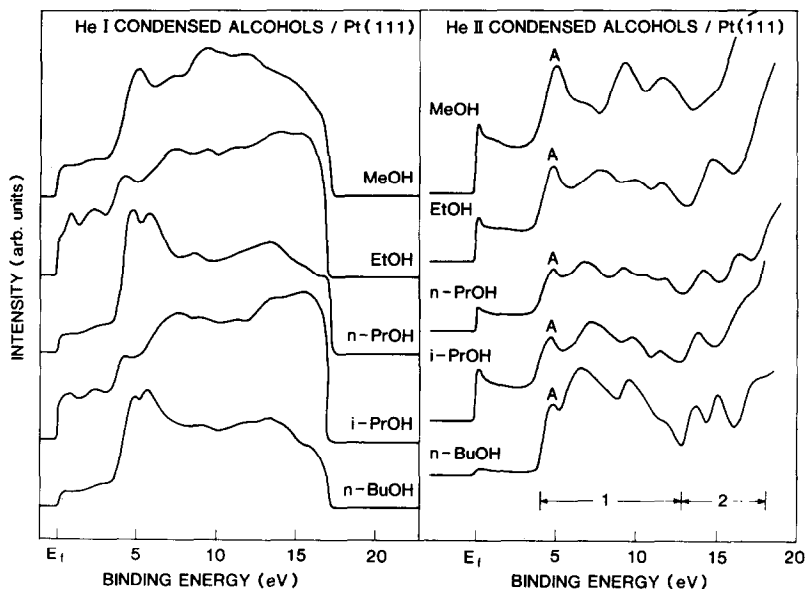


Fig. 8. UPS (He I and He II) spectra of multilayer films of the alcohols adsorbed on Pt(111) at 100 K. Orbital A is the oxygen lone pair.

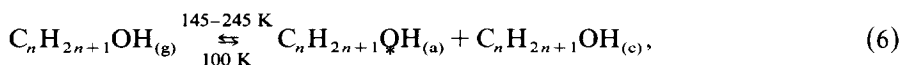
“p-type” orbitals, or orbitals built up from combinations of oxygen and carbon 2p orbitals and H 1s orbitals. As pointed out by Peel [16], each alcohol should have $2n + 3$ molecular orbitals and $2n + 3$ photoelectron bands in region 1. The five orbitals of methanol and the seven bands of ethanol have been seen in the gas phase. In the condensed phases of fig. 8 we count four bands for methanol and five for ethanol in fig. 8. The higher alcohols obviously have considerable overlap of the $2n + 3$ orbitals expected, and are not worth assigning.

The data we wish to extract from fig. 8 are the agreement of the condensed phase spectra with the known gaseous spectra. It is more difficult, however, to identify and distinguish between the monolayer alcohol phases with UPS, due to the interference of the strong d-band features of Pt. The multilayer spectra of fig. 8 are only well resolved because of considerable attenuation of the Pt d-band, due to the overlayer film.

4. Discussion

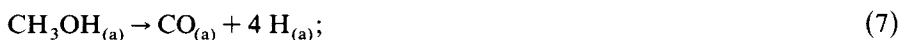
From the preceding data, we propose a mechanism of alcohol adsorption and dissociation. Each alcohol adsorbs into a monolayer phase with a high sticking probability at 100 K. Further exposures increase the coverage into the

multilayer regime:

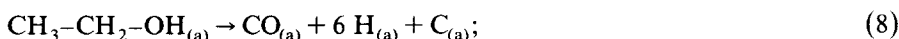


where * = weak lone pair bond to Pt and (c) = condensed phase. Desorption of the multilayer phase precedes the monolayer phase as the temperature is raised from 145–245 K. On the clean surface, each alcohol dissociates during the monolayer desorption with a probability of < 10%. The reaction products consist of a mixture of CO, H, C and CH_x fragments adsorbed on the surface. Only two gaseous products, CO + H_2 are desorbed, the excess carbon being left on the platinum surface at temperatures up to 600 K. The dissociation mechanisms are listed below:

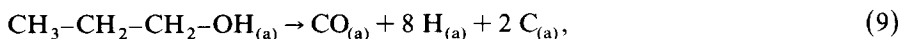
Methanol



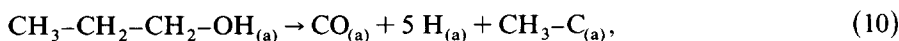
Ethanol



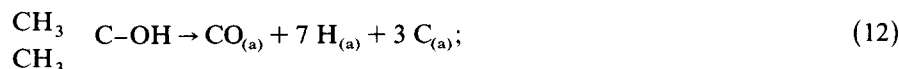
Propan-1-ol



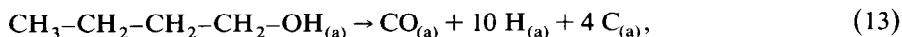
also



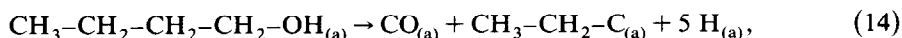
Propan-2-ol



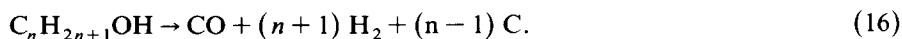
Butan-1-ol



also

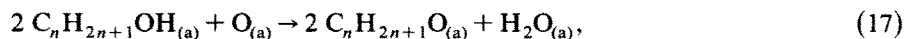


The total reaction and desorption products may be written as:



For reactions involving oxygen, only water (H_2O) was observed as a product. Two pathways are responsible for water formation: reaction with the alcohol

OH group and the hydrogen-oxygen reaction



4.1. The adsorbed molecular phases

Both the multilayer and the monolayer states were identified from TPRS, ΔV , XPS and UPS measurements. The monolayer phase gave a distinct thermal desorption peak (figs. 1 and 2), a large surface potential of $+1.5 \text{ V} \pm 0.1$ (figs. 1 and 2), a constant O 1s binding energy of 532.0 eV, and characteristic UPS features of the molecular alcohol. The multilayer phases of all the alcohols had a distinct thermal desorption peak at a lower temperature than the monolayer. In addition, the surface potential ΔV was only slightly more positive than the monolayer (0.2–0.3 V) and the XPS O 1s binding energy *increased* by up to 0.6 eV due to less extra-atomic relaxation. UPS valence spectra of the alcohols in the multilayer phase agreed well with gas phase UPS spectra.

Multilayer and monolayer alcohol heats of adsorption must be dependent on different forces. We can explain the peak temperatures in table 1 by a simple theory. Assume that the heat of adsorption in the alcohol monolayer is dominated by the oxygen lone pair orbital bond to the Pt (surface). An additional contribution to ΔH_{ads} will come from a Van der Waals bonding of the alkyl groups to the Pt surface

$$\therefore \Delta H_{\text{ads}}^{\text{ROH}} \sim E_{\text{Pt-O}} + E_{\text{Pt-R}}, \quad (20)$$

where $E_{\text{Pt-O}}$ = lone pair oxygen-Pt bond contribution and $E_{\text{Pt-R}}$ = Van der Waals bonding of alkyl groups to Pt surface contribution.

Since water, the simplest alcohol, contains no alkyl groups and bonds in an identical way to alcohols on Pt(111) [14], it should have the lowest heat of adsorption. In table 1 the monolayer desorption temperatures show 170 K for H₂O increasing sequentially to 245 K for n-butanol. The heat due to the lone pair interaction $E_{\text{Pt-O}}$ is therefore approximately 10 kcal mole⁻¹. For n-butanol, an extra 5 kcal mole⁻¹ may be attributed to the Van der Waals bonding of the long chain to Pt. Another factor which may contribute to the linear change in adsorption heat from H₂O to n-butanol is the variation in acidity due to the electron donating properties of the alkyl group. We feel that the Van der Waals interaction between the alkyl groups and the Pt surface would be a more significant contribution to the heat. This is supported by the fact that n-butane adsorbed on Pt(111) [19] has an adsorption heat of 8.2 kcal mole⁻¹. Further evidence for Van der Waals bonding to Pt is detailed in a separate paper [23].

Multilayer desorption temperatures, on the other hand, reflect the hydrogen

bonding in the solid or liquid alcohol phase, and should scale with the boiling points of the alcohols. In table 1, water, which boils at the same temperature as n-propanol, has a similar multilayer desorption temperature (160 K), whereas their monolayer desorption temperatures are separated by 60 K. The leading edge of the multilayer desorption is a measure of the vapor pressure at a particular temperature and should be dependent only on ΔH_{sub} .

4.2. Alcohol dissociation

From the CO and H₂ traces of figs. 1 and 2 and the peak temperatures of table 1, we can conclude that:

- (a) The desorption peaks for H₂ from 310–350 K and CO from 440–480 K are rate-limited desorption of hydrogen and CO respectively.
- (b) The total decomposition probability is < 10% for an initially saturated monolayer.

Rate-limited desorption of CO and H₂ may be inferred purely from the peak temperatures, which are very close to those we measured for pure H₂ and CO adsorption on Pt(111) at low coverage. We also calibrated the desorbed H₂ and CO intensities with respect to a saturated Pt(111) surface to arrive at the dissociation probability. In addition to the main CO and H₂ peaks in figs. 1 and 2, extra shoulders are observed at higher temperatures. For CO desorption from methanol/ethanol, a high temperature state is observed near 520 K which we attribute to CO desorption from step sites. This peak is suppressed in the higher alcohol spectra probably because the carbon generated during dissociation blocks these step sites.

