Characterization of Ethanol and 1,2-Ethanediol Adsorbates on Platinized Platinum with Fourier Transform Infrared Spectroscopy and Differential Electrochemical Mass Spectrometry

J. F. E. Gootzen,* W. Visscher, and J. A. R. van Veen

Department of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The irreversible adsorption of ethanol and 1,2-ethanediol on platinized platinum has been studied with Fourier transform IR spectroscopy (FTIRS) and differential electrochemical mass spectrometry (DEMS) in perchloric acid electrolyte. The adsorption was found to be dissociative for both ethanol and 1,2-ethanediol. During adsorption 1,2-ethanediol is completely dehydrogenated to adsorbed CO. For ethanol it was concluded that carbon species are formed in addition to adsorbed CO. Part of this residue is hydrogenated at low potential to methane.

Introduction

The electrochemical oxidations of 1,2-ethanediol and particularly ethanol on platinum are of considerable interest because of their role as model compounds for the study of the adsorption and electrooxidation behavior of organic species on platinum. Electrochemical studies can also provide useful information with respect to the platinum-catalyzed oxidation of alcohols with molecular oxygen in the liquid phase.

The electrooxidation of ethanol over platinum yields carbon dioxide, acetic acid, and acetaldehyde,[1−6] as was found with spectroscopic methods. Several studies have been conducted to elucidate the structure of the irreversibly adsorbed species that are present on platinum after removal of the ethanol solution. The results are rather contradictory and can be divided into three categories. (i) Dissociation of the carbon−carbon bond occurs during adsorption, leading to the formation of adsorbed CO. This was suggested on the basis of differential electrochemical mass spectrometry (DEMS)[7] and voltammetry.[8−11] (ii) Dissociative as well as nondissociative adsorption was proposed on the basis of electrochemical thermal desorption mass spectrometry (ECTDMS)[2] and Fourier transform infrared spectroscopy (FTIRS).[12,13] (iii) Only nondissociative adsorption occurs, leaving the carbon−carbon bond intact. This conclusion was based on DEMS measurements.[1]

The formation of adsorbed CO was also observed during bulk electrooxidation of ethanol with FTIR spectroscopy[3−6,14] and potential modulated reflectance spectroscopy.[15] Electrochemically modulated infrared spectroscopy (EMIRS)[16] data suggested that in the presence of bulk ethanol dissociative as well as non-dissociative adsorption occurs.

The electrooxidation of 1,2-ethanediol over platinum gives glycolic acid and carbon dioxide as bulk products in acid medium, as found with spectroscopic methods.[17] The formation of adsorbed CO in the presence of bulk 1,2-ethanediol has been observed with FTIRS[6,17] and electrochemically modulated infrared spectroscopy (EMIRS).[18]

It is remarkable that the possible presence of CH_x groups next to adsorbed CO has only been mentioned by a few authors.[7,9,15] In this paper we therefore investigate the irreversibly formed adsorbate of ethanol and 1,2-ethanediol with FTIR spectroscopy and DEMS to establish if adsorbed CH_x groups are formed by dissociative adsorption. Also some experiments with dichloromethane and ethane were conducted to study the possible formation of CH_x groups from these compounds.

Experimental Section

Infrared measurements were performed with a Biorad FTS 45A spectrometer, equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. All spectra were recorded with 4 cm^{-1} resolution.

The electrochemical cell, made of glass, was placed on top of the sample room and was equipped with a CaF$_2$ prism with 65° beveled edges, to obtain a high reflection angle. The electrode consisted of a platinum disk of 9 mm diameter attached to a copper screw, by which it is connected to the electrode holder consisting of a copper interior embedded in PTFE. The infrared beam is focused on the electrode by one flat and one ellipsoidal mirror, with which the optimal spot size could be obtained. A polarizer is placed in the sample room to obtain p-polarized light.

DEMS measurements were performed with a Leybold Quadruvac PGA 100 mass spectrometer. The experimental setup is similar to the one described previously.[19] The products were examined for CO$_2$ (CO$_2$$^+$; m/e = 44), CH$_4$ (CH$_3$$^+$; m/e = 15) and C$_2H_6$ (C$_2$H$_4$$^+$; m/e = 28).

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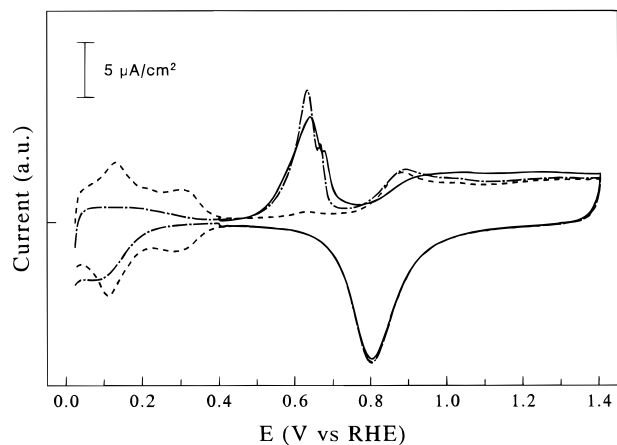(9) Cases, F.; Morallon, E.; Vázquez, J. L.; Perez, J. M.; Aldaz, A. *J. Electroanal. Chem.* **1993**, *350*, 267.
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Figure 1. Cyclic voltammogram of ethanol adsorbate: (─) 'direct' oxidation; (-··-) 'indirect' oxidation; (- - -) blank. Adsorption at 0.4 V in 1 mM ethanol. Electrolyte 0.5 M HClO₄. Scan rate 5 mV/s. Real area 177 cm² .
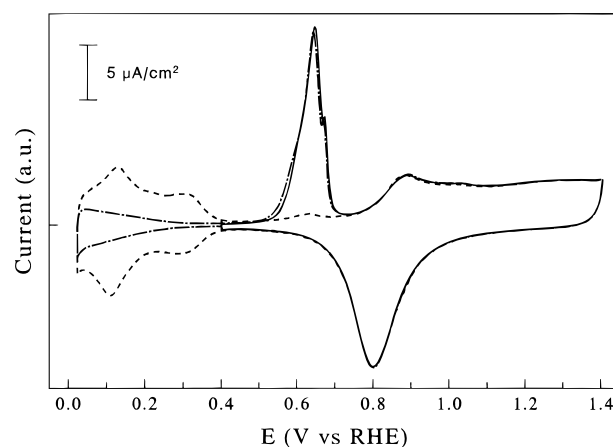

