Adsorption and Dehydrogenation of Alcohols and Ethers on Platinum (111)

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The adsorption of 11 alcohols (C_1–C_4) and ethers (C_1–C_5) has been studied on Pt(111) with temperature-programmed reaction spectroscopy (TPRS). Each molecule adsorbed sequentially into two distinct states at 100 K, a monolayer phase and a multilayer phase. Temperature programming the layers from 100 to 800 K desorbed most (>90%) of the parent molecule intact. The remaining (<10%) monolayer fraction dehydrogenated to form adsorbed CO, H, and CH_x fragments. A comparison of H_2 desorption spectra revealed the various contributions from atomic hydrogen and decomposition of CH_x fragments. The desorption temperatures for the multilayer and monolayer states may be interpreted by a simple model. Whereas the multilayer desorption temperature depends primarily on the heat of sublimation (a monotonic function of the boiling point), the monolayer desorption temperature was dependent on the sum of contributions from both the oxygen lone-pair bond to platinum and weak bonding between the surface and one of the alkyl side chains. A comparison is made between the low-pressure dehydrogenation observed here and reaction over supported Pt catalysts at high pressures.

1. INTRODUCTION

The bonding and reactivity of oxygenated hydrocarbons on transition metal surfaces is of particular interest. Alcohols, particularly methanol, may be synthesized over Pd (*1*) and Rh (*2*) supported metal catalysts at high pressures from CO and H_2. Alcohols may also dehydrogenate or dehydrate on Pt and other metals at atmospheric pressure to form ethers and hydrocarbons (*3*). At low pressures, under UHV conditions, most organic molecules containing CH and CO bonds completely dehydrogenate on single crystal group VIII metals to adsorbed CO, H, and C, with some of the hydrogen generated by decomposition of CH_x intermediates. Examples include methanol dehydrogenation on Pt(111) (*4*) and a similar reaction on Ru (*5*), Pd (*6*), and other metals with a high heat of adsorption

of CO and H. It is generally accepted that the dehydrogenation reaction below room temperature on the metals is facilitated by the high chemisorption heats for the products (CO, H). We have commented previously (*7*) that complete dehydrogenation is highly likely because the residence time of any adsorbed species is extremely long and there is adequate time for dissociation to occur. An example of this is the inability of methanol to oxidize to formaldehyde on Pt(111) in UHV but the same reaction occurring rapidly near atmospheric pressure over a supported Pt catalyst (*3, 4*). Formaldehyde is almost certainly formed under UHV conditions but is completely dehydrogenated because it is formed near 200 K where it is relatively strongly adsorbed.

In a recent work, we have examined the adsorption of C_1–C_4 alcohols on Pt(111) and their reaction pathways on clean and oxygenated surfaces (*8*). We observed interesting trends in the monolayer desorption temperatures and the hydrogen desorption peaks. In this paper we complete a compre-

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hensive study of the reactivity of alcohols, ethers, and water adsorbed on Pt(111). All of these molecules have a common bonding orbital, the out-of-plane oxygen lone-pair orbital (9). We have investigated the effects of the hydrocarbon chain length on the heat of adsorption, and demonstrate that there is an increasing contribution to the heat with increasing chain length. We also examine the hydrogen desorption spectra of all the molecules and show that hydrocarbon intermediates must be formed by dissociation. Finally, we compare the complete dehydrogenation observed on Pt(111) with the reactions of alcohols over a supported Pt catalyst at higher pressures (3), and point out some of the difficulties in attempting to simulate catalytic reactions at UHV pressures.

2. EXPERIMENTAL

All experiments were performed in a stainless-steel UHV system consisting of a turbomolecular-pumped six-way cross (6-in.-o.d. flanges). On the ports of the cross were a quadrupole mass spectrometer, a molecular beam dual gas dosing system (microcapillary arrays), and a liquid nitrogen-cooled sample manipulator. The base pressure of the system was in the 10^{-10} Torr range and consisted almost entirely of hydrogen. A Pt(111) crystal was suspended via tantalum heating wires, and could be heated from 100 to 1400 K. The crystal was cleaned in flowing O_2 (5×10^{-8} Torr, 850°C) and the cleanliness checked by the amplitudes of the molecular and atomic desorption peaks (10). When the atomic oxygen recombination peak was reproducible, the crystal was judged to be clean, in accordance with previous work (10).

