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Spectroscopic Investigation of the Adsorbates of Benzyl Alcohol on Palladium

Ricardo M. Souto, José L. Rodríguez, and Elena Pastor*

*Departamento de Química Física, Universidad de La Laguna,
E-38071 La Laguna, Tenerife, Spain*

Teresa Iwasita

*Instituto de Química de São Carlos, Universidad de São Paulo CP780,
13560-970 São Carlos, São Paulo, Brazil*

The nature of the adsorbates formed when benzyl alcohol interacts with palladium in 0.1 M HClO$_4$ was studied via *on-line* differential electrochemical mass spectroscopy (DEMS), in situ Fourier transform infrared spectroscopy (FTIR), and cyclic voltammetry. Oxidative and reductive stripping experiments, as well as adsorbate displacement by CO, render valuable information concerning the nature of the adsorbed residues. Using isotope-labeled $^{12}C_6H_5^{13}CH_2OH$, it was possible to discriminate the respective behavior of the alcohol group and the aromatic ring. Adsorbate yields were found to strongly depend on the adsorption potential. Toluene, benzene, and CO are the residues formed from benzyl alcohol on palladium in the hydrogen adsorption/absorption range, whereas the intact benzyl alcohol molecule and benzoate seem to be the main species adsorbed on a hydrogen-free electrode.

1. Introduction

As a part of a systematic research project, the adsorption of organic compounds at platinum, palladium, and gold surfaces from aqueous solutions have been the center of our interest in recent years.[1–6] Data measured on different metallic substrates render information on the effect of the catalyst upon the reactivity of the organics. For these investigations, differential electrochemical mass spectrometry (DEMS)[7,8] has provided valuable hints toward the knowledge of the nature of the organic adsorbates.

In this context, we have recently initiated the study of the electrochemical behavior of benzyl alcohol (BA) on some noble metal electrodes. This molecule contains two reactive centers, the aromatic ring and the alcohol group, allowing therefore one to study the combined effect of these two interesting groups. The goal of this work is to investigate the nature of the adsorbed species remaining on the electrode surface after replacing the organic-containing solution by pure electrolyte in a flow-cell experiment.

A previous study on the adsorption characteristics of BA at platinum can be found in the literature,[9] in which voltammetric results were analyzed in combination with ex-situ data obtained via vibrational and Auger spectroscopies. The applicability of DEMS to study the reactivity of some aromatic compounds at noble metal electrodes was demonstrated by Baltruschat and co-workers.[10–14]

We have recently reported DEMS data comparing the adsorption and reactivity of BA on palladium and platinum.[5,6] From the oxidative stripping of the residues it was found that adspecies are strongly bonded to both electrodes, undergoing complete oxidation to CO$_2$ at platinum but incomplete oxidation at palladium. In addition, for adsorption potentials (E_{ad}) in the hydrogen region, formation and adsorption of toluene was observed on both metals. Adsorbate yields were found to depend on the substrate and on the E_{ad}.[5]

In the present paper, additional DEMS data and in situ Fourier transform IR spectroscopy (FTIRS)[15–18] give information on the nature and reactivity of the adsorbed species from BA at palladium electrodes. This study includes the use of labeled benzyl alcohol ($^{12}C_6H_5^{13}CH_2$-OH) and displacement of BA adsorbates by CO.

* Corresponding author. E-mail: epastor@ull.es. Phone: (34922) 318028. Fax: (34922) 318002.

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2. Experimental Section

2.1. Instrumentation. DEMS experiments have been performed with a working electrode consisting of a porous metallic layer of Pd sputtered on a microporous semipermeable membrane (Scimat, average thickness 60 μm, porosity 50%, mean pore size 0.17 μm). This membrane forms the interface between the electrochemical cell and the ion source of the mass spectrometer. The geometric area of the electrode was 0.64 cm^2, and the real area, calculated from the charge involved in the reduction of the palladium oxide, was 16 cm^2. The electrochemical cell was completed with a Pd wire as counter electrode and a reversible hydrogen electrode (rhe) in 0.1 M HClO$_4$ as reference electrode. All the potentials in the text are referred to this value.

The DEMS cell was a small flow-cell containing approximately 2 cm^3 of electrolyte solution. This cell was directly attached to the vacuum chamber containing the mass spectrometer (Balzers QMG 112) with a Faraday cup detector.[19] Volatile species generated at the electrode evaporate at the pores of the membrane into the vacuum and are detected by the mass spectrometer with a time constant of ca. 1 s. This time constant is small enough to allow mass spectrometric cyclic voltammograms (MSCVs) for selected mass-to-charge ratios (m/z) to be recorded in parallel to cyclic voltammograms (CVs) at a scan rate of 0.01 V s^{-1}. Experimental details of the method have been presented elsewhere.[4,8,19]

The Fourier transform IR spectrometer was a Bruker FS 66 provided with a mercury−cadmium telluride detector. Parallel (p) polarized IR light was employed. A glass cell with a 60° CaF$_2$ prism at its bottom was used. The working electrode was a Pd disk placed on one of the prism faces. The cell and experimental arrangements were described previously.[20]

Spectra were computed from the average of 128 scans obtained with a resolution of 8 cm^{-1} and are presented as the reflectance ratio R/R_0, where R and R_0 are the reflectances measured at the sample and the reference potentials, respectively. In this way, bands pointing upward (positive bands) are related to species which are present in a greater amount at the reference potential, whereas bands pointing downward (negative bands) correspond to species in a greater amount at the sample potential.

