

# Adsorption of C<sub>3</sub> Alcohols, 1-Butanol, and Ethene on Platinized Platinum As Studied with FTIRS and DEMS

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The irreversible adsorption of several C<sub>3</sub> alcohols, 1-butanol, and ethene on platinized platinum has been studied with Fourier transform IR spectroscopy (FTIRS) and differential electrochemical mass spectrometry (DEMS) in perchloric acid electrolyte. Apart from 2-propanol, all studied alcohols display C–C(O) dissociative adsorption as the only pathway active in the formation of irreversible adsorbates. 1,2,3-Propanetriol is the only compound that is fully converted to adsorbed CO, while all other primary alcohols generate hydrocarbon adspecies in addition to CO. No further C–C bond breaking is observed in these hydrocarbon adspecies, which were found to be highly dehydrogenated. The hydrocarbon species can be fractionally hydrogenated off the surface to form corresponding gaseous compounds. 2-Propanol and ethene do not undergo C–C dissociation to form CO but are dehydrogenated considerably. For 2-propanol and ethene it was found that a small amount of oxygen incorporation occurs on the C<sub>1</sub> position, followed by decarbonylation to form CO.

## Introduction

The study of the electro-oxidation of simple alcohols on platinum was initially urged by the possible application of these substances in the direct fuel cell.<sup>1</sup> Nowadays, methanol is regarded as the best candidate for application in fuel cells and is thus the most widely studied compound. 1,2-Ethanediol and ethanol have received less attention, and studies concerning C<sub>3</sub> alcohols have been reported even less frequently. In spite of their unfitness for fuel cells, the number of studies concerning alcohol compounds has increased steadily over the past years, due to a growing fundamental interest in the adsorption and oxidation behavior of these compounds. Electrochemical studies can generate relevant information for the selective oxidation of alcohol compounds with molecular oxygen on platinum catalysts in the liquid phase. Small alcohols can fulfill the role of model compounds in the study of larger alcohols like for example  $\alpha$ -D-glucose or methyl- $\alpha$ -D-glucopyranoside.

The recent development of both infrared and mass spectroscopic techniques suitable for the solution phase has enabled a more systematic study of the adsorption and oxidation behavior of alcohols, offering the possibility of gathering molecular information that had been impossible for electrocatalytic researchers so far. Several aspects of the adsorption behavior of primary and secondary alcohols have been clarified with these spectroscopic techniques and will be summarized here.

It has been well established with FTIRS that adsorbed CO is formed during the adsorption of various primary alcohols and polyols: ethanol,<sup>2–5</sup> 1,2-ethanediol,<sup>3,4,6</sup> 1-propanol,<sup>3,7,8</sup> 1,2- and 1,3-propanediol,<sup>3</sup> 1,2,3-propanetriol,<sup>3</sup>

1-butanol,<sup>3</sup> and 2-propen-1-ol.<sup>9</sup> We will refer to this type of reaction as C–C(O) dissociative adsorption or decarbonylation. The IR data were used only in a single report to establish the CO coverage, ranging from 0.9 for methanol to 0.35 for 1-butanol.<sup>3</sup> The formation of adsorbed CO in the adsorption of primary alcohol and polyol compounds has been suggested also on the basis of cyclic voltammetry.<sup>10–13</sup>

Non-C–C(O) dissociative adsorption of primary alcohols has been reported in a number of cases to occur simultaneously with C–C dissociative adsorption. For ethanol,<sup>2</sup> 1-propanol,<sup>8</sup> and 2-propen-1-ol,<sup>9</sup> C–H vibrations were observed that were ascribed to nondissociated adspecies. Most primary alcohols form adsorbates that are susceptible to reduction at potentials in the hydrogen region, and it has been found with differential electrochemical mass spectrometry (DEMS) that gaseous compounds are formed as a result. These products give information on the composition of the adsorbates. It is reported for ethanol that ethane is formed in addition to methane in the ratio 1:6,<sup>2</sup> in contrast with others who only found methane.<sup>4,14,15</sup> For 1-propanol, ethane and propane were found in the ratio 3.5:1.<sup>8</sup> These results show that in some cases nondissociative adsorption occurs in addition to dissociative adsorption. It was further proposed for ethanol<sup>2</sup> and 1-propanol<sup>8</sup> that the nondissociated adspecies can undergo C–C(O) bond cleavage during reduction, leading to an increased CO coverage and methane and ethane formation, respectively. This means that the degree of non-C–C dissociative adsorption is higher than indicated by the reduction products found with DEMS. Due to contrasting results, the issue is still open whether solely C–C dissociative adsorption occurs or dissociative and nondissociative adsorption occur simultaneously.

So far only few data have been reported that give information on the exact composition of the alkyl groups

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that are formed in the C–C(O) dissociative adsorption of primary alcohols. For ethanol we suggested previously that oxidation of the CH<sub>x</sub> group to C and CO occurs.<sup>4</sup> In the case of 1-propanol, C<sub>2</sub>H<sub>6,ads</sub><sup>7</sup> and C<sub>2</sub>H<sub>5,ads</sub><sup>8</sup> adspecies were proposed, whereas also dissolution of the adspecies has been proposed.<sup>10</sup>

There is general agreement for secondary alcohols that no C–C dissociation occurs during adsorption.<sup>3,7,11,16,17</sup> This conclusion is supported by the observation that no CO is formed during adsorption and that reduction of the 2-propanol adsorbate results in formation of propane.<sup>16</sup> Several adsorbate structures were proposed for 2-propanol,<sup>16</sup> but more data are necessary to clarify this point.

Ethane was found with DEMS to be the main product in the reduction of ethene adsorbates, indicating that no C–C bond breaking has occurred. Isotope experiments have shown that the adsorption of ethene on Pt(110) is accompanied by partial oxygen uptake, while the adsorbates on Pt(111) do not undergo oxygen uptake.<sup>14</sup>

In this paper we investigate for several primary alcohols and polyols whether the adsorption on platinized platinum is solely C–C(O) dissociative or dissociative and nondissociative adsorption occur simultaneously. In a previous paper<sup>4</sup> we concluded for 1,2-ethanediol and ethanol that the C–C dissociative adsorption on platinized platinum is the only pathway that is active in the formation of irreversible adsorbates. We will also deal with the point of the proposed C–C(O) bond dissociation during adsorbate reduction, since this is important in the issue of dissociative versus nondissociative adsorption. Little is known about the composition of the coadsorbates that are formed in addition to CO and we will focus on this point. Therefore we aim to determine the degree to which these adspecies dehydrogenate.

The adsorbates formed from 2-propanol and ethene are studied to compare the extent of dehydrogenation in the case of non-C–C dissociative adsorption with that occurring in dissociative adsorption. Fourier transform IR spectroscopy (FTIRS), differential electrochemical mass spectrometry (DEMS), and cyclic voltammetry are used to characterize the irreversible adsorbates.