Figure 2. Cyclic voltammogram of 1,2-ethanediol adsorbate; (─) 'direct' oxidation; (-··-) 'indirect' oxidation; (- - -) blank. Adsorption at 0.4 V in 1 mM 1,2-ethanediol. Electrolyte 0.5 M HClO₄. Scan rate 5 mV/s. Real area 177 cm².

Electrochemical measurements were performed with an Autolab PGSTAT 20 computer-controlled potentiostat. A Hg/Hg₂SO₄ electrode was used as a reference electrode. All potentials will be referred to the reversible hydrogen electrode (RHE). All measurements were performed with platinized platinum that was prepared by electrodeposition in 0.05 M H_2PtCl_6 + 0.01 M HCl on smooth platinum. A deposition current of 10 mA/cm² was used on a substrate of 2.5 cm². Before deposition the substrate was cleaned in a gas—oxygen flame at 1000 °C. Platinized platinum was chosen, since the high area enables accurate assessment of both the charges involved in redox processes and the amount of product detected with the mass spectrometer. The electrode area was determined from the charge involved in the oxidation of the adsorbed hydrogen of a cyclic voltammogram obtained in 0.5 M HClO₄.

Different electrodes were used for DEMS, FTIRS, and cyclic voltammetry, as indicated in the text. Before each measurement 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 HClO₄ was used, and for cyclic voltammetry and the DEMS measurements 0.5 M HClO₄ was used. Oxygen was removed from the electrolyte with argon.

Adsorption was carried out at 0.4 V for 10 min in ethanol (Merck p.a.) or 1,2-ethanediol (Merck p.a.) solutions. In the case of dichloromethane (Merck p.a.) 100 μL was added to the blank electrolyte. Ethane (Hoek Loos, purity 2.6) and CO (Hoek Loos, purity 4.7) were adsorbed at 0.4 V for 10 min by bubbling through the solution. After adsorption the electrolyte was replaced by blank electrolyte, while the electrode was kept at the adsorption potential.

Results

Cyclic Voltammetry. A cyclic voltammogram of the ethanol adsorbate, formed at 0.40 V from 1 mM electrolyte, is shown in Figure 1. The dashed curve represents the blank electrolyte. If the anodic scan is started at the adsorption potential, referred to as 'direct' oxidation, a peak is present at 0.641 V with a shoulder at 0.679 V. This peak resembles the oxidation peak of adsorbed CO.[20] A broad wave is present in the oxide region that is not terminated at the reverse potential. The amount of charge associated with oxidation of adsorbate in a second cycle is only very small. If the scan is started in the cathodic direction at the adsorption potential, a reduction wave is observed in the hydrogen region at potentials below 0.20 V. The subsequent anodic scan displays an oxidation peak that has narrowed and shifted to 0.633 V with a shoulder at 0.667 V. The broad oxidation wave in the oxide region

has decreased. This procedure is referred to as 'indirect' oxidation. The total oxidation charge, including the oxidation peak at low potential as well as the broad wave at higher potential, has decreased from 229 μC/cm² for the 'direct' oxidation to 186 μC/cm² for 'indirect' oxidation. The platinum area was established from the oxidation charge of adsorbed hydrogen in a cyclic voltammogram obtained in blank electrolyte.
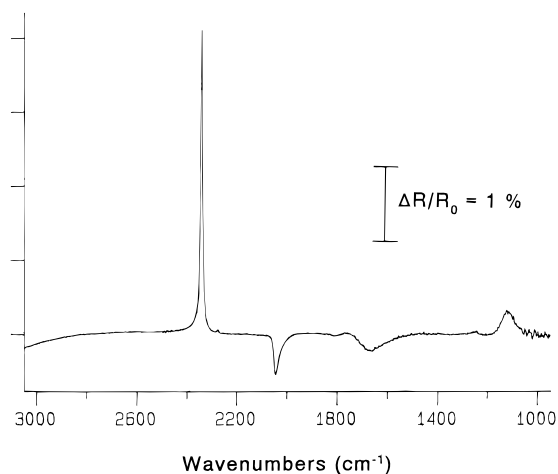
The charge involved in the reduction, Q_{red}, can be determined by subtracting the charge involved in the anodic part of the scan below 0.40 V from the charge involved in the cathodic part of the scan below 0.40 V. The cathodic part of the scan consists of both reduction of adsorbate and formation of adsorbed hydrogen from solution protons on uncovered platinum sites. The anodic part of the scan only consists of oxidation of adsorbed hydrogen. Subtracting both values gives the charge involved in reduction; $Q_{red} = 50$ μC/cm². The charge involved in the oxidation of adsorbed hydrogen has decreased to 20% of the value in the voltammogram of the blank electrolyte. This means that after reduction below 0.20 V still 80% of the platinum sites are covered with ethanol adsorbate. Note that the hydrogen liberated during adsorption by C—H bond breaking is immediately oxidized to H⁺ at the adsorption potential of 0.4 V and is thus not involved in the reactions described here.