Each gas was a high purity organic reagent, degassed in small glass bottles by freeze–thaw cycles with pumping. The equilibrium vapor (1–20 Torr) of each liquid was expanded into a miniconflat cross connected to a leak valve. Doses of gas (5×10^{-9} Torr background for ~30 sec) through the microcapillary array were sufficient to produce at least three monolayers adsorbed on the Pt(111) surface at 100 K, as judged by thermal desorption. Care was taken to position the doser beam so that only the front face of the crystal was exposed. In this way complete resolution of the multilayer and monolayer states was obtained.

The crystal temperature was ramped at 5 K sec^{-1} with a linear temperature programmer, and a mass multiplexer simultaneously monitored the parent alcohol, H_2 and CO mass fractions, storing the data via pulse counting on a signal averager memory (1 K). Checks were also made for other desorbed mass fractions (e.g., CO_2) but none was found. The signal averager data were converted to paper tape and further processed on a separate computer.

After a particular run, the Pt(111) crystal was regenerated by oxygen cleaning and annealing. This was necessary in the case of larger molecules ($>C_2$) because some carbon was always formed by dissociation.

3. RESULTS

3.1. Monolayer and Multilayer Adsorption States

Eleven compounds were adsorbed on Pt(111) at 100 K to form approximately three layers. Temperature-programmed desorption was then used to separate the monolayer desorption peak from the multilayer (second and subsequent layers) peak. We adsorbed the following alcohols: methanol, ethanol, propanol, isopropanol, n-butanol, and the ethers: dimethyl, diethyl, n-propyl, isopropyl, n-butyl, and n-amyl ether. Data for water adsorption was also measured (11). With the exception of dimethyl ether, which was found not to adsorb at 100 K, each molecule gave two distinct peaks in the thermal desorption spectrum. Data for methanol are shown in Fig. 1, and are representative of the other alcohols and ethers. In Fig. 1, two peaks are seen, a large, low-temperature peak near 145 K and a second, smaller peak near 190 K. These peaks are labeled the "multi-
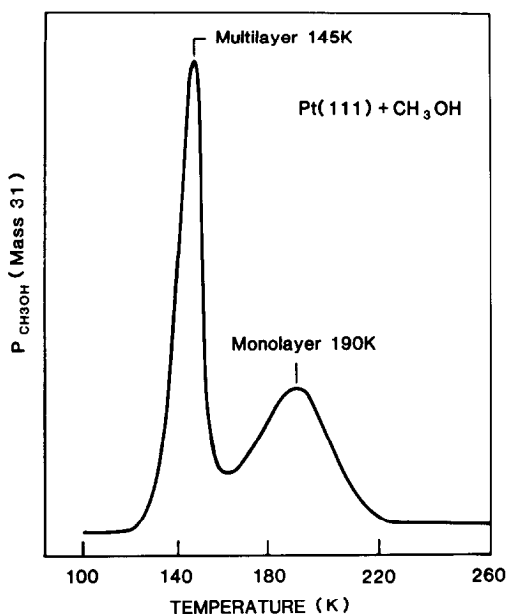
FIG. 1. Temperature-programmed desorption of methanol condensed on clean Pt(111) at 100 K. Approx. three layers of methanol were adsorbed. The heating rate was 5 K sec^{-1}.

layer" and "monolayer," respectively. We observed that as the exposure was varied, the high-temperature peak always filled *first* and saturated in intensity, then with increasing exposure the sharp low-temperature peak grew in intensity. Due to the narrow line width of the multilayer peak, the peak maximum temperatures were only slightly exposure dependent, and we therefore arbitrarily limited the exposure to about three monolayers in all cases. The monolayer peak maximum temperatures were therefore measured at saturation monolayer coverage. Having established the existence of separate first layer (or monolayer) and multilayer desorption states we list the measured peak maxima in Table 1, together with the boiling points of the respective 11 compounds.