## Experimental Section

Infrared measurements were performed with a Biorad FTS 45A spectrometer, equipped with a liquid-nitrogen-cooled MCT detector. All IR spectra were recorded with 4 cm<sup>−1</sup> resolution. The bottom of the electrochemical cell consists of a CaF<sub>2</sub> prism with 65° beveled edges. The platinum electrode has a diameter of 9 mm and is embedded in a PTFE holder. P-polarized light has been used in all IR measurements. DEMS measurements were performed with a Leybold Quadruvac PGA 100 mass spectrometer. The details of the experimental setup are given in a previous report.<sup>18</sup> The products were examined for carbon dioxide (*m/z* = 44, CO<sub>2</sub><sup>+</sup>), methane (*m/z* = 15, CH<sub>3</sub><sup>+</sup>), ethane (*m/z* = 30, C<sub>2</sub>H<sub>6</sub><sup>+</sup>), propene (*m/z* = 42, C<sub>3</sub>H<sub>6</sub><sup>+</sup>), propane (*m/z* = 44, C<sub>3</sub>H<sub>8</sub><sup>+</sup>), butene (*m/z* = 56, C<sub>4</sub>H<sub>8</sub><sup>+</sup>), and butane (*m/z* = 58, C<sub>4</sub>H<sub>10</sub><sup>+</sup>). Electrochemical measurements were performed with an Autolab PGSTAT 20 computer-controlled potentiostat. A Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode was used as a reference electrode. All potentials will be referred to RHE. All measurements were performed with platinized platinum that was obtained by electrodeposition from a 0.05 M H<sub>2</sub>PtCl<sub>6</sub> + 0.01 M HCl solution on smooth platinum. A deposition current of 10 mA/cm<sup>2</sup> was used for the DEMS gauze electrode, while 0.5 mA/cm<sup>2</sup> was used for the IR electrode. The electrode areas, determined from the hydrogen desorption region in the cyclic voltammogram, were 53 and 10 cm<sup>2</sup>, respectively. Platinized platinum was chosen in order to minimize the influence

of impurities on the adsorption process as well as to increase the mass signals in the DEMS technique. Potential cycling between 0 and 1.5 V was carried out until a stable voltammogram was obtained. Electrolytes were prepared using ultrapure water (18.2 MΩ) obtained with an Elga water purification system. In the infrared experiments 0.1 M HClO<sub>4</sub> was used, and for cyclic voltammetry and the DEMS measurements 0.5 M HClO<sub>4</sub> was used. Oxygen was removed from the electrolyte with Argon 4.6.

Adsorption experiments were performed at 0.4 V for 10 min with 1 or 5 mM concentrations of the various alcohol compounds. The potential of 0.4 V was chosen on one hand high enough to enable adsorption in the absence of adsorbed hydrogen, which might react with the adspecies, and on the other hand low enough to suppress oxidation reactions of the adsorbate. The adsorption current has nearly decreased to zero after 10 min, indicating that the time was long enough for the adsorption to be complete. Ethylene (Hoek Loos, purity 2.7) and CO (Hoek Loos, purity 4.6) were bubbled through the solution for 10 min. All other chemicals, p.a. quality, were obtained from Merck. After adsorption the electrolyte was replaced by blank electrolyte while keeping the electrode at the adsorption potential.

## Results

**DEMS and Cyclic Voltammetry.** After adsorption of the alcohol compound at 0.4 V for 10 min, followed by replacement of the alcohol-containing solution by fresh electrolyte, a scan is started in the anodic direction and subsequently the mass signal for CO<sub>2</sub> is recorded. This procedure will be referred to as 'direct' oxidation. Combining the DEMS and cyclic voltammetry results gives the number of electrons, *n*<sub>ox</sub>, liberated in the adsorbate oxidation per formed CO<sub>2</sub> molecule. This requires calibration of the mass spectrometer for CO<sub>2</sub>, which is carried out by measuring the oxidation of adsorbed CO to CO<sub>2</sub> in a reference experiment. This yields the calibration factor *K*<sub>CO</sub> according to

$$K_{\text{CO}} = \left( \frac{Q_{\text{ox}}}{Q_{\text{mass}}/\text{CO}} \right)$$

where *Q*<sub>ox</sub> is the coulometric charge involved in the oxidation of CO to CO<sub>2</sub> and *Q*<sub>mass</sub> represents the integrated mass current  $\int i_{\text{mass}} dt$ . The *n*<sub>ox</sub> value for 1,2,3-propanetriol can then be obtained from the value *Q*<sub>ox</sub>/*Q*<sub>mass</sub> measured for the alcohol oxidation according to

$$n_{\text{ox}} = \left( \frac{Q_{\text{ox}}}{Q_{\text{mass}}} \right)_{1,2,3\text{-propanetriol}} \frac{1}{K_{\text{CO}}} n_{\text{ox}}^{\text{CO}}$$

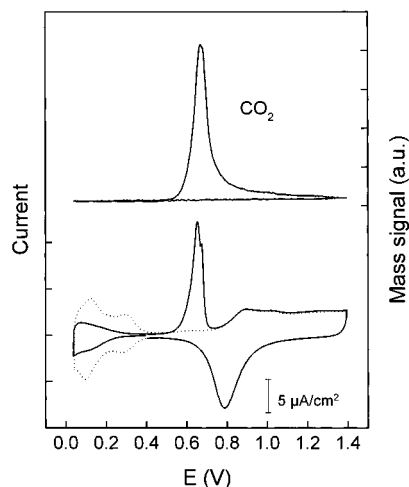
where *n*<sub>ox</sub><sup>CO</sup> = 2 electrons per CO<sub>2</sub> molecule. In contrast with the 'direct' oxidation, the scan can also be started in the cathodic direction after adsorption at 0.4 V followed by electrolyte exchange. This procedure will be referred to as 'indirect' oxidation. Concomitantly the mass response for possible reduction products can be followed during the reduction. In the subsequent anodic scan the CO<sub>2</sub> mass response is followed again.

Figure 1 shows the current and CO<sub>2</sub> (*m/z* = 44) mass response for the indirect oxidation of 1,2,3-propanetriol adspecies. No reduction of the adspecies is observed in the potential region below 0.4 V, and as a result the oxidation profiles for 'direct' and 'indirect' oxidation are the same. An oxidation peak is observed in the double-layer region at 0.65 V. This peak resembles that of the oxidation of 1,2-ethanediol adsorbates very well, which were shown to consist solely of adsorbed CO.<sup>4</sup> The dotted line represents the second cycle, which equals the cyclic voltammogram for platinized platinum in fresh 0.5 M HClO<sub>4</sub>. The charge involved in the oxidation was 114 μC/cm<sup>2</sup>, and 82% of the hydrogen sites were blocked after

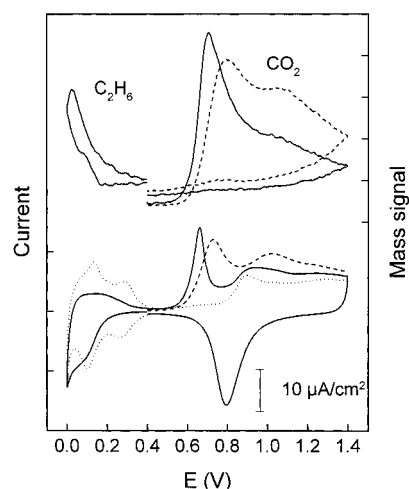
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**Figure 1.** Combined cyclic voltammogram and DEMS measurement of 1,2,3-propanetriol adsorbates: 'indirect' oxidation (—); blank (···); adsorption at 0.4 V in 1 mM 1,2,3-propanetriol; electrolyte, 0.5 M  $HClO_4$ ; scan rate, 5 mV/s;  $m/z = 44$  ( $CO_2^+$ ).

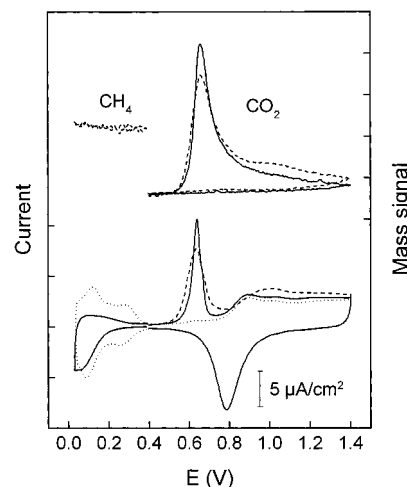


**Figure 2.** Combined cyclic voltammogram and DEMS measurement of 1-propanol adsorbates: 'direct' oxidation (---); 'indirect' oxidation (—); blank (···); adsorption at 0.4 V in 10 mM 1-propanol; electrolyte, 0.5 M  $HClO_4$ ; scan rate, 10 mV/s;  $m/z = 44$  ( $CO_2^+$ );  $m/z = 30$  ( $C_2H_6^+$ ).