The voltammogram of 1,2-ethanediol adsorbate formed at 0.4 V from 1 mM 1,2-ethanediol shows only an oxidation wave at 0.643 V with a shoulder at 0.670 V, as shown in Figure 2. Again the anodic peak resembles the oxidation of adsorbed CO, but it is less broad than in the case of ethanol. In contrast with ethanol no reduction can be observed at low potential and no broad oxidation wave is present at high potential. The total oxidation charge is 218 μC/cm², and from the anodic part of the scan below 0.40 V it follows that 87% of the platinum sites are covered with 1,2-ethanediol adsorbate.
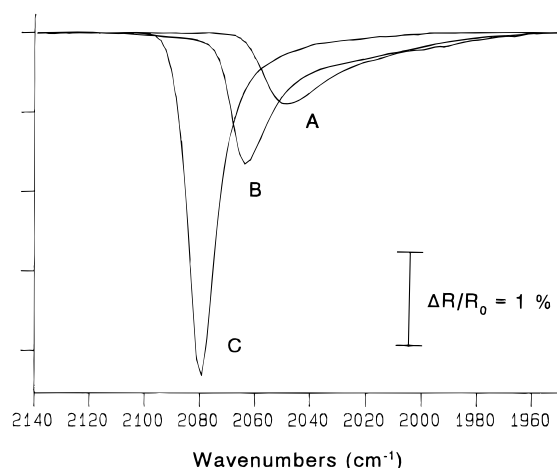
IR Experiments. Infrared spectra were obtained by subtracting the single-beam spectra measured before (R_0) and after (R_1) oxidation of the adsorbate. The first single-beam spectrum was obtained at the adsorption potential; the second was obtained at a potential of 0.75 V or at the adsorption potential after an excursion to 1.4 V. The IR spectrum of the ethanol adsorbate is shown in Figure 3 and is given as $\Delta R/R_0$ ($\Delta R = R_0 - R_1$). Besides the positive-going ClO₄⁻ vibration at 1120 cm⁻¹,[21] a negative-going

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Figure 3. Infrared spectrum of ethanol adsorbate, obtained after adsorption at 0.4 V in 1 mM ethanol. Electrolyte 0.1 M $HClO_4$. Resolution 4 cm^{-1}. Reference potential 0.4 V after potential excursion to 1.4 V.

Figure 4. CO vibrations obtained after adsorption of 1 mM ethanol (A), 1 mM 1,2-ethanediol (B), and CO (C) in 0.1 M $HClO_4$. Resolution 4 cm^{-1}. Reference potential 0.75 V.

CO vibration at 2044 cm^{-1} [22] and a positive-going band of CO_2 at 2344 cm^{-1} are observed. The negative-going band at 1650 cm^{-1} is due to an uncompensated H_2O bending mode. Upon magnification of the spectrum a small band is observed at 1805 cm^{-1}, which can be assigned to bridge bonded CO.[22] No C-H bands were observed within the detection limit of 0.01%T in the C−H stretch region.

The IR spectrum of the 1,2-ethanediol adsorbate is virtually the same as those for the ethanol adsorbates. Figure 4 compares the spectra of adsorbed CO as obtained in the case of ethanol, 1,2-ethanediol, and gaseous CO. For both alcohols the amount of adsorbed CO formed during adsorption is lower than that for gaseous CO. Concurrently the vibrations are shifted to lower wavenumbers, as expected for lower coverages. The vibration frequency and integrated absorbance data are given in Table 1. The data suggest a considerable amount of adsorbed CO formed for both alcohols, with 1,2-ethanediol generating a higher amount than ethanol. The increase of the alcohol concentration from 1 mM to 1 M results in a small shift of the vibration frequency to higher wavenumbers. The small shift shows that the CO coverage increases only to a small extent in going from 1 mM to 1

Table 1. Vibration Frequencies and Integrated Absorbance of CO Obtained after the Adsorption of Ethanol, 1,2-Ethanediol, and CO[a]

	frequency (cm^{-1})		integrated Absorbance (au)
	1 mM	1 M	1 mM
ethanol	2044	2048	0.43
1,2-ethanediol	2054	2060	0.64
CO	2080	2080	1

[a] The absorbance of CO is taken as unity.

M. It has indeed been found that at a concentration of 1 mM ethanol a nearly maximal adsorbate coverage is obtained.[23]

The calculation of the CO coverage from the integrated absorbance is admittedly difficult, since it is known from FTIRS studies in ultrahigh vacuum on single crystals[24−28] that the integrated absorbance is not linearly related to the CO coverage. The relation between the integrated absorbance and the CO coverage for polycrystalline platinum would have to be established in separate experiments. Moreover, it is uncertain whether coadsorbates are present in the case of ethanol and 1,2-ethanediol that might have some influence on the vibrational properties of CO. Nevertheless we feel that it is possible to obtain the CO coverage with IR spectroscopy by approximation.