2.2. Chemicals. The solutions were prepared with Millipore-MilliQplus water (18.2 MΩ cm) and analytical grade chemicals. The base electrolyte was 0.1 M HClO$_4$. The concentration of benzyl alcohol was 1×10^{-3} M. For displacement experiments, CO was driven through the pure electrolyte during 20 min to obtain a CO-saturated solution. Some test experiments necessary to support the interpretation of BA data were conducted using either 0.01 M methanol or 5×10^{-3} M toluene in base electrolyte.
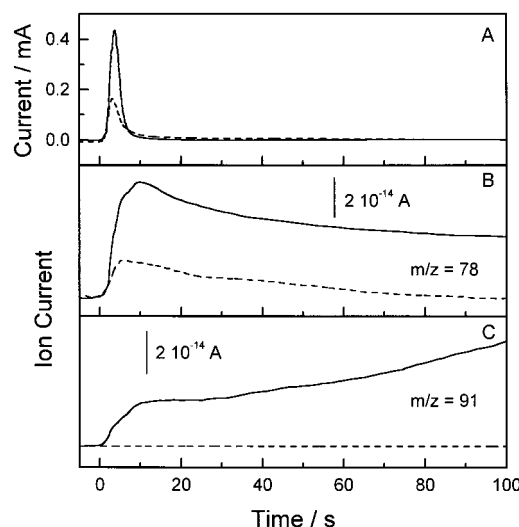
All experiments were performed at room temperature (ca. 22 °C). Solutions were deoxygenated thoroughly with purified argon (99.998%).

2.3. Experimental Procedure. BA was adsorbed on the Pd electrode at a potential E_{ad} in the range $0.20 \leq E_{ad} \leq 0.60$ V. The complete experimental procedure was as follows:

(I) Adsorption. After activation of the electrode by potential cycling at 0.01 V s^{-1} in the supporting electrolyte solution between 0.30 and 1.50 V, the potential was stopped during the anodic scan at E_{ad}, and the benzyl alcohol-containing solution was admitted in the cell. Faradic current (and ion current responses for DEMS studies) were recorded during adsorption.

(II) Elimination of Bulk Benzyl Alcohol. After an adsorption time of 5 min, the solution was completely replaced by pure base electrolyte under potential control. To ensure a complete electrolyte replacement, about 10 times the volume needed to fill the cell was allowed to flow through.

(III) Displacement Experiments. In displacement experiments of benzyl alcohol or toluene adsorbates with CO, following steps I and II, the CO-containing solution was admitted in the cell for 5 min and then bulk CO was eliminated by rinsing the cell with the base electrolyte solution several times.

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Figure 1. Faradaic current and ion current transients recorded during adsorption of BA at selected E_{ad} on Pd electrodes in 0.1 M HClO$_4$: (−) $E_{ad} = 0.20$ V; (- - -) $E_{ad} = 0.40$ V; (A) current transient; ion current transients (B) for $m/z = 78$ (benzene) and (C) for $m/z = 91$ (toluene).

(IV) Stripping of the Adlayer. After steps I−III, the residues were oxidized or reduced by potential scans in the positive- or negative-going potential direction.

3. Results and Discussion

3.1. Adsorption of Benzyl Alcohol. Anodic current transients were observed during the adsorption of benzyl alcohol at all E_{ad}. As shown in Figure 1A for BA adsorption at 0.20 and at 0.40 V, the current exhibits a sharp peak during the first 15−20 s. The corresponding charge, Q_t, was ca. 80 μC cm^{-2} (referred to real area) for experiments at 0.20 and 0.25 V. Since the Pd electrode is partially covered by hydrogen at these potentials, this charge must be related to the displacement of adsorbed hydrogen as protons in addition to the charge involved in the formation of adspecies. A lower charge was obtained for $E_{ad} = 0.40$ V, i.e., 40 μC cm^{-2}. Due to the relatively low amount of adsorbed hydrogen at this potential, we can infer that this charge is mainly due to some oxidation processes of BA during adsorption. In addition, for both regions, there might be a small fraction of charge due to double-layer effects.