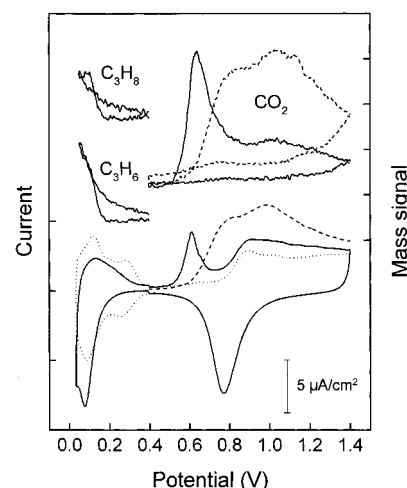
adsorption. For the oxidation of these adspecies it was found that  $n_{ox}$  is 1.9 e/ $CO_2$ .

It is shown in Figures 2–6 for the various compounds that different oxidation profiles are observed for the 'direct' and 'indirect' oxidation as a result of the preceding reduction during the latter. For all these compounds, the oxidation charge involved in the 'direct' oxidation is higher than that in the 'indirect' oxidation, as shown in Table 1, and this observation implies that in the reduction adsorbates are removed from the surface. This is confirmed by the DEMS measurements that are discussed below.

In the 'direct' oxidation of 1-propanol, represented by the dashed line in Figure 2, an oxidation peak is found at 0.73 V in the double-layer region, followed by a broad oxidation wave that extends throughout the oxide region with a maximum at 1.02 V. At the reverse potential the oxidation wave is not completed, as shown by the dashed line in Figure 2. The oxidation is accompanied by formation of  $CO_2$  ( $m/z = 44$ ). In the 'indirect' oxidation, represented by the solid line in Figure 2, a reduction is observed below 0.2 V that is accompanied by the formation of ethane ( $m/z = 30$ ). A small contribution at  $m/z = 15$  was observed, and this could be fully ascribed to the



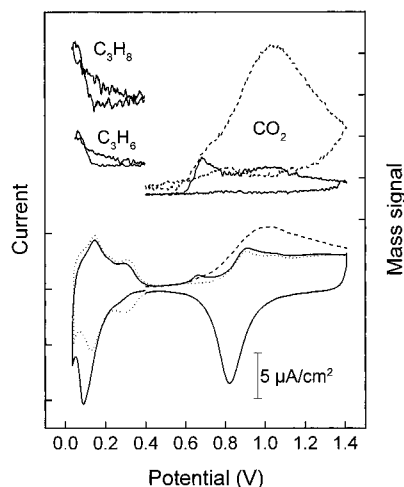
**Figure 3.** Combined cyclic voltammogram and DEMS measurement of 1,3-propanediol adsorbates: 'direct' oxidation (---); 'indirect' oxidation (—); blank (···); adsorption at 0.4 V in 5 mM 1,3-propanediol; electrolyte, 0.5 M  $HClO_4$ ; scan rate, 5 mV/s;  $m/z = 44$  ( $CO_2^+$ );  $m/z = 15$  ( $CH_3^+$ ).



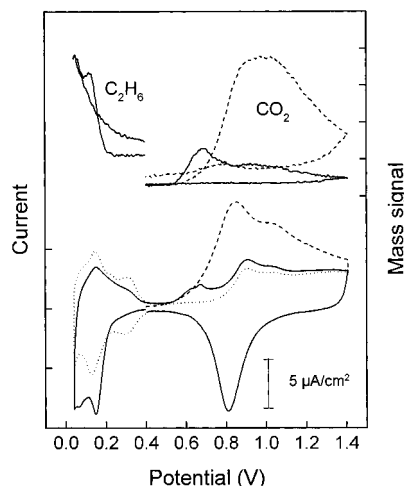
**Figure 4.** Combined cyclic voltammogram and DEMS measurement of 1-butanol adsorbates: 'direct' oxidation (---); 'indirect' oxidation (—); blank (···); adsorption at 0.4 V in 5 mM 1-butanol; electrolyte, 0.5 M  $HClO_4$ ; scan rate, 5 mV/s;  $m/z = 44$  ( $CO_2^+$ ,  $C_3H_8^+$ );  $m/z = 42$  ( $C_3H_6^+$ ).

fragmentation of ethane. This indicates that no methane is formed during reduction of the adsorbate. Only a small signal was found for propane at  $m/z = 44$  in the hydrogen adsorption region, where reduction of the adsorbates occurs. After taking into account the fragmentation patterns and relative ionization probabilities, the ratio of ethane to propane was found to be roughly 50:1. Several scans had to be carried out to complete the reduction; 95  $\mu C/cm^2$  was involved in the first cycle, and after five cycles the total charge was 131  $\mu C/cm^2$ . The charge involved in the reduction,  $Q_{red}$ , given in Table 1, could be determined by subtracting the anodic part of the scan below 0.4 V, due to oxidation of adsorbed hydrogen, from the cathodic part of the scan below 0.4 V, due to hydrogenation and formation of adsorbed hydrogen. The oxidation peak in the double-layer region, recorded after reduction of the adsorbate, has narrowed and shifted 0.07 V in the negative direction with respect to the 'direct' oxidation to 0.66 V. The form of this peak now resembles the oxidation peak of adsorbed  $CO$ ,<sup>19</sup> and the concomitant  $CO_2$  production has changed similarly (cf. Figure 2 upper part). It follows

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**Figure 5.** Combined cyclic voltammogram and DEMS measurement of 2-propanol adsorbates; 'direct' oxidation (---); 'indirect' oxidation (—); blank (···); adsorption at 0.4 V in 5 mM 2-propanol; electrolyte, 0.5 M HClO<sub>4</sub>; scan rate, 5 mV/s;  $m/z = 44$  (CO<sub>2</sub><sup>+</sup>, C<sub>3</sub>H<sub>8</sub><sup>+</sup>);  $m/z = 42$  (C<sub>3</sub>H<sub>6</sub><sup>+</sup>).



**Figure 6.** Combined cyclic voltammogram and DEMS measurement of ethene adsorbates; 'direct' oxidation (---); 'indirect' oxidation (—); blank (···); adsorption at 0.4 V by bubbling ethene; electrolyte, 0.5 M HClO<sub>4</sub>; scan rate, 5 mV/s;  $m/z = 44$  (CO<sub>2</sub><sup>+</sup>);  $m/z = 30$  (C<sub>2</sub>H<sub>6</sub><sup>+</sup>).

**Table 1. Charge Involved in the 'Direct' and 'Indirect' Oxidation of Various Alcohol Compounds and Ethene after Adsorption at 0.4 V**

compound	$Q_{ox}$ direct oxidation (μC/cm <sup>2</sup> )	$Q_{ox}$ indirect oxidation (μC/cm <sup>2</sup> )	$Q_{red}$ (μC/cm <sup>2</sup> )
1-propanol	564	354	131
1,3-propanediol	371	248	83
1,2,3-propanetriol	114		
2-propanol	389	116	98
1-butanol	649	304	115
ethene	793	149	192

further from the anodic branch of the hydrogen region that still 73% of the Pt–H sites are blocked after reduction of the adsorbate. The number of electrons,  $n_{ox}$ , liberated per CO<sub>2</sub> molecule was found to be 3.5 for the 'direct' oxidation and 3.1 for the 'indirect' oxidation.