In order to establish some trends in the data of Table 1, we have plotted all the monolayer and multilayer temperatures against the boiling points of the liquid compounds (*12*) in Fig. 2. Some immediate correlations can be seen in Fig. 2. First, the

multilayer temperatures of all of the molecules (including water) are a smooth function of the boiling point. We have drawn a curve of best fit through the data points in the lower section of Fig. 2. By extrapolating the curve it is easy to see why dimethyl ether does not condense on Pt(111) at 100 K. With a boiling point of only 248 K we would predict a multilayer desorption peak at <100 K. As will be discussed later, this multilayer temperature–boiling point correlation is not a universal curve for all organic molecules, but is valid for the alcohols, ethers and water, or compounds of the type ROR. Since the condensed phase of the organic molecules on Pt(111) is similar in chemical bonding to the solid, or ice phases of the respective organics (*4*) such a correlation is not surprising. The multilayer peak temperature is the temperature required to raise the vapor pressure to ~1 × 10^{-9} Torr and should be related directly to the heat of sublimation. The heat of sublimation is in turn a monotonic function of the boiling point (heat of vaporization) of the liquid. Therefore, the intermolecular forces acting in the condensed phase on Pt(111) are simi-
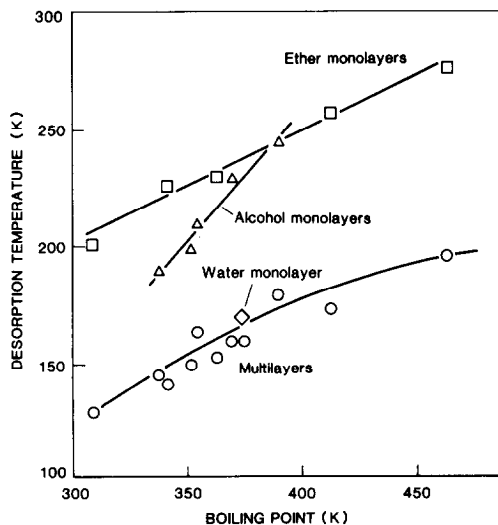

FIG. 2. Multilayer and monolayer peak desorption temperatures for alcohols, ethers, and water adsorbed on Pt(111) at 100 K, as a function of the boiling point of the liquid compounds. The heating rate was 5 K sec^{-1}.

TABLE 1

Data for Alcohols and Ethers Adsorbed on Platinum(111) at 100 K

Molecule	Formula	Boiling[a] point (K)	Multilayer desorption (K)	Monolayer desorption (K)	Hydrogen desorption maxima[b] (K)
Water	H_2O	373	160	170	—
Methanol	CH_3OH	339	145	190	350
Ethanol	C_2H_5OH	351	150	200	350
n-Propanol	C_3H_7OH	370	160	230	320, 450
i-Propanol	C_3H_7OH	356	165	210	320
n-Butanol	C_4H_9OH	389	180	245	310, 410
Dimethyl ether	$(CH_3)_2O$	248	Not adsorbed[c]		—
Diethyl ether	$(C_2H_5)_2O$	308	129	210	330
n-Propyl ether	$(C_3H_7)_2O$	363	153	230	320, 410, 475
Isopropyl ether	$(C_3H_7)_2O$	341	141	227	330, 410
n-Butyl ether	$(C_4H_9)_2O$	413	174	258	320, 400, 430
n-Amyl ether	$(C_5H_{11})_2O$	463	196	266	325, 380, 410, 465

[a] At atmospheric pressure.

[b] Peak location determined from the integral H_2 desorption spectrum without any deconvolution.

[c] Sample temperature 100–150 K.

lar to the intermolecular forces in the solid or liquid organics.

In Fig. 2 we can see, however, that the monolayer temperatures do not all fall on the one curve. Both the ethers and alcohols form a separate linear plot with boiling point, but the lines are of different slopes. Water does not fall on either line, but lies close to the multilayer curve. One might expect the forces in the monolayer to be quite different to those in the multilayer. It is known that all of the R–O–R-type compounds bond to metals via the oxygen lone-pair orbital (out-of-plane p-type). There is also EELS evidence of hydrogen bonding between the methyl group of methanol and a Pt(111) surface in the adsorbed monolayer (4).

In Fig. 3, we have correlated all of the monolayer desorption temperatures, including water with a simple parameter: the number of carbon atoms in the longest alkane group of the molecule. For normal alcohols or ethers this is simply n in the formula $C_nH_{2n+1}OH$ or $(C_nH_{2n+1})_2O$. For isopropyl alcohol and ether the carbon number is two, with zero for water. A good

linear fit is obtained for the monolayer temperatures, with all values within ±10% of the line.