The adsorption process is accompanied by the production of volatile species as detected by DEMS. Depending on E_{ad}, benzene and toluene are detected during BA admission (see Figure 1B,C for $E_{ad} = 0.20$ and 0.40 V). The formation of benzene is followed by the signal for $m/z = 78$ ([C$_6$H$_6$]$^{.+}$, Figure 1B) and that of toluene by $m/z = 91$ ([C$_6$H$_5$CH$_2$]$^+$, Figure 1C). The mass signals exhibit a time-dependent behavior that extends well beyond the duration of the current transient in Figure 1A. Additional m/z ratios were also checked, but no other compounds were found. Both $m/z = 78$ and 91 recover the background level after exchange with the base electrolyte.

The production of toluene, which only occurs in the presence of adsorbed hydrogen, continues as long as BA is present in the bulk of the solution. Thus the results in Figure 1C can be described by the following equation:

$$C_6H_5CH_2OH + 2(H)Pd \rightarrow C_6H_5CH_3 + H_2O + 2Pd \quad (1)$$
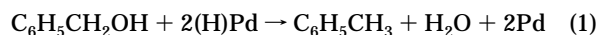
Equation 1 represents not the mechanism but the total process producing toluene during BA interaction with (H)-Pd. Since toluene is detected in a DEMS experiment, we
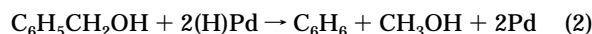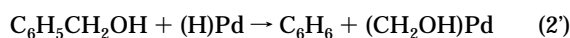
infer that it goes into the solution. However, as we shall see in the next section, a fraction of toluene remains adsorbed at the surface.

The fact that the quantity of toluene slowly increases with time (Figure 1C) could be explained by an increasing contribution of absorbed hydrogen to replenish the layer of adsorbed hydrogen Pd(H). For this effect, it is thinkable that reaction 1 may provoke acceleration of hydrogen diffusion to the surface of the metal.

On the other hand, the amount of benzene ($m/z = 78$) grows and passes through a maximum a few seconds after beginning of adsorption and then decays slowly (Figure 1B). Benzene is observed at all potentials studied here; its yield strongly decreases as E_{ad} is set to more positive values (only small amounts are produced above 0.40 V). The formation of benzene must be accompanied by the simultaneous formation of a C_1 species. Taking into account that the amount of benzene is higher at 0.20 V and decreases as the adsorption potential is set to more positive values, we suggest that Pd(H) is involved in benzene formation. Tentatively, we write as possible reactions forming benzene

$$C_6H_5CH_2OH + 2(H)Pd \rightarrow C_6H_6 + CH_3OH + 2Pd \quad (2)$$

or

$$C_6H_5CH_2OH + (H)Pd \rightarrow C_6H_6 + (CH_2OH)Pd \quad (2')$$

One of the problems to prove the first of these possibilities via DEMS is the difficulty to detect the main ion current for methanol ($m/z = 31$) in the presence of species also contributing to this signal (for example, benzyl alcohol molecules). We have tested the adsorption behavior of methanol on Pd and observed that it does not adsorb on Pd at 0.20 V, but it adsorbs at 0.40 V.

Reactions 2 or 2' can also be suggested for adsorption at 0.40 V but to a limited extent in view of the much lower amount of Pd(H) at this potential.

3.2. Oxidation of the Adsorbed Species Formed from Benzyl Alcohol. During a potential scan up to 1.50 V, BA adsorbates formed at all E_{ad} studied produce only CO_2 ($m/z = 44$) and benzene ($m/z = 78$). Typical CVs and MSCVs are given in Figure 2. Inspection of this figure indicates great changes in the shape of the CVs and the MSCVs with the adsorption potential. For adsorption at 0.20 V, a sharp peak is observed at ca. 0.90 V (Figure 2A) and the MSCVs for CO_2 (Figure 2B) closely match this oxidation peak. When BA is adsorbed at $E_{ad} \geq 0.35$ V, the voltammogram presents less-marked features, and the CO_2 signal widens, extending toward the Pd oxide region. Although the potential is scanned to the onset of oxygen evolution, complete elimination of the organic adlayer in the form of CO_2 requires several scans (not shown).

Desorption of benzene exclusively occurs during the first potential scan and starts at $E > 0.80$ V during the positive-going run, i.e., in the potential range of oxide formation (Figure 2C). Its production diminishes as E_{ad} is set to more positive values, approaching values close to zero for $E_{ad} \geq 0.50$ V. The integrated ion charges for CO_2 and benzene are given in Table 1.