Figure 3 shows the results for 1,3-propanediol. It is clear by comparison with Figure 2 that the doubled number of hydroxyl moieties on 1,3-propanediol is responsible for a lower oxidation wave in the oxide region, and the oxidation profile therefore resembles the CO oxidation more than that of 1-propanol. The oxidation profile can

**Table 2.  $n_{ox}$  (e/CO<sub>2</sub>) Values for the 'Direct' and 'Indirect' Oxidation of Various Alcohol Adsorbates Determined with DEMS after Adsorption at 0.4 V**

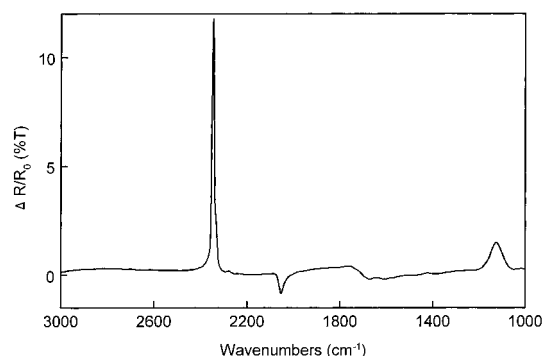
compound	$n_{ox}$ direct oxidation	$n_{ox}$ indirect oxidation
1-propanol	3.5	3.1
1,3-propanediol	2.5	2.2
1,2,3-propanetriol	1.9	
2-propanol	3.8	5.2
1-butanol	3.7	3.6
ethene	4.0	3.7

be regarded as intermediate between those of 1-propanol and 1,2,3-propanetriol. In the 'direct' and 'indirect' oxidation a peak is observed at 0.64 V. As shown in Table 1, the charge involved in the reduction is lower for 1,3-propanediol than for 1-propanol, demonstrating that a lower fraction of the adsorbate is sensitive toward hydrogenation. The only product observed in the reduction is methane. The  $n_{ox}$  values found were 2.5 e/CO<sub>2</sub> for the 'direct' oxidation and 2.2 e/CO<sub>2</sub> for the 'indirect' oxidation, the latter being close to the value of 2 e/CO<sub>2</sub> for adsorbed CO.

The effect of increasing the chain length by a single carbon atom can be seen when cyclic voltammograms for 1-butanol and 1-propanol are compared. For 1-butanol, a broad double peak with maxima at 0.8 and 1.04 V is observed in the 'direct' oxidation, as shown in Figure 4. When compared to the 'direct' oxidation profile of 1-propanol, the oxidation peak in the double-layer region is less pronounced and has become a shoulder that is shifted 0.07 V in the anodic direction. The relative contribution of oxidation in the oxide region has increased with respect to that of 1-propanol while the charge involved in the reduction is relatively lower than that for 1-propanol. In the 'indirect' oxidation a well defined CO-like peak is present in the double-layer region at 0.61 V. This peak is smaller than that for the 'indirect' oxidation of 1-propanol. The  $n_{ox}$  values found were 3.7 e/CO<sub>2</sub> for the 'direct' oxidation and 3.6 e/CO<sub>2</sub> for the 'indirect' oxidation. The reduction of the adsorbate at 0.08 V is accompanied by propene ( $m/z = 42$ ) and propane ( $m/z = 44$ ) formation. Only a small contribution was found for butane at  $m/z = 58$  in the hydrogen adsorption region, where reduction of the adsorbates occurs. After taking into account the fragmentation patterns and relative ionization probabilities, the (propene + propane)/butane ratio was found to be roughly 100:1. No methane or ethane was observed after correction for the fragmentation of propane.

The 'direct' and 'indirect' oxidation profiles obtained from 2-propanol in Figure 5 demonstrate that this secondary alcohol behaves quite differently from primary alcohols. A broad wave is present in the 'direct' oxidation in the oxide region, with a maximum at 1.02 V, while only a small contribution is visible in the double-layer region. It is shown in Table 1 that the charge involved in the 'direct' oxidation is much lower than that for 1-propanol and a larger fraction of the adsorbate is susceptible toward hydrogenation, which leads to the formation of propene ( $m/z = 42$ ) and propane ( $m/z = 44$ ). In the 'indirect' oxidation a small oxidation peak is found at 0.65 V, indicating that a small amount of CO might have been formed. The  $n_{ox}$  values found were 3.8 e/CO<sub>2</sub> for the 'direct' oxidation and 5.2 e/CO<sub>2</sub> for the 'indirect' oxidation.

The 'direct' and 'indirect' oxidation profiles of ethene adsorbates formed at 0.4 V are given in Figure 6. In the 'direct' oxidation a broad wave starts at 0.5 V and extends throughout the oxide region and is clearly not completed at the reverse potential of 1.4 V. The wave contains a maximum at 0.85 V and a shoulder at 1.04 V. However, in the double layer, where CO-like adsorbates are expected,

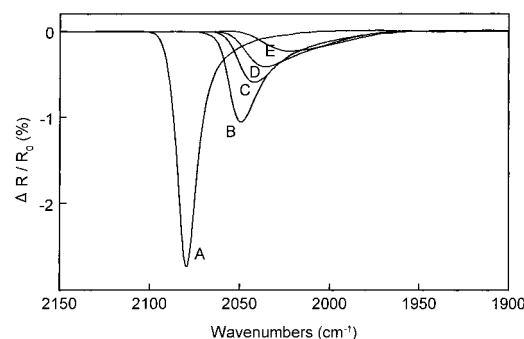


**Figure 7.** Infrared spectrum of 1,2,3-propanetriol adsorbate, obtained after adsorption at 0.4 V in 1 mM 1,2,3-propanetriol: electrolyte, 0.1 M  $\text{HClO}_4$ ;  $E_0 = 0.4$  V;  $E_1 = 0.4$  V after potential excursion to 1.4 V; resolution,  $4\text{ cm}^{-1}$ .

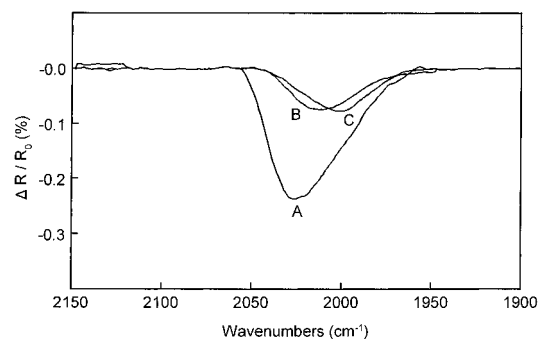
a relatively low oxidation current is established. When 'indirect' oxidation is performed, a large reduction peak is present at 0.15 V, which is accompanied by the formation of ethane ( $m/z = 30$ ) and a small amount of butane ( $m/z = 58$ ). It follows from the anodic scan that after reduction only 16% of the hydrogen adsites are covered with adsorbate. In the subsequent scan a small oxidation peak is present in the double-layer region at +0.68 V, combined with a broad wave extending from 0.8 to 1.4 V in the oxide region. From this observation it follows that the majority of the ethene adsorbates are removed from the surface during the reduction reaction. The  $n_{\text{ox}}$  values found were 4.0  $\text{e}/\text{CO}_2$  for the 'direct' oxidation and 3.7  $\text{e}/\text{CO}_2$  for the 'indirect' oxidation.