The formation of the adsorbed species from 1 M ethanol was studied in situ with FTIRS by raising the electrode potential from 0.05 to 0.30 V and to 0.40 V, recording a spectrum at each potential. At 0.05 V no chemisorption of ethanol occurs, as shown by the absence of an anodic current when the ethanol solution is contacted with the platinum electrode; hence, the spectrum recorded at 0.05 V can be used as a reference spectrum. The results are shown in Figure 5. At 0.30 V adsorption of ethanol occurs, as indicated by the CO vibrations at 2040 cm^{-1} from linear CO and at 1845 cm^{-1} from bridge bonded CO.[22] No other positive-going bands are observed. At 2984 cm^{-1} a negative-going C−H band[4] is observed, indicative of the disappearance of ethanol from the solution.

At 0.40 V the vibration at 2053 cm^{-1} implies further formation of linear CO. The bands that appear at 1717, 1395, and 1285 cm^{-1} are indicative of acetic acid formation.[4] Note that the acetic acid was accumulated in the thin layer during 5 min, the time that was required for the adsorption of ethanol. At 0.40 V a positive-going band at 2343 cm^{-1} is observed that demonstrates the formation of CO_2. Again the disappearance of a C−H vibration at 2984 cm^{-1} is observed.

Attempts to observe the hydrogenation products from the ethanol adsorbate formed at potentials below 0.20 V did not succeed; no C−H vibrations or other vibrations could be found within the detection limit of 0.01%T, probably due to the low concentration of hydrogenation products in the thin layer and a low absorptivity of the C−H bands.

Differential Electrochemical Mass Spectrometry (DEMS). Figure 6 shows the mass signals of CO_2 for the oxidation and of CH_4 for the reduction of ethanol adsorbate. When 'indirect' oxidation is performed, a small amount of methane is detected at potentials below 0.25 V. No ethane

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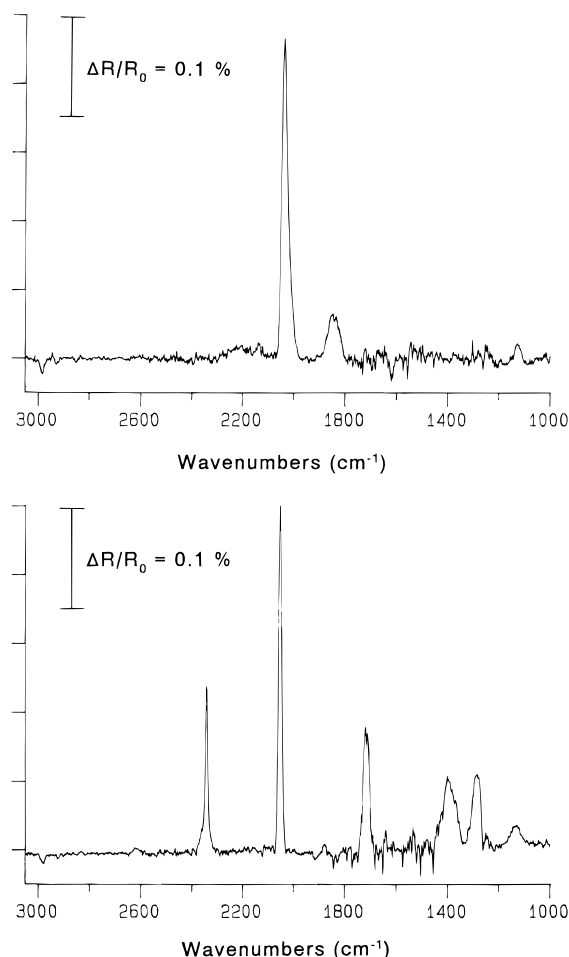(23) Bruijn, de F. A.; Kuster, B. F. M.; Marin, G. B. Submitted to *J. Catal.*

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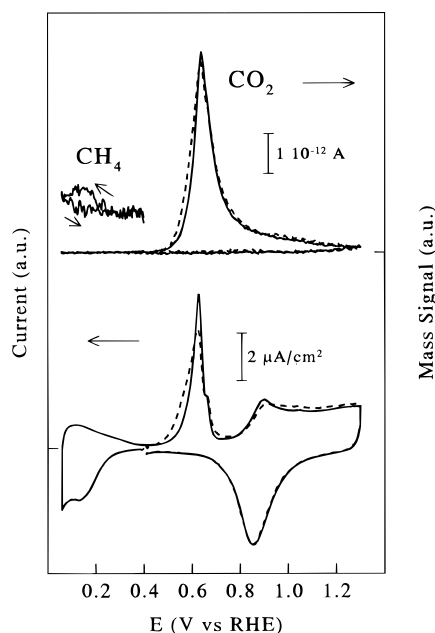(25) Crossley, A.; King, D. A. *Surf. Sci.* **1980**, *95*, 131.

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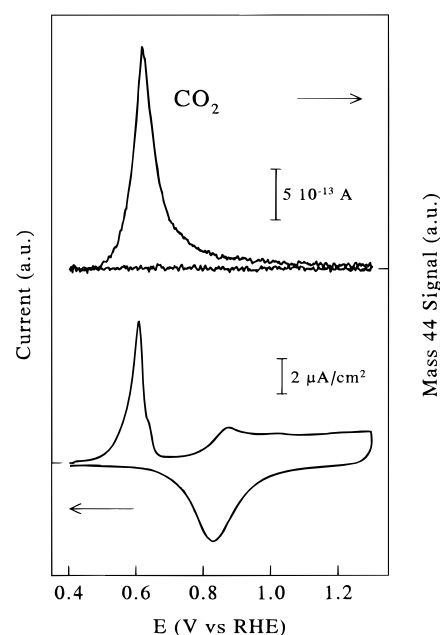
Figure 5. IR spectra obtained at 0.3 V (top spectrum) and 0.4 V (bottom spectrum) in 1 M ethanol. Resolution 4 cm^{-1}. Reference potential 0.05 V.