Hydrogen desorption also shows high temperature states for n-propanol and n-butanol near 450 K and 410 K respectively. We attribute these peaks to the rate-limited dissociation of the ethylidyne (CH₃–C) and propylidyne (CH₃–CH₂–C) species, respectively [19]. With reference to eqs. (10) and (14), when molecular CO is cleaved from these alcohols, a C₂ and C₃ species will be formed. The desorption peak temperatures observed in this work are very similar to those observed by Salmeron and Somorjai [19] for ethylene and propylene adsorption on Pt(111). Salmeron observed peaks near 490 and 440 K for ethylene and propylene decomposition on Pt(111) and there is supporting EELS evidence for both the ethylidyne and propylidyne intermediates [19].

On the clean surface, therefore, all of the alcohols dissociate to adsorbed CO and atomic hydrogen above their desorption temperature. In addition surface carbon is formed from ethanol, propanol and butanol. For propan-1-ol and butan-1-ol, cleavage of the C–C bond nearest the C–O group results in the formation of some ethylidyne and propylidyne species which decompose to adsorbed C and H near 450 and 410 K respectively. From the relative areas of the hydrogen desorption peaks we estimate a constant probability of 30% for ethylidyne and propylidyne formation when propan-1-ol and butan-1-ol dissociate, respectively.

Although we were unable to determine exactly when the alcohols dissociate, we believe that the dissociation occurs during the monolayer desorption, and that no other intermediates are involved besides the ones already mentioned. The work function results showed very little variation after the monolayer desorption, and the variations that did occur could be accounted for by desorption of CO and H₂ (with the residual values being due to surface carbon).

4.3. Reaction with atomic oxygen

Two possible mechanisms of water formation may be proposed. Atomic oxygen on Pt(111) is highly basic and reacts readily with the acidic alcohol proton [20]. Examples of oxygen basicity include water formation by titration of atomic oxygen with carboxylic acids and alcohols [21] on metal surfaces. Second, the reaction between oxygen and atomic hydrogen on Pt(111) proceeds readily in the temperature range 120 K and higher [22]. In a previous study we observed a transient-methoxy (CH₃O) intermediate by reaction of CH₃OH and O/Pt(111) [6]. The methoxy intermediate decomposed to CO and H above 170 K, however. In the present work we believe that alkoxy formation occurs for all alcohols, but the intermediates decompose rapidly near the monolayer desorption temperatures. In addition, some oxygen also reacts with the atomic hydrogen formed by alcohol dissociation. We observed a high temperature tail in the H₂O desorption which indicated some water evolution up to 250 K. From the reduction in H/CO ratio we determined a value of $\theta_o/\theta_a \approx 1.3$. That is roughly 1.3 oxygen atoms react with each dissociated alcohol molecule to form water. The magnitude of this ratio means there must be contributions from both the reaction with the acidic OH proton (one proton per alcohol) and the atomic hydrogen reaction (from dissociated alcohols). Oxygen, however, does not affect the *selectivity* of the alcohol decomposition to any extent. We still observed the same peak temperatures for CO and H₂ desorption in all of the alcohols on the oxygenated surface.

5. Conclusions

Alcohols (C₁-C₄) adsorb on Pt(111) in a monolayer state characterized by a weak heat of adsorption (11-15 kcal mole⁻¹). Bonding of each alcohol is through the oxygen lone-pair orbital with an increasing Van der Waals contribution from the carbon chain interaction with the surface. During the monolayer desorption, a parallel dissociation reaction (< 10%) is observed resulting in adsorbed CO, H and C. In addition to complete dissociation, a parallel cleavage of a C-C bond (30% probability) generates small amounts of ethylidyne (CH₃-C) and propylidyne (CH₃-CH₂-C) intermediates from n-

propanol and n-butanol, respectively. Reaction with atomic oxygen extracts hydrogen from the alcohol (as water) in two ways: removal of the acidic OH proton or reaction with atomic hydrogen from alcohol dissociation. Apart from water formation, no new intermediates or reaction products were observed. The desorption kinetics of H_2 and CO from Pt(111) are essentially identical to the respective gases adsorbed on the surface. Blocking of step sites occurs with carbon deposition from the higher alcohols. Finally H_2 desorption shows high temperature peaks for the normal C_3 and C_4 alcohols indicating small concentrations of hydrocarbon intermediates (CH_3-C , CH_3-CH_2-C).

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