Two conclusions are immediately apparent from the data in Fig. 3. First, all alcohols and ethers have a monolayer desorption temperature higher than water (170 K), and water, therefore, is the lowest member of the series in Fig. 3. Second, the monolayer desorption temperature is a linear function of the carbon number, or the length of the side chain. With ethers only one side chain appears to determine the desorption temperature. In the discussion we quantify this relationship in terms of approximate adsorption heats and show that the heat of adsorption (~ activation energy for desorption) can be expressed as a base value determined by the strength of the Pt–oxygen lone-pair bond, plus a platinum–alkane group bonding contribution which is a linear function of the side carbon chain length. It is important to note that the ethers do not desorb at the same temperature as an alcohol of comparable molecular weight. In the discussion we also comment on the lack of adsorption of dimethyl ether
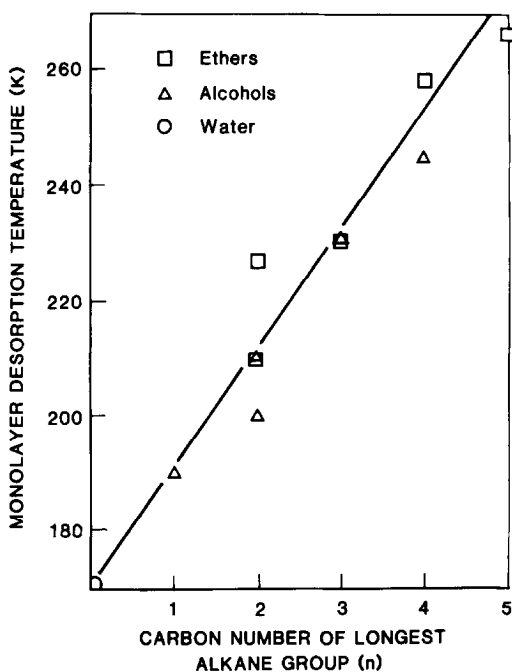
on Pt(111) at 100 K. From Fig. 3 we would predict a similar desorption temperature (190 K) for dimethyl ether as methanol, based on the side chain theory.

In summary, two distinct correlations are observed: the multilayer states are a smooth function of the boiling point and the monolayer states are a linear function of the carbon number of the alcohol or ether.

3.2. Decomposition Reactions

All of the alcohols and ethers were found to undergo dehydrogenation as the temperature was ramped from 100 to 600 K. Only two desorption products were observed above 270 K, H_2 and CO. Data for the alcohols have already been published (8). CO desorption in all cases occurred as a single peak near 440–480 K, which is the normal desorption temperature for CO/Pt(111). Hydrogen desorption, however, was more diagnostic and exhibited multiple features, depending on the adsorbed molecule. We

have determined in previous work (8) that the total CO and H_2 desorbed may be accounted for by fractionation of individual organic molecules, and the H/CO ratio desorbed is proportional to the H/CO ratio in the parent molecule (8). Also, the total dissociation probability is <10% of the original monolayer and >90% of the parent molecule desorbs intact. The total coverage of CO and H is therefore much smaller than the saturation values.

Hydrogen desorption data for the normal alcohols and ethers are shown in Fig. 4. Water does not dissociate on the clean Pt(111) surface (11) and has been omitted. The hydrogen results (which have been approximately normalized in intensity) show a main desorption maximum near 310–350 K and a series of smaller maxima up to 475 K which depend on the chain length of the
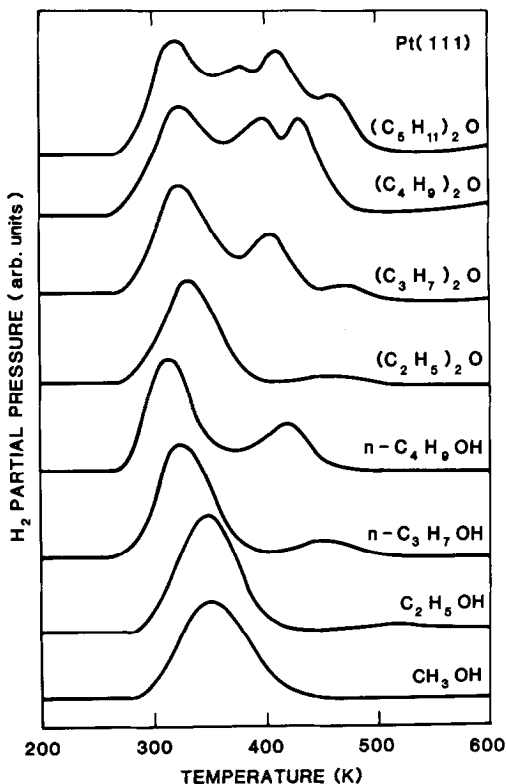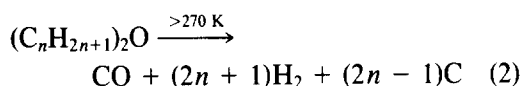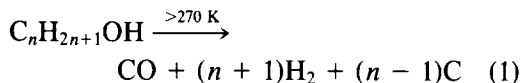