3.3. Consecutive Adsorption of CO: Displacement of the Adsorbed Species Formed from Benzyl Alcohol. In these experiments, preadsorbed residues formed from BA were displaced by introducing a CO-saturated solution under potential control at E_{ad}. Faradic current and ion current transients for selected m/z values were recorded over 5 min. At $E_{ad} = 0.20$ V, CO admission causes the desorption of benzene and toluene, as shown by the
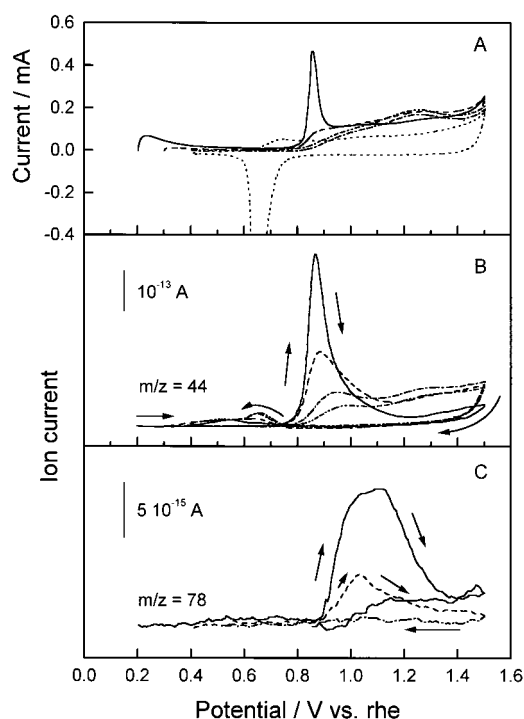
Figure 2. Electrooxidation of the residues formed at Pd after adsorption from a 1×10^{-3} M BA solution followed by electrolyte exchange with 0.1 M $HClO_4$ at different E_{ad}, $v = 0.01$ V s^{-1}: (A) CVs; (B) MSCVs for CO_2; (C) MSCVs for benzene; (—) 0.20 V; (- - -) 0.30 V; (- · -) 0.40 V; (- ·· -) 0.60 V; (···) CV in pure supporting electrolyte.

solid lines in Figure 3B,C, thus indicating that part of the benzene and toluene molecules formed when BA interacts with Pd remains adsorbed on the surface. At 0.40 V only benzene is displaced. The amount of benzene displaced by CO at $E_{ad} = 0.20$ V is proportional to the integral under the ion current transient given in Figure 3B, which amounts to 4.1×10^{-13} C. Integration of the corresponding ion current for toluene gave a yield of 3.0×10^{-13} C.

For BA residues formed at $E_{ad} = 0.40$ V, the only substance produced during CO admission is benzene, as shown by the dashed line in Figure 3B, its yield being now clearly smaller than for $E_{ad} = 0.20$ V. No other time-dependent mass signals related to other compounds were found at any of these potentials.

For all potentials, displacement of the BA adsorbates with CO produced cathodic current transients as those shown in Figure 3A. Since CO adsorbs without electron transfer, the cathodic currents could indicate that inter-action of the metal with the π-system of the aromatic molecules causes a partial electron donation from the adsorbate to the substrate. For this transfer, a flat orientation of these molecules should be necessary. This charge must be recovered when CO forces the desorption of the organic molecules. The fact that the value of the cathodic charge involved in the transient is higher at 0.40 V than at 0.20 V can be justified if a superimposed anodic process takes place, which is less important at 0.40 V than at 0.20 V. Such a process could be the oxidative desorption of coadsorbed hydrogen.

The adsorbed residues after the displacement experiments were oxidized during a positive potential scan up to 1.50 V. For $E_{ad} = 0.20$ V, the CV and MSCV for CO_2 exhibit a single peak at ca. 0.88 V reproducing the form of the voltammograms for adsorbed CO on Pd. A somewhat different behavior was observed for the residues of the displacement experiment at $E_{ad} = 0.40$ V. In this case, in

Table 1. Integrated Charge Densities Related to the Evolution of CO_2, Toluene, and Benzene at Different E_{ad} Values during the Experiments Described in Section 3

	integrated ion charges				
	$E_{ad} = 0.20$ V			$E_{ad} = 0.40$ V	
	$CO_2/10^{12}$ C	benzene/10^{13} C	toluene/10^{13} C	$CO_2/10^{12}$ C	benzene/10^{13} C
anodic stripping	11.6	4.7		26.6	2.0
displacement with CO		4.1	3.0		1.8
labeled BA/$^{13}CO_2$	6.4			4.8	
labeled BA/$^{12}CO_2$	5.3			21.8	
electroreduction		0.5	3.5		11.8
anodic stripping after electroreduction	10.8	5.2		12.3	7.3
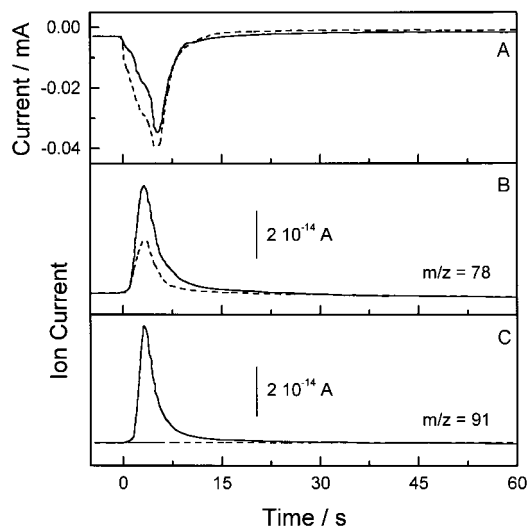
Figure 3. Faradaic current and ion current transients during displacement with CO of the adsorbates obtained from BA at (—) $E_{ad} = 0.20$ V and (- - -) $E_{ad} = 0.40$ V, on Pd electrodes in 0.1 M $HClO_4$: (A) current transients; (B) ion current transients for $m/z = 78$ (benzene); (C) ion current transients for $m/z = 91$ (toluene).