Figure 6. DEMS measurement obtained after adsorption at 0.4 V in 1 mM ethanol. Electrolyte 0.5 M HClO$_4$. 'Direct' (- - -) and 'indirect' oxidation (—). Scan rate 2 mV/s. $m/e = 44$ (CO$_2$). $m/e = 15$ (CH$_4$). Real area 79 cm^2.

could be detected. The amount of carbon dioxide formed in the 'indirect' oxidation is somewhat lower than that in the 'direct' oxidation. The number of electrons, n_{ox}, liberated per formed CO$_2$ molecule can be calculated from

Figure 7. DEMS measurement obtained after adsorption at 0.4 V in 1 mM 1,2-ethanediol. Electrolyte 0.5 M HClO$_4$. Scan rate 2 mV/s. $m/e = 44$ (CO$_2$). Real area 79 cm^2.

the DEMS measurements. This requires calibration of the mass spectrometer for CO$_2$; this is carried out by measuring the oxidation of adsorbed CO to CO$_2$ in a reference experiment. This yields the calibration factor K_{CO}

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

where Q_{ox} is the coulometric charge involved in the oxidation of CO to CO$_2$ and Q_{mass} represents the integrated mass current $\int i_{mass}\,dt$. The n_{ox} value for ethanol can then be obtained from the value Q_{ox}/Q_{mass} measured for the alcohol oxidation according to
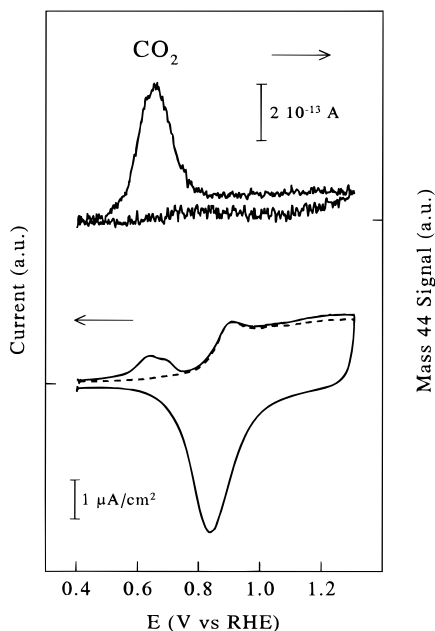
$$n_{ox} = \left(\frac{Q_{ox}}{Q_{mass}}\right)_{ethanol}\frac{1}{K_{CO}}n_{ox}^{CO}$$

with $n_{ox}^{CO} = 2$ electrons per CO$_2$ molecule. The n_{ox} values were found to be 2.5 for the 'direct' oxidation of the ethanol adsorbate and 2.2 for the 'indirect' oxidation. The margin of error of these n_{ox} values is estimated to be 0.1.
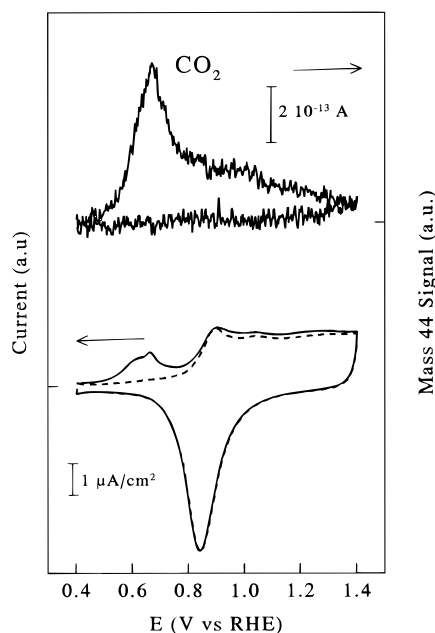
Figure 7 shows the DEMS results for adsorbed 1,2-ethanediol, which generates a higher amount of carbon dioxide than adsorbed ethanol. A value of 2.1 electrons per CO$_2$ molecule was found. No hydrogenation products such as methane or ethane could be detected during the cathodic scan.

DEMS results for the irreversible adsorbates of dichloromethane and ethane are shown in Figures 8 and 9. Because of the low solubility of both dichloromethane and ethane only low adsorbate coverages were found. The n_{ox} values for the dichloromethane and ethane adsorbates were found to be respectively 3.2 and 3.3 electrons per CO$_2$ molecule.

Coulometry. The charge Q_{ads}, liberated during the adsorption, was determined at 0.30 V with coulometry, since infrared spectroscopy showed that no bulk oxidation products are formed at that potential. Adsorption was carried out in solutions of 1 mM ethanol or 1,2-ethanediol for 10 min. After adsorption the total charge released during direct oxidation of the adsorbate Q_{ox} is determined

Figure 8. DEMS measurement obtained after adsorption of dichloromethane in 0.5 M $HClO_4$. 'Direct' oxidation (—) and blank (- - -). Scan rate 2 mV/s. $m/e = 44$ (CO_2). Real area 79 cm^2.
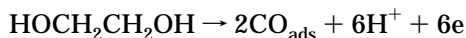

Figure 9. DEMS measurement obtained after adsorption of ethane in 0.5 M $HClO_4$. 'Direct' oxidation (—) and blank (- - -). Scan rate 2 mV/s. $m/e = 44$ (CO_2). Real area 79 cm^2.
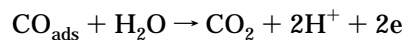
in a cyclic voltammogram. The ratio of the adsorption charge and the total oxidation charge for 'direct' oxidation Q_{ads}/Q_{ox} was 1.3 for ethanol and 1.5 for 1,2-ethanediol.