FIG. 4. Hydrogen desorption spectra for alcohols and ethers adsorbed on Pt(111). The heating rate was 5 K sec⁻¹. All spectra have been approximately normalized.
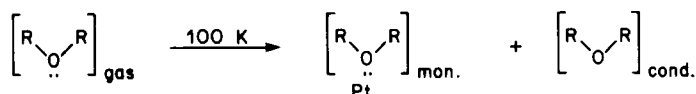
alcohol or ether. Omitted in Fig. 4 are broad, shallow maxima peaking at even higher temperatures (>600 K), observed for the higher ethers. The peak maxima are listed in Table 1. We can summarize the desorption products as a total dehydrogenation of less than 10% of the initially adsorbed monolayer:

$$C_nH_{2n+1}OH \xrightarrow{>270 \text{ K}}$$
$$CO + (n + 1)H_2 + (n - 1)C \quad (1)$$

$$(C_nH_{2n+1})_2O \xrightarrow{>270 \text{ K}}$$
$$CO + (2n + 1)H_2 + (2n - 1)C \quad (2)$$

4. DISCUSSION

4.1. Molecular Adsorption States

All of the alcohols and the ethers studied adsorbed into two separate adsorption states. First the monolayer was filled, then the condensed (ice) phase formed with increasing exposure at 100 K.

$$\left[\begin{array}{c} R \diagdown O \diagup R \\ \vdots \end{array} \right]_{gas} \xrightarrow{100 \text{ K}} \left[\begin{array}{c} R \diagdown O \diagup R \\ \vdots \\ Pt \end{array} \right]_{mon.} + \left[\begin{array}{c} R \diagdown O \diagup R \end{array} \right]_{cond.}$$

There is spectroscopic evidence (6) that the highest occupied molecular orbital, the oxygen out-of-plane lone-pair is the bonding orbital involved in the monolayer state. In the multilayer state we would expect the intermolecular forces to be similar to those in the ice phases of the respective organics. In a previous EELS study of methanol condensed on Pt(111) (4) we demonstrated that the vibrational spectra of methanol were different in the two states; in particular there was less hydrogen bonding between alcohol molecules in the monolayer and an increased interaction of the methyl group with the Pt surface.

In the data of Fig. 2, all of the multilayer desorption temperatures fitted on a curve that was related to the boiling point of the molecule. An explanation of this curve is as follows: the multilayer desorption peak temperature is approximately the temperature required to achieve a measurable ($\sim 1 \times 10^{-9}$ Torr) vapor pressure of the organic above the ice phase (before it is pumped away). If we assume the Clausius–Clapeyron equation to be valid, then

$$\log P = \frac{-\Delta H_{sub.}}{2.303RT} + \text{constant.} \quad (3)$$

We would also expect $\Delta H_{sub.}$ to be related to the boiling point of the liquid, since both depend on intermolecular forces in the condensed phase. A monotonic function of multilayer temperature versus boiling point is therefore expected.

The monolayer desorption temperatures, on the other hand, were dependent primarily on the carbon chain length and not on the boiling point. From the graph of Fig. 3, the monolayer desorption temperature is related by the relationship,

$$T_M(K) \cong 170 + 21n \quad (4)$$

where T_M = monolayer desorption temperature (K) and n = carbon number, or number of carbon atoms in longest side chain of R–O–R molecule. Assuming that the monolayer desorption is first order (13) and the activation energy for desorption is approximately equal to the heat of adsorption of the alcohol or ether, we can rewrite Eq. (4) in terms of an adsorption heat (see appendix for details)

$$\Delta H_{mon} \cong 10.0 + 1.3n \text{ kcal mole}^{-1} \quad (5)$$

where ΔH_{mon} = heat of adsorption in monolayer and n = carbon number as defined above.