addition to the voltammetric anodic peak observed at 0.84 V due to the CO_{ad} component, a broad current feature in the Pd oxide region, also producing CO_2, suggests the presence of other residues which cannot be displaced by CO. The nature of these species will be discussed later in section 3.6.

To differentiate the behavior of toluene and benzene at 0.20 V, we have performed additional CO-displacement experiments after adsorbing toluene at this potential. Displacement caused a cathodic current transient and the desorption of toluene as the only organic species.

3.4. Oxidation of the Adsorbed Species Formed from Labeled Benzyl Alcohol on Palladium. Using ^{13}C-labeled benzyl alcohol it is possible to monitor the behavior of the alcohol group and the aromatic ring. The MSCVs given in Figure 4 were obtained during the stripping of the adsorbates from $^{12}C_6H_5$ at $E_{ad} = 0.20$ and 0.40 V. The mass signals for $m/z = 45$ and $m/z = 44$ are related to $^{13}CO_2$ and $^{12}CO_2$, respectively. From these results the following facts are noteworthy:

(i) The aromatic ring is more difficult to oxidize ($^{12}CO_2$ $m/z = 44$) than the alcohol group ($^{13}CO_2$ $m/z = 45$). The former signal is displaced to higher potentials and continues being produced during the second and subsequent scans.

(ii) The $^{13}CO_2$ yields are dependent on the adsorption potential, amounting 6.4×10^{-12} C at $E_{ad} = 0.20$ V and 4.8×10^{-12} C at $E_{ad} = 0.40$ V. For both adsorption potentials the oxidation reaction is completed during the first positive-going potential scan.

(iii) The shapes of the mass profiles for $m/z = 44$ ($^{12}CO_2$), which originates from the oxidation of the aromatic
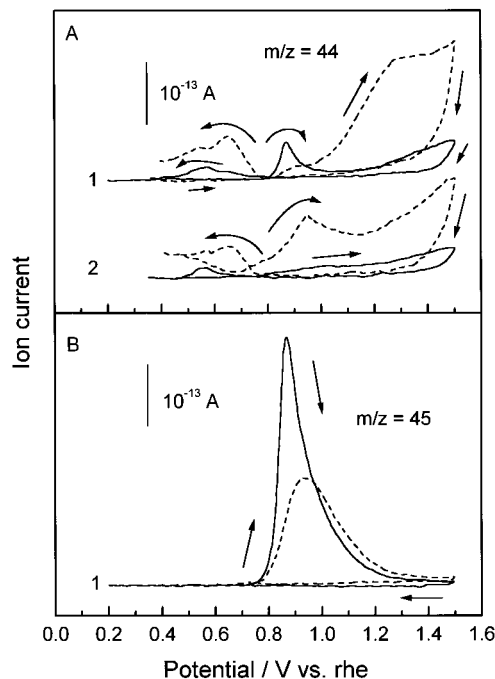
Figure 4. Electrooxidation of preadsorbed $^{12}C_6H_5{}^{13}CH_2OH$ at Pd after adsorption from a 10^{-3} M BA solution followed by electrolyte exchange with 0.1 M $HClO_4$ at (—) $E_{ad} = 0.20$ V and (- - -) $E_{ad} = 0.40$ V, $v = 0.01$ V s^{-1}: (A) MSCVs for $^{12}CO_2$ ($m/z = 44$); (B) MSCVs for $^{13}CO_2$ ($m/z = 45$). Numbers 1 and 2 refer to the first and second potential scans, respectively.

ring, are strongly dependent on the adsorption potential. For $E_{ad} = 0.40$ V, i.e., in the absence of surface hydrogen, $^{12}CO_2$ production extends for $E > 1.05$ V and is also observed during the reverse scan (Figure 4A, dashed line). Conversely, for $E_{ad} = 0.20$ V, i.e., in the presence of adsorbed/absorbed hydrogen, only small amounts of ^{12}-CO_2 are formed at $E > 1.05$ V (Figure 4A, solid line). Complete oxidation of the adsorbates requires five potential cycles (only two are shown), and the total ion charges are 5.3×10^{-12} C at $E_{ad} = 0.20$ V and 21.8×10^{-12} C at $E_{ad} = 0.40$ V. All integrated ion current values are collected in Table 1.