**Infrared Spectroscopy.** Infrared spectra, given as  $\Delta R/R_0$  ( $\Delta R = R_0 - R_1$ ), were obtained by subtracting the single-beam spectra that were obtained at the adsorption potential before ( $R_0$ ) and after ( $R_1$ ) a potential excursion to 1.4 V. The spectrum obtained for 1,2,3-propanetriol is shown in Figure 7. At  $1120\text{ cm}^{-1}$  a positive-going band from  $\text{ClO}_4^-$  (ref 20) is observed, due to an increase in concentration as a result of migration processes involved in the oxidation of the 1-propanol adsorbate. Apart from this band, the only IR bands observed were a negative-going band at  $2054\text{ cm}^{-1}$ , due to linearly adsorbed CO,<sup>21</sup> a positive-going band at  $2344\text{ cm}^{-1}$ , which originates from the formation of  $\text{CO}_2$  present in the thin layer, and a broad band around  $1650\text{ cm}^{-1}$  due to an uncompensated water bending mode. No C-H bands could be observed in the wavenumber region around  $3000\text{ cm}^{-1}$ . The infrared spectra obtained for 1-propanol, 1,3-propanediol, and 1-butanol are virtually the same as those for 1,2,3-propanetriol. Figure 8 compares the spectra in the  $1900\text{--}2100\text{ cm}^{-1}$  range obtained after adsorption of the various alcohols with the spectrum obtained after adsorption of pure CO. The alcohol-derived CO vibrations are substantially lower and broader than the CO vibrations obtained from pure CO; additionally, they have shifted to lower wavenumbers, as is expected for lower CO coverages. In the case of 2-propanol and ethene only small CO vibrations were observed at  $2100\text{ cm}^{-1}$ , as shown in Figure 9, where the spectrum for 1-butanol is given for comparison.

The integrated CO absorbances give a good indication of the CO coverage formed after adsorption of the various compounds. It has been reported for FTIRS studies in ultra high vacuum on platinum single crystals that the integrated CO absorbance is not linearly related to the



**Figure 8.** Infrared spectrum in the wavenumber region of linear adsorbed CO after adsorption of CO (A), 5 mM 1,2,3-propanetriol (B), 1,3-propanediol (C), 1-propanol (D), and 1-butanol (E): electrolyte, 0.1 M  $\text{HClO}_4$ ;  $E_0 = 0.4$  V;  $E_1 = 0.4$  V after potential excursion to 1.4 V; resolution,  $4\text{ cm}^{-1}$ .



**Figure 9.** Infrared spectrum in the wavenumber region of linear adsorbed CO after adsorption of 1-butanol (A), 2-propanol (B), and ethene (C): electrolyte 0.1 M  $\text{HClO}_4$ ;  $E_0 = 0.4$  V;  $E_1 = 0.4$  V after potential excursion to 1.4 V; resolution,  $4\text{ cm}^{-1}$ .

**Table 3. Integrated Absorbance of the CO Vibration Observed after Adsorption of Various Compounds at an Adsorption Potential of 0.4 V**

compound	vibration frequency ( $\text{cm}^{-1}$ )	integrated absorbance (au)
CO	2080	1
1-propanol	2040	0.38
1,3-propanediol	2048	0.53
1,2,3-propanetriol	2054	0.69
1-butanol	2025	0.30
2-propanol	2101	0.07
ethene	2000	0.06

CO coverage.<sup>22–26</sup> It must also be considered that coadsorbates next to CO might alter the vibrational properties of CO to some extent with respect to those of pure CO adlayers. The data are shown in Table 3, taking the absorbance of gaseous CO as unity. It can be concluded that 1,2,3-propanetriol generates the highest amount of CO, followed by 1,3-propanediol, 1-propanol, and 1-butanol. Ethene and 2-propanol yield very small CO coverages. The amount of CO formed after adsorption of ethanol described in a previous study<sup>4</sup> is intermediate between those for 1-propanol and 1,3-propanediol. The amount of CO formed in the adsorption of 1,2-ethanediol is equal to that from 1,2,3-propanetriol.<sup>4</sup> Leung and Weaver<sup>3</sup> have determined CO coverages in the presence of the reactant alcohol with FTIRS, and they reported higher coverages than in our measurements: between

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0.9 for methanol and 0.35 for 1-butanol. However the trend in the CO coverage for various alcohol compounds is the same as in our case.

It is remarkable that for all substances reported here no C–H vibrations were observed in the wavenumber region between 2800 and 3000  $\text{cm}^{-1}$  within the detection limit of 0.01%T. This is in contrast with previous reports for ethanol,<sup>2</sup> 1-propanol,<sup>8</sup> and 2-propanol,<sup>16</sup> where C–H bands of 0.04, 0.15, and 0.04%T were found, respectively. The noise level in our measurements is low enough to detect vibrations with the typical intensities between 0.05 and 0.15%T, observed for methyl and ethyl species on platinum in ultra high vacuum.<sup>27,28</sup> We studied the hydrogenation of the alcohol adsorbates with IR to see if the products that are formed during reduction can be observed while they are trapped in the thin layer. We found for 2-propanol a small C–H band at 2920  $\text{cm}^{-1}$  of 0.03%T after stepping the potential from  $-0.3$  to  $-0.65$  V.

It was reported previously that hydrogenation of ethanol and 1-propanol adsorbates results in CO formation during reduction together with methane and ethane.<sup>2,8</sup> This reaction is important for the interpretation of the product distribution in DEMS during reduction. We found also that cycling through the hydrogen region resulted in an increase of the integrated CO absorbance when the electrode was in the thin layer configuration during reduction. However, FTIRS shows that the increase of the CO vibration is accompanied by a disappearance of  $\text{CO}_2$  in the thin layer, as shown by a negative band at 2343  $\text{cm}^{-1}$ . To examine whether the CO increase was only due to reduction of  $\text{CO}_2$  that has accumulated in the thin layer, we performed an experiment in which the reduction was carried out while the electrode was positioned in the bulk of the solution. After the reduction, the electrode was brought in the thin layer configuration to record the IR subtract spectrum. This spectrum was compared with one obtained without previous hydrogenation of the adsorbate, and only a small 3  $\text{cm}^{-1}$  shift of the CO vibration to lower wavenumbers was observed upon reduction, while the integrated absorbances were equal. The small shift is probably due to the removal of coadsorbates during the reduction. This experiment clearly demonstrates that the increase of the CO vibration that is found when the electrode is in the thin layer configuration during reduction is indeed due to reduction of  $\text{CO}_2$  that has accumulated in the thin layer.

### Discussion

**1,2,3-Propanetriol.** The adsorption of 1,2,3-propanetriol yields a considerable amount of CO, as detected with FTIRS. This indicates that 1,2,3-propanetriol undergoes decarbonylation during adsorption. The  $n_{\text{ox}}$  value of 1.9 electrons per  $\text{CO}_2$  molecule, found with DEMS, implies that this decarbonylation reaction is complete and thus CO is the only adsorbate formed according to



Afterward the adsorbate is oxidized in the cyclic voltammogram according to



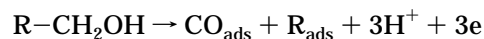
The conclusion that 1,2,3-propanetriol completely decarbonylates is supported by the absence of an adsorbate

reduction in the cyclic voltammogram at potentials in the hydrogen region. Complete decarbonylation during adsorption was also found for 1,2-ethanediol,<sup>4</sup> and we conclude that this adsorption behavior is general for all small alcohols that contain an OH moiety on every carbon atom. Adsorbed CO was also observed for 1,2,3-propanetriol in 0.1 M NaOH electrolyte on the basal planes of platinum using cyclic voltammetry and EMIRS.<sup>12</sup> No investigations have been carried out so far concerning the irreversible adsorbates of 1,2,3-propanetriol formed at low pH. From the charge  $Q_{\text{ox}}$  involved in the direct oxidation in combination with the  $n_{\text{ox}}$  value of 2e/ $\text{CO}_2$  a coverage of 0.53 CO molecules per platinum atom can be calculated, using the relation

$$\theta = \frac{Q_{\text{ox}}}{Q_{\text{H}}^{\circ} n_{\text{ox}}}$$

where  $Q_{\text{H}}^{\circ}$  is the charge involved in the hydrogen desorption in blank sulfuric acid electrolyte. This CO coverage is nearly equal to that found for 1,2-ethanediol<sup>4</sup> but lower than that after adsorption of pure CO at 0.4 V, which is established from cyclic voltammetry to be 0.7. The lower coverage with respect to adsorption of CO can be ascribed to the ensemble effect: above a certain coverage the ensembles of uncovered platinum atoms will become too small for dissociative adsorption. The integrated CO absorption measured with FTIRS, as shown in Table 3, is in agreement with the CO coverage calculated from the oxidation charge in the cyclic voltammogram. Whereas oxidation charges give CO coverages of 0.53 and 0.7 for 1,2,3-propanetriol and pure CO, FTIRS gives integrated CO absorbances of 0.69 and 1.