Discussion

1,2-Ethanediol. The observation of substantial amounts of adsorbed carbon monoxide with IR spectroscopy for 1,2-ethanediol indicates that this molecule adsorbs dissociatively on platinized platinum. The ratio Q_{ads}/Q_{ox} of 1.5 and the n_{ox} value of 2.1 electrons per CO_2 measured with DEMS clearly show that adsorbed CO is the only irreversible adsorbate that is formed according to

$$HOCH_2CH_2OH \rightarrow 2CO_{ads} + 6H^+ + 6e$$

The adsorbed carbon monoxide is oxidized at higher potential according to

$$CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e$$

This conclusion is in agreement with previous reports for 1,2-ethanediol that observed CO in the presence of 1,2-ethanediol in solution.[6,17,18] However, no investigations have been carried out so far concerning the irreversible adsorbate in acid electrolyte.

From the oxidation charge Q_{ox} in combination with n_{ox} = 2.1 a coverage of 0.52 CO molecules per platinum atom can be calculated using the equation

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

where Q_H° is the charge involved in the oxidation of adsorbed hydrogen in a voltammogram obtained in 0.5 M $HClO_4$. The integrated CO absorbances for 1,2-ethanediol and CO data in Table 1 are in agreement with the calculated CO coverage of 0.52 for 1,2-ethanediol, given that the CO coverage for gaseous CO was found to be 0.7 in separate experiments. In our view the lower CO coverage for 1,2-ethanediol is connected to spatial requirements for the dissociation of C−C and C−H and O−H bonds during adsorption. Energetically the breaking of the C−C, C−H, and O−H bonds forms apparently no obstacle on the route to CO formation. The formation of the platinum−carbon bond and the multiple C−O bond must be the driving force for this process.

We encounter a discrepancy between cyclic voltammetry and IR spectroscopy when the hydrogen blocking due to CO adsorbates from 1,2-ethanediol is analyzed in terms of linear and bridge bonded CO. The hydrogen adsorption has decreased 87% of its original value, and so, on average, every CO molecule blocks 1.67 (0.87/0.52) hydrogen sites. When it is assumed that linear adsorbed CO displaces one hydrogen atom and bridge bonded CO displaces two hydrogen atoms, the displacement ratio H/CO = 1.67 indicates that 67% of the adsorbed CO is bridge bonded and 33% is linearly bonded. However our IR experiments reveal only a small fraction of bridge bonded CO while the majority is linear bonded CO.

We must consider though that it has recently been shown for compressed CO adlayers on Pt(111) electrodes that in IR spectroscopy considerable intensity transfer from the multiple bonded CO vibration to the linear bonded CO vibration can occur due to dynamic dipole−dipole coupling.[29] The ratio of the integrated absorbances for linear and bridge bonded CO was a factor of four higher than expected on the basis of STM measurements. The phenomenon of intensity transfer has also been found in IR studies that were carried out in ultrahigh vacuum (UHV).[24] However, even when the different cross sections for linear and bridge bonded CO are included, our IR results are not in agreement with the cyclic voltammetry results that suggest that 67% is bridge bonded and 33% is linearly bonded CO. Such a discrepancy between the IR and voltammetry results has also been noted in the case of adsorbed CO formed after CO_2 reduction in phosphate buffer at pH = 6.8,[30] and the authors suggested the presence of IR insensitive species such as side-on adsorbed CO, a concept that has been introduced previously.[31]

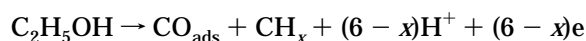(29) Villegas, I.; Weaver, M. J. *J. Chem. Phys.* **1994**, *101*, 1648.
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Another possible cause of error is the reconstruction of the surface, as reported for a Pt(110) single-crystal electrode.[32] The clean Pt(110)-(1×1) surface reconstructs partially into the Pt(110)-(2×1) plane, which has a higher density of surface atoms. For the hydrogen adsorption 148 μC/cm^2 is expected for the (1×1) surface and 222 μC/cm^2 is expected for the missing row reconstructed (2×1) surface. In the presence of adsorbed CO the surface reconstruction is lifted,[33] and this can lead to the situation that linear adsorbed CO apparently blocks 1.5 hydrogen atoms. However, in contrast with sulfuric acid, reconstruction is only observed to a minor degree in perchloric acid[32] and it can therefore not explain the discrepancy that we observed between voltammetry and IR spectroscopy.

Also the assumption that linear CO displaces one hydrogen atom and bridge bonded CO two hydrogen atoms might be somewhat oversimplified. Connected to this is the assumption that hydrogen atoms are adsorbed atop, although this has never been demonstrated. STM work has shown that even on Pt(111) CO adlayers can have a complicated structure like ($\sqrt{19}\times\sqrt{19}$)R23.4°-13CO with a CO coverage of 0.68.[29] Part of the CO molecules are bonded asymmetrically in between atop and bridging geometries. The behavior of asymmetrically bonded CO in IR spectroscopy is typically linear, but it might possibly prevent the adsorption of two hydrogen atoms.