Such a simple relationship for the adsorption heat or desorption activation energy may be explained by a bonding model. We

assume that the oxygen lone-pair orbital interaction with platinum has a value of approximately 10 kcal mole^{-1} (42 kJ mole^{-1}). Water has an adsorption heat of approximately 10 kcal mole^{-1} on Pt(111) (*11*) and desorbs near 170 K. Bonding of the alcohols to Pt(111) must involve an additional weak van der Waals-type bond between the alkyl group and the platinum surface (1.3

kcal/mole of carbon atoms), and similarly with the ethers. For the ethers, however, only one of the side chains appears to give this additional contribution to the adsorption heat, and we propose that the ethers are adsorbed with one hydrocarbon chain parallel and interacting with the metal surface and one extended away from the surface as shown below:

Water   H∖ ∕H   Alcohols   H∖ ∕R   Ethers   R∖ ∕R
           O   O   O
           Pt   Pt   Pt   Pt   Pt
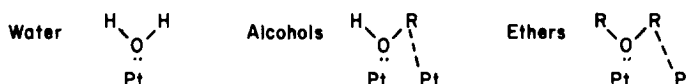
In summary, the dominant contribution to the adsorption heat for alcohols and ethers is the oxygen lone-pair (10 kcal mole^{-1}, 170 K) with an additional contribution of 1.3 kcal mole^{-1} per carbon atom due to van der Waals, or dispersion forces between the alkyl chain and the Pt surface. The magnitudes of these numbers should be put into context, however, against the known heats of adsorption of oxygen and alkanes on Pt(111). Atomic oxygen on Pt(111) recombines to molecular oxygen near 700 K (*10*) and has an adsorption heat of approximately 50 kcal mole^{-1} (200 kJ mole^{-1}). The Pt–O bond vibrates near 490 cm^{-1} in EELS measurements on Pt(111) and is known to be quite covalent in character (*7*). By contrast the weak lone-pair bond observed in the present work is 10 kcal mole^{-1} and the vibrational frequency was found to be too low to be measured for the Pt–O bond between molecular CH$_3$OH and Pt(111) (*7*). We therefore stress the weak nature of the oxygen lone-pair platinum interaction for molecularly adsorbed alcohols and ethers: the interaction cannot be considered a true covalent bond, as in the case of atomic oxygen.

The value of 1.3 kcal mole^{-1} per carbon atom for the alcohols and ethers is of the right order of magnitude for physical adsorption of an alkane chain on a Pt(111) surface. Salmeron and Somorjai (*16*) have ob-

tained desorption activation energy values of 8.2 and 10.2 kcal mole^{-1} for *n*-butane and *n*-pentane adsorption on Pt(111) which is 2 kcal mole^{-1} per carbon atom. It is difficult to rationalize, however, why only one of the ether side chains should determine the desorption temperature on Pt(111). The simplest explanation is a bonding model involving asymmetric bonding of the ether on Pt(111), although any model of an ether molecule will show that it is physically possible to lay both alkyl chains close to the Pt surface while still maintaining the lone-pair bond. We can therefore comment on a second possibility that the ether desorption may be from a state in which only one half of the molecule (including the oxygen atom) is in a surface potential well. Such a state is possible if each alkane chain vibrates with a low frequency about the central oxygen lone-pair bond, and the desorption state essentially comes from a state "frozen" into one of two configurations. More vibration spectroscopic (EELS) data are needed on this system to examine the adsorbed monolayer states and to search for CH "soft" modes indicative of interaction between the alkyl group and the Pt surface.

4.2. Alcohol and Ether Dissociation on Pt(111)

The hydrogen desorption spectra of Fig. 4 may be interpreted in terms of two kinds

of surface species. The main H_2 peak near 310–350 K is the normal rate-limited recombination of adsorbed hydrogen atoms. Recombination of H_2 on clean Pt(111) occurs at the same temperature range. A second piece of evidence for hydrogen recombination comes from oxygen titration experiments. If the Pt(111) surface is covered with preadsorbed atomic oxygen, the 300–350 K H_2 peak is attenuated as the atomic hydrogen is removed as water near 170 K (for alcohols), and 205 K (for ethers). However, the H_2 peaks at higher temperatures were not affected by preadsorbed oxygen and must be due to a different kind of hydrogen-containing species.

We propose that all of the high-temperature H_2 peaks (~350 K) in Fig. 4 are due to meta-stable hydrocarbon intermediates which are formed when CO is split off the alcohols and ethers. The hydrogen desorbed is therefore rate-limited decomposition of adsorbed CH_x species, with the carbon remaining on the surface and hydrogen recombining to H_2 as soon as the CH bonds have been broken.