**1-Propanol, 1,3-Propanediol, and 1-Butanol—Qualitative Consideration.** Our data indicate for these alcohol compounds that decarbonylation is the dominant pathway in the formation of irreversible adsorbates. As shown in Table 3, FTIRS demonstrates that considerable amounts of  $\text{CO}_{\text{ads}}$  are formed, and this indicates that C–C dissociation occurs according to



It is clear that CO cannot be the only product, since not enough OH groups are present on these alcohol compounds to enable full conversion to  $\text{CO}_{\text{ads}}$ , as was observed for 1,2,3-propanetriol and 1,2-ethanediol.<sup>4</sup> The  $n_{\text{ox}}$  values in Table 2 for 1-propanol, 1,3-propanediol, and 1-butanol show indeed that CO is not the only adsorbate, since  $n_{\text{ox}}$  values higher than two are indicative of adsorbates other than CO. For instance, a  $\text{CH}_x$  group is characterized by an  $n_{\text{ox}}$  value of  $(4 + x)$  e/ $\text{CO}_2$ . Note that the  $\text{R}_{\text{ads}}$  species can undergo further oxidation reactions, and we will discuss the composition of these adspecies below. The mechanism is likely to proceed via initial adsorption via the lone pair of the oxygen atom, followed by oxidation of the hydroxyl proton and C–H protons and subsequently C–C dissociation to give CO.

Our DEMS measurements show that, in contrast with some earlier reports,<sup>2,8,9</sup> the decarbonylation mechanism is the only pathway active in the formation of irreversible adsorbates. The products formed in the adsorbate reduction give important information on the composition of the coadsorbates that are formed next to CO. In the case of 1-propanol, ethane was observed as by far the major reduction product, while hardly any propane was found. This demonstrates that C–C(O) dissociative adsorption must be the dominant adsorption pathway, since non-dissociative adsorption would lead to a considerable

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amount of propane in the reduction. The absence of methane shows that these C<sub>2</sub> adspecies do not dissociate further into C<sub>1</sub> species. The same conclusion also holds for the other compounds: 1,3-propanediol and 1-butanol. In the case of 1,3-propanediol, methane was observed as the only reduction product, indicating that CO and CH<sub>x</sub> adspecies have been formed during adsorption. For 1-butanol, the major products found in the reduction are propene and propane, demonstrating that 1-butanol is transformed into CO<sub>ads</sub> and a C<sub>3</sub> species.

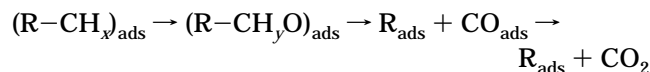
Our finding for 1-propanol contrasts with the results of Pastor et al., who found ethane and propane in the ratio of 3.5:1,<sup>8</sup> whereas we find 50:1. This difference might be connected with the type of electrode used: whereas we used platinized platinum grids, Pastor et al. used electrodes that were obtained by deposition of a DODUCO Pt lacquer suspension on Teflon. It is possible that the distribution of crystal faces is different from that of our electrodes. They further concluded on the basis of FTIRS that dissociation of the C–C(O) bond can occur not only at the adsorption potential but also during reduction of the adsorbate, resulting in the formation of CO and ethane. However, we established that the increase of the integrated CO absorption that was observed after reduction of the adsorbate originated from the reduction of CO<sub>2</sub> to CO<sub>ads</sub> that was present in the thin electrolyte layer. A control experiment in which the reduction of the adsorbate was carried out while the electrode was pulled back from the CaF<sub>2</sub> window proved that the CO coverage does not increase during reduction of the 1-propanol adsorbates. These experiments clearly show that the mechanism in which the C–C(O) bond is broken during reduction of the adsorbate is not active in our situation. Therefore we can safely conclude that the products formed during adsorbate reduction for the various compounds can be assigned to dissociated species that were already present after adsorption.

It is important to note that there is always a fraction of the adsorbate, apart from CO, that is not subject to hydrogenation. It is difficult to obtain information on the composition of these species. We can establish though that it concerns C<sub>x</sub>H<sub>y</sub> species, as indicated by the broad oxidation wave in the oxide region, which is atypical for adsorbed CO. In addition, the *n*<sub>ox</sub> values exceeding 2 e/CO<sub>2</sub> for the 'indirect' oxidation, shown in Table 2, confirm that hydrocarbon adspecies remain present after reduction, since they are characterized by *n*<sub>ox</sub> values higher than 4 e/CO<sub>2</sub>. Probably graphite formation causes the insensitivity toward hydrogenation of these adspecies.

The few data that have been reported on the adsorption of primary and secondary alcohols on platinum in ultrahigh vacuum show that the adsorption mechanisms in ultrahigh vacuum and in the liquid phase are quite similar. Thermal desorption spectrometry (TDS) demonstrated for ethanol, 1-propanol, and 1-butanol that decarbonylation occurs at temperatures below room temperature on Pt(111),<sup>29</sup> Pd(111),<sup>30</sup> and Pd(110).<sup>31</sup> No evidence was found for nondissociative adsorption or splitting of the C–O bond. In the case of ethanol, CH<sub>x</sub> species are formed in addition to CO.<sup>29–31</sup> No clear conclusions could be drawn on the composition of the carbon residue that was formed from 1-propanol and 1-butanol. On Pd(111) ethylene was formed during TDS of 1-propanol adsorbates, indicating that C<sub>2</sub> species are formed in the decarbonylation.<sup>30</sup> The decarbonylation mechanism was also found to be active

at room temperature for 2-propen-1-ol,<sup>32</sup> for 2-propen-1-al,<sup>32</sup> and even for a cyclic compound such as furan on Pd(111).<sup>33</sup>

In general, our results show that C–C bond breaking only occurs when an oxygen atom is present at the C<sub>1</sub> position, so that CO formation can occur. The C<sub>2</sub> and C<sub>3</sub> species that are formed from 1-propanol and 1-butanol, respectively, do not display C–C bond breaking, due to the absence of an oxygen atom at the C<sub>1</sub> position. We conclude from this that the high adsorption energy of CO is the driving force for the dissociative adsorption. In our opinion, these observations can be generalized; the oxidation of hydrocarbons to carbon dioxide on platinum at room temperature proceeds via oxygen incorporation on the C<sub>1</sub> position of the hydrocarbon, followed by decarbonylation and further oxidation to CO<sub>2</sub> according to



**1-Propanol, 1,3-Propanediol, and 1-Butanol—Quantitative Analysis.** Quantitative analysis of the data obtained with DEMS and cyclic voltammetry gives valuable information on the (i) adsorbate coverages and (ii) composition of the coadsorbed C<sub>x</sub>H<sub>y</sub> species. Analysis of the charge *Q*<sub>ox</sub> involved in the oxidation of the adsorption products, given in Table 1, in combination with the *n*<sub>ox</sub> value obtained with DEMS, given in Table 2, gives the coverage of C atoms, present in the form of CO or C<sub>x</sub>H<sub>y</sub> adsorbates according to  $\theta = Q_{ox}/(n_{ox} Q_H^\circ)$ , where *Q*<sub>H</sub><sup>°</sup> is the charge involved in hydrogen desorption in blank electrolyte. For 1-propanol, 1,3-propanediol, 1-butanol, and ethene, respectively,  $\theta$  values of 0.75, 0.67, 0.82, and 0.92 were found. These coverages are considerably higher than the coverages obtained for ethanol,<sup>4</sup> 1,2-ethanediol,<sup>4</sup> and 1,2,3-propanetriol; 0.44, 0.52, and 0.53, respectively.