Ethanol. In the case of ethanol all data point in the direction of dissociative adsorption as the only pathway leading to irreversible adsorbates, as was also found for 1,2-ethanediol. The substantial amount of CO observed with IR spectroscopy demonstrates that dissociative adsorption occurs. The integrated CO absorbance is only 30% lower than that for 1,2-ethanediol, where dissociative adsorption was demonstrated to be the only pathway, leading to $\theta_{CO} = 0.52$. The first step in dissociative ethanol adsorption is probably the partial dehydrogenation of the molecule followed by dissociation of the C–C bond, resulting in adsorbed CO and CH$_x$ according to

$$C_2H_5OH \rightarrow CO_{ads} + CH_x + (6-x)H^+ + (6-x)e$$
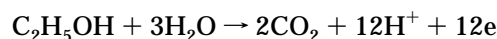
The formation of methane in the reduction of the adsorbate layer shows that CH$_x$ species are present after adsorption, and the absence of ethane formation strongly suggests that nondissociated C$_2$ species are not present. In a previous report a small amount of ethane was observed in addition to methane.[13] The n_{ox} value of 2.5 obtained for ethanol confirms that CO is not the only adsorbate and supports the claim that CH$_x$ groups are present. Our conclusion that dissociative adsorption is the only adsorption pathway leading to irreversible adsorbates is in agreement with those of several others,[7–11] as opposed to nondissociative adsorption as the only pathway.[1] A combination of dissociative and nondissociative adsorption has also been suggested.[2,12,13]

Only a few data are available on the adsorption of ethanol on platinum in ultrahigh vacuum. Thermal desorption spectrometry demonstrated that dissociation of adsorbed ethanol molecules in CO and CH$_x$ takes place at room temperature on Pt(111),[35] Pd(111),[36] and Pd(110).[37] The CH$_x$ group is dehydrogenated to surface carbon on

platinum, in contrast with palladium, where the CH$_x$ group desorbed as CH$_4$. These data show that the adsorption mechanism under ultrahigh vacuum conditions is very similar to that for adsorption in the liquid phase.

Before analyzing the n_{ox} value of 2.5 found with DEMS, we will show that the data found with coulometry are in good agreement with the DEMS results. FTIRS and DEMS have shown that CO$_2$ is the only product formed in the oxidation of the irreversible adsorbate layer, whereas IR spectroscopy has shown that at the adsorption potential of 0.3 V used in the coulometry experiments no acetic acid is formed. This means that the obtained adsorption charge Q_{ads} can be completely ascribed to adsorption. Therefore, the Q_{ads}/Q_{ox} ratio of 1.3 found with coulometry suggests that of the 12 electrons liberated in the total oxidation of an ethanol molecule to CO$_2$ according to
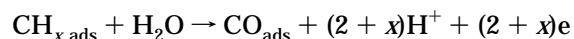
$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e$$

6.8 electrons are liberated during adsorption and 5.2 are liberated in the oxidation of the adsorbate. Since 2 CO$_2$ molecules are formed in the oxidation of a single ethanol adsorbate, 2.6 electrons per CO$_2$ molecule are released. This value is in good agreement with the value of 2.5 found with DEMS.

Quantitative analysis of the n_{ox} value of 2.5 found with DEMS shows that a follow-up oxidation from CH$_x$ to CO can occur after dissociation. Formation of equal amounts of CO and CH$_x$ during adsorption would result in n_{ox} values between 3 ($x = 0$) and 4.5 ($x = 3$), according to

$$n_{ox} = \frac{n_{ox,CO} + n_{ox,CH_x}}{2}$$

taking $n_{ox,CO} = 2$ and $n_{ox,CH_x} = (4 + x)$. Since no methane was observed during the adsorption, it must be concluded that the observed n_{ox} value of 2.5 does not originate from the removal of CH$_x$ species during adsorption but from a follow-up reaction of CH$_x$. This means that a fraction of the CH$_x$ species is oxidized to CO$_{ads}$; such a reaction mechanism has been proposed recently:[7]

$$CH_{x\ ads} + H_2O \rightarrow CO_{ads} + (2+x)H^+ + (2+x)e$$

The conclusion that CH$_x$ species can be oxidized to CO is supported by the DEMS data that we obtained for dichloromethane and ethane. The low n_{ox} values of 3.2 for dichloromethane and 3.3 for ethane can only be caused by the presence of adsorbates with low n_{ox} values like CO. The CH$_3$ group of ethanol and the CH$_2$ group from dichloromethane seem to behave quite similarly upon adsorption, as follows from a quantitative analysis of the n_{ox} number for ethanol. In the case of ethanol both the adsorbates formed from the CH$_3$ and CH$_2$OH groups contribute evenly to the n_{ox} value of 2.5, and both contributions can be calculated when it is assumed that the conversion of the CH$_2$OH group to CO$_{ads}$ is complete using

$$\frac{n_{ox,CH_3} + n_{ox,CH_2OH}}{2} = 2.5$$

It follows from this relation that, for the contribution of the adsorbate from the CH$_3$ group $n_{ox,CH_2OH} = 3.0$ electrons per formed CO$_2$ molecule. This number is close to the value of 3.2 found for the irreversible adsorbates from dichloromethane, demonstrating that the oxidation be-

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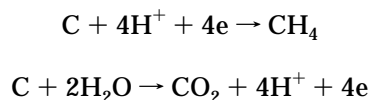havior of the CH_3 group of ethanol is similar to that of the CH_2 group from CH_2Cl_2.