In the previous alcohol paper (8) we proposed that for the higher alcohols (propanol and butanol), stable ethylidyne (CH_3–C) and propylidyne (CH_3–CH_2–C) species were responsible for the two hydrogen maxima near 450 and 410 K, respectively, in Fig. 4. Salmeron and Somorjai (14) observed similar rate-limited decomposition of ethylidyne and propylidyne species by chemisorbing ethylene and propylene on Pt(111) (14). The only hydrocarbon species which is known to be stable on Pt(111) above 300 K are the alkylidyne groups (14). We believe that the ether decomposition spectra of Fig. 4 are more complicated than the alcohol spectra because carbon chains of different lengths are split off the ether when CO forms as opposed to only a single alkyl group from the adsorbed alcohol. We can summarize the mechanism as follows:

$$\underline{\text{Alcohols}} \quad C_nH_{2n+1}OH_{ads} \begin{array}{c} \;\;\nearrow^{a}\;\; C_nH_{2n+1}OH_{gas} \\ \xrightarrow{\;b\;} CO_{ads} \;+\; 2(n+1)H_{ads} \;+\; nC_{ads} \\ \;\;\searrow^{c}\;\; \\ CO_{ads} \;+\; (C_{n-1}H_{2n-3})_{ads} \;+\; 5H_{ads} \end{array} \qquad (6)$$

Step (c) results in a small fraction of adsorbed alkylidyne intermediates which decompose above 350 K, and step (b) produces adsorbed H which desorbs near 350 K.

$$\underline{\text{Ethers}} \quad (C_nH_{2n+1})_2O_{ads} \begin{array}{c} \;\;\nearrow^{a}\;\; (C_nH_{2n+1})_2O_{gas} \\ \xrightarrow{\;b\;} CO_{ads} \;+\; 2(2n+1)H_{ads} \;+\; 2nC_{ads} \\ \;\;\searrow^{c}\;\; \\ CO_{ads} \;+\; (C_nH_{2n-1})_{ads} \\ \;+\; (C_{n-1}H_{2n-3})_{ads} \;+\; 6H_{ads} \end{array} \qquad (7)$$

The ether decomposition route must involve at least one carbon–carbon and one carbon–oxygen bond scission to form adsorbed CO and hence at least two hydrocarbon species may be generated. In the spectra of Fig. 4, propyl ether has two high-temperature maxima, corresponding approximately to the C_3 and C_2 decomposi-

tion temperatures. Butyl ether has two maxima which represent a C_4 and a C_3 fragment and amyl ether three maxima corresponding approximately to a C_5, C_4, and C_2 species. To support the case for the hydrocarbon intermediates, we adsorbed 1-pentene and 1-butene on Pt(111) and examined the H_2 desorption spectra. We have plotted the data in Fig. 5. The 1-butene decomposition was almost identical to that measured by Salmeron and Somorjai (*14*) for 2-butene, with a small burst of H_2 near 280 K and a major maximum near 380 K. According to Salmeron (*14*) the C_4, C_3, and C_2 alkylidyne species each decompose in the temperature range 350–500 K with a temperature which decreases with increasing carbon number. These are marked as bars in Fig. 5. Our data for 1-pentene show that a single C_5 species is not generated, but peaks corresponding to a C_5, C_4, and C_2 species are produced. The decomposition of pentene therefore shows that C_5 species (pentylidyne) are not as stable as the C_4 and lower species and multiple pathways of decomposition to lower fragments must occur. In Fig. 5 we have also observed the tail of H_2 desorption from 500 to 750 K which has been attributed to CH bond breaking

from residual CH fragments on the Pt surface (*14*). In summary, the data in Fig. 5 and that of Salmeron show a linear sequence of decomposition temperatures (decreasing with increasing carbon number) for alkylidyne decomposition on Pt(111).

Referring back to Fig. 4, it is now clear that the mechanism of alcohol and ether decomposition does involve formation of either one or two hydrocarbon fragments for alkyl side chains up to C_4 in length, as outlined in Eqs. (6) and (7). However, for amyl ether and 1-pentene, a mixture of C_5, C_4, and C_2 species is generated because the C_5 species are less stable. There is always a certain amount of high-temperature (500–700 K) hydrogen evolution from CH decomposition for all of the higher alcohols and ethers ($>C_4$).