Analysis of the DEMS data can give the *n*<sub>ox</sub> values of the C<sub>x</sub>H<sub>y</sub> species formed for the various alcohol compounds, providing information on their composition. We can infer from the experimental *n*<sub>ox</sub> value for 1,3-propanediol that the CH<sub>x</sub> group initially formed in the adsorption is fractionally oxidized to CO, as was also found for ethanol.<sup>4</sup> The *n*<sub>ox</sub> value of the C<sub>1</sub> fragment can be derived from the *n*<sub>ox</sub> value of 2.7 found with DEMS, assuming that the transformation of the two OH moieties to CO<sub>ads</sub> is complete. A value of 3.5 e/CO<sub>2</sub> is found using the relation  $\frac{2}{3}n_{ox}^{CO} + \frac{1}{3}n_{ox}^{C1} = n_{ox}^{DEMS}$ , with *n*<sub>ox</sub><sup>CO</sup> = 2 and *n*<sub>ox</sub><sup>DEMS</sup> = 2.7. An *n*<sub>ox</sub> value lower than 4 can only be caused by COH or CO adspecies, of which the former is highly unlikely, since it was absent for adsorbates from 1,2-ethanediol<sup>4</sup> and 1,2,3-propanetriol. Thus it can be concluded that the C<sub>1</sub> species is partially oxidized to CO, a reaction that was also observed for ethanol, although to a somewhat higher extent.<sup>4</sup> Recent FTIRS experiments<sup>34</sup> using <sup>13</sup>CH<sub>3</sub>CH<sub>2</sub>OH demonstrated that the formation of <sup>13</sup>CO<sub>ads</sub> started at 0 V vs SCE, confirming our conclusions. Ultrahigh vacuum experiments have shown that the reaction between CH and CH<sub>2</sub> species with adsorbed oxygen atoms on Pt(111) occurs at temperatures above 200 K.<sup>35</sup>

The *n*<sub>ox</sub> value of 3.5 found for 1-propanol can be divided into the separate contributions of the CO and C<sub>2</sub> species that are formed out of a single 1-propanol molecule. Since 1 and 2 CO<sub>2</sub> molecules are formed in the oxidation of the

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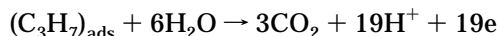
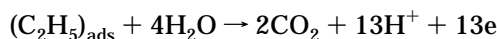
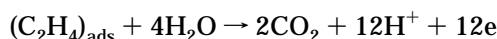
CO and C<sub>2</sub> groups, respectively, the contribution of the C<sub>2</sub> group to the  $n_{\text{ox}}$  value of 1-propanol can be obtained using the relation  $1/3 n_{\text{ox}}^{\text{CO}} + 2/3 n_{\text{ox}}^{\text{C}_2} = n_{\text{ox}}^{\text{DEMS}}$ , with  $n_{\text{ox}}^{\text{CO}} = 2$  and  $n_{\text{ox}}^{\text{DEMS}} = 3.5$ . In this way  $n_{\text{ox}} = 4.3 \text{ e/CO}_2$  is calculated for the C<sub>2</sub> group.

The  $n_{\text{ox}}$  value for the C<sub>3</sub> adsorbate formed from 1-butanol can be calculated in the same way. Using the relation  $1/4 n_{\text{ox}}^{\text{CO}} + 1/4 n_{\text{ox}}^{\text{C}_3} = n_{\text{ox}}^{\text{DEMS}}$ , with  $n_{\text{ox}}^{\text{CO}} = 2$  and  $n_{\text{ox}}^{\text{DEMS}} = 3.7 \text{ e/CO}_2$ , gives  $4.3 \text{ e/CO}_2$  for the C<sub>3</sub> group.

The  $n_{\text{ox}}$  values for the C<sub>2</sub> and C<sub>3</sub> adspecies from 1-propanol and 1-butanol, respectively, are very close to the  $n_{\text{ox}}$  value of 4.0 e/CO<sub>2</sub> found for ethene. This shows that the nonCO adspecies formed from both propanol and butanol have a similar composition to that of the ethene adsorbates. The  $n_{\text{ox}}$  values, being close to 4 e/CO<sub>2</sub>, are characteristic for completely dehydrogenated carbon according to



In the case that these adspecies would have retained all hydrogen atoms, it would have been found that  $n_{\text{ox}} = 6$  for ethene,  $n_{\text{ox}} = 6.5$  for ethyl, and  $n_{\text{ox}} = 6.3$  for propyl adspecies according to



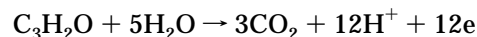
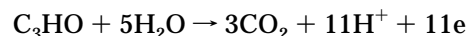
Sun et al.<sup>7</sup> and Pastor et al.<sup>8</sup> suggested on the basis of the observation of C–H stretch vibrations just below 3000 cm<sup>−1</sup> with FTIRS that C<sub>2</sub>H<sub>6,ads</sub> and C<sub>2</sub>H<sub>5,ads</sub>, respectively, were formed in the adsorption of 1-propanol. In our experiments we did not observe any C–H vibrations with FTIRS. However, note that on some occasions three uncompensated C–H bands below 3000 cm<sup>−1</sup> appeared in the spectra, that originate from adsorbed hydrocarbons on the mirrors inside the FTIR spectrometer. These vibrations are clearly visible in a single-beam spectrum recorded in the absence of alcohol adsorbates, which indicates that they are of considerable intensity. These bands appear in the spectrum when the baseline has changed as a result of the transport of solvated ions through the thin layer, which accompanies any electrochemical reaction. The mechanical instability of the thin layer also readily causes changes in the base line, resulting in the appearance of the C–H bands. This phenomenon makes the assignment of observed C–H bands in the literature tentative. In agreement with the absence of C–H bands in the IR spectra, our DEMS and voltammetry results show that the hydrocarbon species are highly dehydrogenated and C<sub>2</sub>H<sub>6,ads</sub> and C<sub>2</sub>H<sub>5,ads</sub> species are therefore unlikely in our case. That 1-propanol is dehydrogenated to a large extent can also be inferred from the ratio  $Q_{\text{ads}}/Q_{\text{ox}}$  of the charges involved in the adsorption and oxidation given in previous reports,<sup>10,13</sup> although the authors come to a somewhat different conclusion on the products of the adsorption reaction.

We must consider the possibility that C<sub>2</sub> and C<sub>3</sub> groups initially formed in the adsorption of 1-propanol, 1-butanol, and ethene incorporate some oxygen. It has been shown with isotope experiments that 25% of the C atoms reacted with oxygen after adsorption of ethene at 0.5 V vs RHE on Pt(110).<sup>14</sup> However, we performed the ethene adsorption at 0.4 V, and we therefore expect a much lower degree of oxygen incorporation. In general, the uptake of oxygen atoms is strongly potential dependent, as for instance with

the oxidation of adsorbed CO that occurs above a certain threshold potential. It is likely that the adsorption potential of 0.5 V used by Schmiemann et al.<sup>14</sup> is at the threshold potential for oxygen incorporation. In the case that oxygen uptake occurs in our experiments, dissociation of the molecule can occur to form CO and CH<sub>x</sub>, just as we found for ethanol.<sup>4</sup> Our experiments reported here show that such a dissociation reaction can occur even at high coverages, and therefore we do not expect C–C(O) species as proposed by Schmiemann et al. to be stable. Indeed, we found a small amount of CO with FTIRS and a small CO-like peak in the 'indirect' oxidation of ethene in Figure 6. From the cyclic voltammogram, the CO coverage can be estimated to be 0.08, which means that  $n_{\text{ox}} = 4.0$  is actually an average value for a mixed adlayer of C<sub>2</sub> species and CO. The contribution of the C<sub>2</sub> can then be calculated to be 4.2 e/CO<sub>2</sub>, which means that the adsorbate consists mainly of highly dehydrogenated species like C<sub>2</sub> and C<sub>2</sub>H, in addition to a small amount of CO.