(iv) The $^{12}CO_2/^{13}CO_2$ ratio, computed from data obtained during five scans, is 4.5 for $E_{ad} = 0.40$ V and 0.8 for $E_{ad} = 0.20$ V. These ratios are well below 6 in agreement with the partial elimination of the aromatic ring during the adsorption in addition to benzene desorption during the potential sweep (see Figure 2C). For the adsorbate formed in the presence of hydrogen (at 0.20 V), the production of CO_2 is mainly related to the oxidation of the CH_2OH group. For $E_{ad} = 0.40$ V, the amount of benzene desorbed during the potential scan up to 1.50 V is lower, which results in a ratio closer to the value for the complete oxidation of BA to CO_2.

**3.5. Electroreduction of the Adsorbed Species Formed from Benzyl Alcohol on Palladium.** Adsorbed
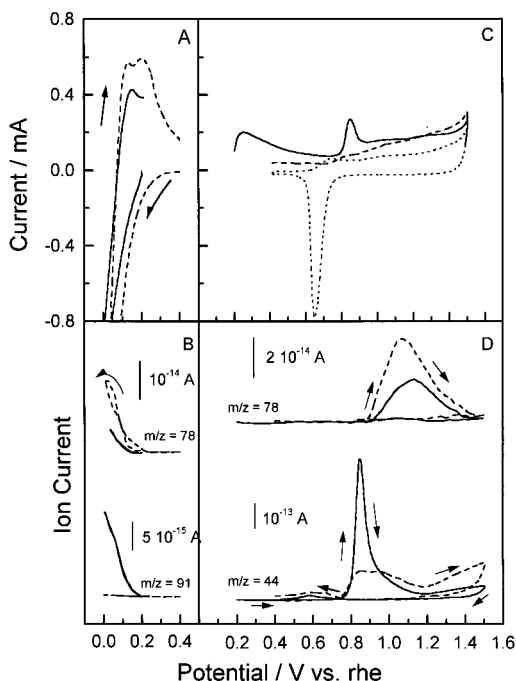
Figure 5. (A) First CV during the reduction of BA residues on Pd electrodes in 0.1 M $HClO_4$. (B) First MSCV for benzene ($m/z = 78$) and toluene ($m/z = 91$) production in the hydrogen region. (C) First CV for the oxidation of the residues remaining on the surface after (A) and (B). (D) Corresponding MSCVs for benzene ($m/z = 78$) and CO_2 ($m/z = 44$). Key: $v = 0.01$ V s^{-1}: (—) $E_{ad} = 0.20$ V; (- - -) $E_{ad} = 0.40$ V.

species from BA undergo desorption when the potential is cycled from E_{ad} toward 0 V (Figure 5 A,B). The only potential-dependent signals observed are $m/z = 78$ and $m/z = 91$, which result from the evolution of benzene and toluene during electroreduction (Figure 5B). The respective yields strongly vary with E_{ad}.

For $E_{ad} = 0.20$ V (Figure 5, solid line) both toluene and benzene (small amounts) are formed (Figure 5B). Total reduction, achieved in two potential cycles, produces integrated MSCV charges of 0.5×10^{-13} and 3.5×10^{-13} C for benzene and toluene, respectively. If the interaction of toluene with the Pd surface takes place through the π-system by donation of electrons to the metal, we can state that as the potential is set more negative, electron donation diminishes, and so does the strength of the interaction, causing toluene desorption. The same behavior should be expected for benzene, but only a very small signal is observed, which indicates that other factors are involved (see later).

Stripping of the remaining residues is shown in Figure 5C,D. The integrated ion charges are collected in Table 1. These charges can be compared with those observed for the direct adsorbate stripping. For $E_{ad} = 0.20$ V only minor differences are observed for benzene and CO_2. That means that most of the residues cannot be electroreduced. Thus, the total amount of CO_2 produced during the oxidative stripping after the electroreduction experiment (10.8×10^{-12} C) is slightly smaller than that obtained in the direct oxidation (11.6×10^{-12} C), the difference exclusively amounting for those residues evolved as toluene during the electroreduction procedure.