Finally, some comments on the use of platinum catalysts in alcohol reactions. Recently, Licht *et al.* (*3*) have measured primary alcohol reaction rates over supported Pt/SiO_2 catalysts. For *n*-butanol, up to 28% yields of di-*n*-butyl ether were found at 190°C (30% conversion) with 62% propane and 10.4% *n*-butane being formed. The dehydrogenation of the alcohol was therefore the dominant reaction, with lesser dehydration to form the ether. *n*-Butane is presumably formed by hydrogenation of butylene (formed by dehydration of the alcohol). These reactions at higher pressures illustrate the difficulty in interpreting UHV experiments in terms of real catalytic conditions. Whereas alcohols completely dehydrogenate on Pt(111) in UHV, ethers may be produced by dehydration on a real catalyst. As we have mentioned before, UHV low-temperature reactions artificially increase the *residence time* of all of the adsorbed species such that total dehydrogenation results. Almost all hydrocarbons adsorbed on Pt(111) at low temperatures decompose to C and H and oxygenated compounds to CO, H, and C. We therefore conclude that low-temperature chemistry on metal crystals in UHV is not necessarily relevant to real conditions. On the other
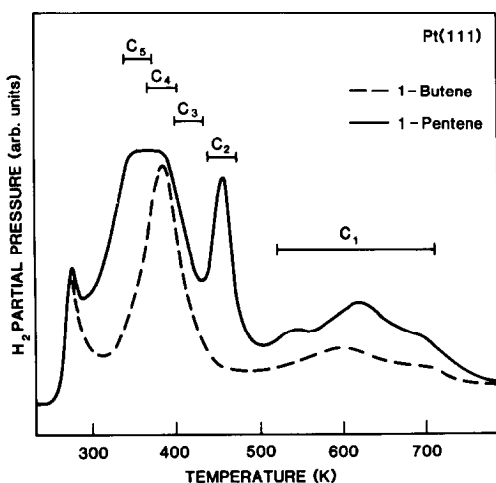

FIG. 5. Hydrogen desorption spectra for 1-butene and 1-pentene adsorption on Pt(111). The bars represent the temperature ranges in which the indicated alkylidyne species decompose. Data (see Ref. (*14*)).

hand some understanding of the systematic trends in reactivity of organic reactants may be obtained from this type of work.

5. SUMMARY

Alcohols, ethers, and water adsorb on platinum (111) at 100 K into monolayer and multilayer states. The multilayer desorption temperature is a function of the boiling point of the compound whereas the monolayer desorption temperature depends on the platinum–oxygen lone-pair bond plus a contribution from surface bonding to one of the alkyl side chains. During temperature programming, a small fraction (<10%) of the adsorbed alcohol or ether dehydrogenates to adsorbed CO, H, and hydrocarbon fragments. Up to C_4, alcohols split off an alkylidyne species of carbon number (n − 1) where n is the alcohol carbon number. Ethers split off two alkylidyne intermediates of carbon number n and (n − 1). For n-amyl ether the C_5 alkylidyne species was unstable and formed a mixture of C_5, C_4, C_2, and C_1 adsorbed species, in agreement with H_2 desorption spectra from 1-pentene adsorption.

A comparison of the low-pressure–low-temperature conditions in this work and real catalytic conditions at higher pressures shows considerable discrepancy in selectivity. We attribute the total dehydrogenation of alcohols and ethers on Pt(111) to the long residence times of the intermediates. Under high-pressure catalysis at elevated temperatures, however, alcohols may be readily dehydrated to ethers and alkenes.

APPENDIX

For first-order desorption processes, Redhead (*15*) has derived the following equation:

$$E_{des} \cong RT_M \left(\ln \frac{\nu T_M}{\beta} - 3.64 \right) \quad (1)$$

where E_{des} = activation energy for desorp-

tion, T_M = monolayer peak desorption temperature, ν = preexponential (constant), and β = heating rate.

Assuming 10^{13} sec^{-1} for ν (an immobile adsorbate) and a heating rate of 5 K sec^{-1}, Eq. (1) simplifies to

$$E_{des} \simeq 60\ T_M\ (cal\ mole^{-1}). \quad (2)$$

Over the temperature range of 100–300 K, Eq. (2) has an accuracy of approx. ±5%. We have used Eq. (2) to calculate the activation energy for desorption and hence the approximate heat of adsorption in the discussion. It should also be noted that Eq. (1) is relatively insensitive to small changes in the $\nu T_M/\beta$ term.

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