**2-Propanol.** The formation of propane and propene as the only products in the electroreduction of 2-propanol adsorbate demonstrates that no substantial C–C bond cleavage occurs. However, a small amount of CO was observed with FTIRS. From the charge that is involved in the small oxidation peak at 0.65 V in the cyclic voltammogram the CO coverage is approximately 0.04. This CO coverage is similar to the CO coverage obtained with ethene. Probably this small amount of CO is formed as a result of oxygen incorporation at the C<sub>1</sub> position of the adsorbate, followed by C–C bond dissociation. From the oxidation charge and the  $n_{\text{ox}}$  value of 3.8 it follows that the coverage of C atoms is 0.48. The low CO coverage shows that additional oxygen incorporation into the 2-propanol residue is only minor, since the C atom coverage of 0.48 is low enough to enable decarbonylation. In this context, it should be noted that the CO coverage for 1,2,3-propanetriol is 0.53. Since the incorporation of oxygen in 2-propanol is small, it is reasonable to assume that this will also hold for ethene.

It follows from the  $n_{\text{ox}}$  value of 3.8 for 2-propanol that the adsorbed residue is highly dehydrogenated. Since oxygen incorporation is believed to be small the  $n_{\text{ox}}$  value originates from species like C<sub>3</sub>HO with 3.7 e/CO<sub>2</sub> or C<sub>3</sub>H<sub>2</sub>O with 4 e/CO<sub>2</sub> according to



This result is in contrast with a previous report<sup>16</sup> that suggests on the basis of FTIRS that 2-propanol adsorbate consists of (CH<sub>3</sub>–C–CH<sub>3</sub>)<sub>ads</sub>, (CH<sub>3</sub>–CH–CH<sub>3</sub>)<sub>ads</sub>, (CH<sub>3</sub>–COH–CH<sub>3</sub>)<sub>ads</sub>, and (CH<sub>3</sub>–CO–CH<sub>3</sub>)<sub>ads</sub>. However, these adsorbates are not present in our situation, since they are characterized by much higher  $n_{\text{ox}}$  values of 6.0, 6.3, 5.7, and 5.3 e/CO<sub>2</sub>, respectively, than the experimentally found value of 3.8. A possible reason for this difference might be the type of electrode used; whereas we used platinized platinum, Pastor et al. used smooth platinum.<sup>16</sup> These electrodes might expose different crystal planes, thus causing a different reactivity.

In addition, it also follows from the reduction and oxidation charges given in Table 1 that the adsorbates of 2-propanol are highly dehydrogenated. The reduction of the adsorbate, which requires 98 μC/cm<sup>2</sup>, results in a decrease of the oxidation charge from 389 to 116 μC/cm<sup>2</sup>. We can conclude from this that for the reduction 98 μC/cm<sup>2</sup> is necessary while for the oxidation of the same adspecies to CO<sub>2</sub> 273 μC/cm<sup>2</sup> (=389–116) is required. Note



that for the proposed adsorbates<sup>16</sup> given above the ratio of the reduction and oxidation charge varies for the four species from 1:19 to 1:4, when complete conversion to propane and carbon dioxide is assumed in the reduction and oxidation, respectively. These ratios deviate considerably from the ratio of 1:2.8 found in our experiments.

Summarizing, we find for all compounds that the hydrocarbon species formed are highly dehydrogenated. UHV studies have shown that considerable dehydrogenation of hydrocarbon species can occur at room temperature. Adsorbed CH<sub>3</sub> species on Pt(111) are subject to dehydrogenation at temperatures above 230 K, and the C–H stretch vibration at 2885 cm<sup>-1</sup> in the IR spectrum has completely disappeared after increasing the temperature to 300 K,<sup>27–37</sup> indicative of considerable dehydrogenation. In accordance with this, complete dehydrogenation of adsorbed CH<sub>2</sub> species, formed from CH<sub>2</sub>Cl<sub>2</sub>, is observed on Pd(100) at 300 K.<sup>37</sup> In UHV adsorbed hydrogen formed during dehydrogenation desorbs in the temperature region between 280 and 350 K. This means that a significant amount of adsorbed hydrogen remains on the surface, enabling an equilibrium to establish itself. In the electrochemical experiments, dehydrogenation is accompanied by oxidation of hydrogen to protons. The energy involved in the oxidation might generate an extra driving force for dehydrogenation. Given these facts, it is not surprising that we find considerable dehydrogenation of adsorbed hydrocarbon species. This result might explain the absence of C–H vibrations in the IR spectra.

Finally, we should like to comment on the relevance of adsorbate studies to the electro-oxidation of alcohols. Leung and Weaver<sup>3</sup> have discussed the poisoning of alcohol electro-oxidation in relation to irreversible adspecies that are formed from the reactant alcohol itself. Since it was found with FTIRS that the electro-oxidation of the alcohol commences at the potential where adsorbed CO is oxidized, the authors concluded that CO was completely responsible for the poisoning of the reaction. They also noted that the inhibition is generally effective even though the initial CO coverage varies substantially with the alcohol compound. The poisoning effect of CO is well-known in the literature.

Our experiments have demonstrated that in the dissociative adsorption of primary alcohols and polyols hydrocarbon species are formed in addition to CO. The redox behavior of these hydrocarbon fragments differs

considerably from that of adsorbed CO, which is oxidized at relatively low potential in the double-layer region, while the hydrocarbon fragments are oxidized at potentials in the oxide region. The hydrocarbon fragments cause a decrease of the active platinum surface in the same way that CO does and contribute therefore considerably to poisoning. In fact for large primary alcohols, like propanol and butanol, the site coverage due to hydrocarbon fragments is probably larger than that for CO. In addition, the lower affinity of these fragments toward oxidation implies that higher potentials are necessary to remove these species. In fact, the necessary potentials are beyond the region where alcohol oxidation proceeds with maximal rate. The presence of these poisoning hydrocarbon fragments nicely explains the observation that even at low CO coverages effective poisoning occurs.<sup>3</sup>

It is well-known that the oxidation of secondary alcohols proceeds with a higher rate than those for most primary alcohols, and this has been ascribed to the absence of adsorbed CO on the surface during reaction.<sup>3</sup> However, our experiments show that irreversible adsorbates are formed from 2-propanol that are oxidized to CO<sub>2</sub> at potentials in the oxide region. These adspecies definitely cause poisoning of the electro-oxidation reaction. That the reaction rate is nevertheless higher than that for primary alcohols and polyols is in our view probably due to a higher fraction of accessible platinum sites in the case of 2-propanol.

## Conclusions

In this study on C<sub>3</sub> alcohols we have shown on the basis of FTIRS, DEMS, and cyclic voltammetry measurements that decarbonylation is by far the dominant pathway active in the formation of irreversible adsorbates from primary alcohols and polyols. In the case of 1,2,3-propanetriol the parent alcohol is completely dehydrogenated to adsorbed CO. The other primary alcohols studied here form in addition to CO a hydrocarbon adspecies that can be partially hydrogenated off the surface to form gaseous compounds. No further C–C bond breaking occurs in these hydrocarbon adspecies after adsorption. It was found for both 2-propanol and ethene that the carbon backbone remains intact upon adsorption. As for the primary alcohols we found that these adspecies are highly dehydrogenated. It was found for 2-propanol and ethene that a small amount of oxygen incorporation occurs on the C<sub>1</sub> position, followed by decarbonylation to form CO.

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