A drastic increase in the amount of benzene is produced during electroreduction from BA residues formed at $E_{ad} = 0.40$ V (see Figure 5, dashed line). Benzene is eliminated during 7 cycles giving a total ion charge of 11.8×10^{-13} C (compare this charge with the value of 2.0×10^{-13} or 1.8×10^{-13} C obtained from direct anodic stripping or
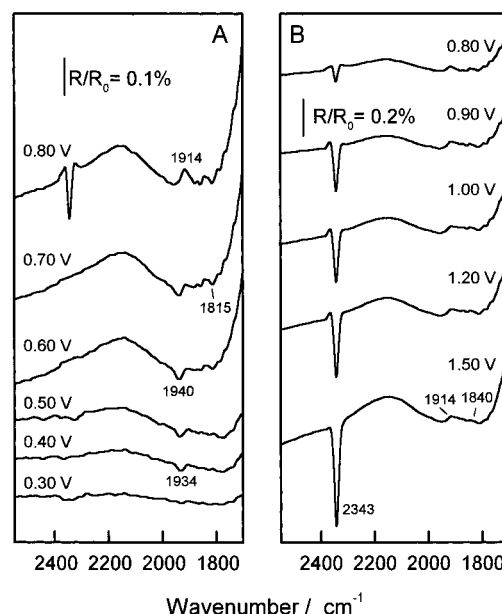

Figure 6. In situ FTIR spectra (*p*-polarized light, 128 scans, 8 cm^{-1} resolution) for the oxidation of the adsorbates formed from BA at $E_{ad} = 0.20$ V (reference potential). Sample spectra were acquired after applying potential steps toward more positive potentials as indicated. For details, see text.

CO-displacement respectively; see Table 1). Additional data were obtained from the oxidation of the residues remaining at the surface after reduction. A potential scan up to 1.50 V showed a 4-fold increase in the amount of benzene and a drastic reduction of CO_2, as compared with the corresponding amounts produced during the direct oxidation (see values in Table 1).

Thus, we conclude that some residue "R" should be formed at 0.40 V, which is transformed at 0.05 V into a species delivering considerable amounts of benzene not only during electroreduction but also during electrooxidation of the remaining residue. The latter process occurs at the expenses of the adsorbate forming CO_2. The nature of "R" will be established in section 3.6.

3.6. FTIR Studies of the Adsorbed Species Formed from Benzyl Alcohol on Palladium. After adsorption of BA from a 1 mM solution at $E_{ad} = 0.20$ V (reference potential) and solution exchange with pure supporting electrolyte, the spectra shown in Figure 6 were obtained. In the spectrum at 0.80 V, the development of two positive bands at 1914 and 1842 cm^{-1} provides evidence that CO_{ad} is one of the species formed at 0.20 V. These bands are not observed for $E_{ad} = 0.40$ V. Since methanol does not adsorb at Pd at $E_{ad} = 0.20$ V, the adsorption process giving rise to a C_1 species is probably better described by reaction 2' forming an adsorbed C_1 species, which reacts further to form adsorbed CO:

$$(CH_2OH)Pd \rightarrow (CO)Pd + 3H^+ + 3e^- \qquad (3)$$
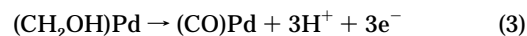
This reaction allows us to explain the behavior of benzene adsorbed from benzyl alcohol. Inspection of Table 1 shows that the amount of benzene evolved during the oxidative stripping of the residues from BA is similar to that displaced by CO. From this result we conclude that benzene desorbs without oxidation during the anodic potential scan. On the other hand, benzene formed at $E_{ad} = 0.20$ V is not desorbed during electroreduction (only very small amounts were detected; see Figure 5B, solid line, for $m/z = 78$). However, previous studies devoted to the adsorption of benzene at polycrystalline Pd have shown
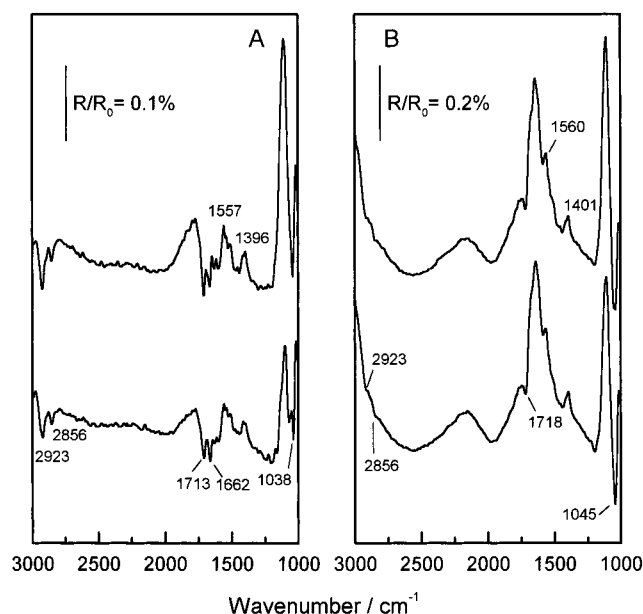
Figure 7. In situ FTIR spectra (p-polarized light, 128 scans, 8 cm^{-1} resolution) for the electroreduction at 0.05 V (sample potential) of the adsorbates formed from BA at $E_{ad} = 0.40$ V (reference potential). Two consecutively recorded spectra are shown (below, first spectrum; above, second spectrum). For details, see text. (B) In situ FTIR spectra (*p*-polarized light, 128 scans, 8 cm^{-1} resolution) obtained after (A) stepping back the potential at 0.40 V. Reference potential: 0.40 V before reduction of the adsorbate. Sample potential: 0.40 V after reduction of the adsorbate at 0.05 V. Two consecutively recorded spectra are shown (below, first spectrum; above, second spectrum). For details, see text.