Combining the n_{ox} value found with DEMS with the voltammetry data gives the total adsorbate coverage as well as possible CO and CH_x coverages. We will show that these data are in agreement with our IR data. It can be calculated from the oxidation charge Q_{ox} in combination with the n_{ox} value of 2.5 that the adsorbate coverage is 0.44 per platinum atom, using the relation $\theta = Q_{ox}/(n_{ox}Q_H°)$. This coverage is somewhat lower than that for 1,2-ethanediol, where 0.52 CO molecules per platinum atom were found. The exact adsorbate composition can be calculated as well from the fractional contribution of the CO and CH_x groups to the n_{ox} value of 2.5, using the relations

$$\frac{\theta_{CO}}{\theta_{CO} + \theta_{CH_x}}n_{ox,CO} + \frac{\theta_{CH_x}}{\theta_{CO} + \theta_{CH_x}}n_{ox,CH_x} = 2.5$$

$$\theta_{CO} + \theta_{CH_x} = 0.44$$

with $n_{ox,CO} = 2$ and $n_{ox,CH_x} = (4 + x)$. From these equations it follows that in the case of C as the coadsorbate ($x = 0$) the CO coverage is 0.33 and for CH_3 as the coadsorbate the CO coverage is 0.40. This result is in good agreement with the IR data presented in Table 1, which show a 33% lower integrated CO absorption for ethanol with respect to 1,2-ethanediol, for which θ_{CO} was established as 0.52.

Evaluation of the charges involved in the reduction and in the 'direct' and 'indirect' oxidation of ethanol in view of the dissociative reaction mechanism gives information on the oxidation state of the CH_x species. As a result of the reduction of the adsorbate, the charge Q_{ox} involved in the 'indirect' oxidation is lower than the charge Q_{ox} for the 'direct' oxidation. The ratio $Q_{red}/\Delta Q_{ox}$ of 1.2 suggests that the hydrogenated species is a carbon species with the average oxidation state zero, since in the reduction as well as the oxidation of elemental carbon four electrons are involved according to

$$C + 4H^+ + 4e \rightarrow CH_4$$

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e$$

It is unlikely that ethanol generates COH species that contribute to hydrogenation at low potentials, since no evidence was found for such a species in the case of 1,2-ethanediol. Therefore it seems appropriate to conclude that elemental carbon is the only species that is hydrogenated to methane at low potentials. It must be noted that only a fraction of the carbon residue is hydrogenated. No firm conclusions can be drawn on the nature of the carbon residues that are insensitive to hydrogenation. The reason for the partial hydrogenation might be the occurrence of carbon islands on the surface that are insensitive toward hydrogenation. Elemental carbon can be formed through further dehydrogenation of CH_x species

according to

$$CH_x \rightarrow C + xH^+ + xe$$
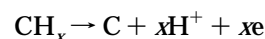
The conclusion that carbon atoms are formed is in accordance with the absence of C−H vibrations in the IR spectrum in Figure 3 within the detection limit of 0.01%T. In contrast with our measurements, C−H vibrations were observed with FTIRS[13] at 2960, 2920, and 2850 cm^{-1} with intensities of approximately 0.1%T that were ascribed to an adsorbed ethoxy species. Electron energy loss spectroscopy (EELS) also observed C−H vibrations after transfer of the electrode to UHV.[34]

IR and thermal desorption studies of CH_3 adspecies on Pt(111) in UHV support our conclusion that complete dehydrogenation of the CH_x species has occurred. IR studies have shown that adsorbed CH_3 moieties on Pt-(111) at 150 K are characterized by a single C−H band at 2885 cm^{-1} of approximately 0.07%T at saturation coverage.[38−40] Adsorbed CH_3 species are subject to dehydrogenation at temperatures above 230 K, and the C-H stretch vibration at 2885 cm^{-1} in the IR spectrum has completely disappeared after increasing the temperature to 300 K,[38−42] indicative of complete dehydrogenation to carbon species. In accordance with this, complete dehydrogenation of adsorbed CH_2 species formed from CH_2Cl_2 is observed on Pd(100) at room temperature.[43] It is characteristic for UHV experiments that adsorbed hydrogen formed in dehydrogenation of methyl fragments desorbs in the temperature region 280−350 K, indicating that at room temperature some adsorbed hydrogen can be present.[38] However, in our electrochemical adsorption experiments at 0.4 V dissociation of C−H bonds is accompanied by oxidation of the hydrogen atom to a proton. The energy involved in the oxidation might generate an extra driving force for C−H dissociation, favoring complete dehydrogenation of CH_x species to carbon.

Conclusions

In the present study we have shown on the basis of FTIRS and DEMS measurements that both 1,2-ethanediol and ethanol adsorb dissociatively. During adsorption 1,2-ethanediol is completely dehydrogenated to CO_{ads}. In the adsorption of ethanol the alcohol group is completely dehydrogenated to CO_{ads}, the methyl group is partially oxidized to CO_{ads} and partially dehydrogenated to a hydrogenable C_{ads} species, and a small fraction is formed that is insensitive toward hydrogenation. The nature of the latter is unknown. Infrared spectroscopy has revealed that for both ethanol and 1,2-ethanediol CO_{ads} is adsorbed mainly linear, in contrast with voltammetry results that suggest the presence of large amounts of bridge bonded CO.

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