that benzene oxidizes to CO_2 although some fraction was also desorbed as the intact molecule.[13] Moreover, benzene was completely desorbed during potential cycling in the hydrogen region.[13] These differences can be explained in terms of the composition of the adlayer: benzyl alcohol adsorbs dissociatively forming a coadsorbed layer containing (at least) benzene and CO. UHV studies[21] have shown that the presence of both species at the surface stabilizes the adlayer, and therefore, in our case benzene oxidizes at more positive potentials in the positive run or cannot be desorbed during the cathodic scan.

The spectra in Figure 6 show that there must be other species reacting to form CO_{ad} in the $0.40 \leq E \leq 0.70$ V potential range, where two negative features at 1934–1940 and 1815 cm^{-1} are observed. Absolute negative bands were obtained at these frequencies when the single beam spectra acquired at these potentials were recalculated with respect to the single beam spectrum measured at 0.80 V. Thus the negative-going CO bands should be considered as due to additional formation of CO at more positive potentials.

IR spectra obtained during the reduction at 0.05 V of BA adsorbates formed at 0.40 V are shown in Figure 7A. The negative features at 2923 and 2856 cm^{-1} are related to the formation of species containing a CH_3 group (these bands are assigned to the asymmetric and the symmetric stretchings of the methyl group, respectively).[22] However, DEMS experiments have shown that no toluene is produced from the adsorbates formed at 0.40 V. Thus, the bands must be related to some other species. On the other hand, the presence of a negative-going band at 1038 cm^{-1},

which can be assigned to the C−O stretching of an alcoholic group,[22] suggests that this and the CH stretching features are related to methanol formation during electroreduction. These bands have been observed in aqueous methanol + $HClO_4$ solutions.[7]

It has to be mentioned that it is very difficult to detect the formation of benzene or related hydrocarbons in FTIR experiments because their characteristic vibrations (the C=C stretch modes) appear in the same region as the bending vibration of water molecules.[22,23] However, in this experiment, a negative-going feature at 1662 cm^{-1}, could be attributed to the production of compounds containing an aromatic group.[3] Indeed these compounds can be detected as they go into the solution, since, as discussed before, the aromatic ring lies flat on the surface in the adsorbed state. In summary, these data suggest that besides benzene also methanol is formed during the electroreduction of the adsorbates.

A possible explanation for these observations is that, for $E_{ad} = 0.40$ V, a substantial amount of benzyl alcohol adsorbs without dissociation. Thus, residues denoted as "R" in section 3.5 seem to be BA molecules. Since benzyl alcohol was not detected during CO admission, we must conclude that it is very strongly adsorbed on the Pd surface. This is probably due to the fact that the interaction implies not only the aromatic ring of the molecule through the π-system but also the oxygen of the alcoholic group. A strong interaction with the substrate can also justify that this adsorbed BA becomes totally oxidized to CO_2 during the direct oxidation of the adsorbate. As pointed out before, total elimination of the CO_2-producing adsorbate required up to 5 potential scans, which is understandable in view of the complexity of the BA molecule.

The foregoing discussion should now be complemented by recalling that most of the total benzene amount desorbs as an intact molecule during the application of a positive potential scan (see Figure 2 and Table 1). We correlate the increase of the amount of benzene shown by DEMS during oxidation of the "reduced" adsorbate to a reaction like (2) occurring at 0.05 V, with adsorbed BA as reactant and producing major amounts of adsorbed benzene:

$$(C_6H_5CH_2OH)Pd + 2(H)Pd \rightarrow (C_6H_6)Pd + CH_3OH \quad (4)$$
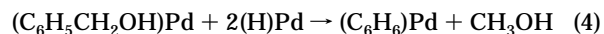
Intact BA molecules seem to be then the main adsorbate present at 0.40 V.

Additional bands are observed in the spectra of Figure 7, namely two positive-going bands at 1557 and 1369 cm^{-1} and a negative one at 1713 cm^{-1}. These features were not observed for adsorption at $E_{ad} = 0.20$ V. Both positive-going bands are associated with the asymmetric and symmetric stretching CO modes of a carboxylate group while the negative going feature indicates the formation of a carbonyl group. The band at 1713 cm^{-1} is assigned to the CO stretching vibration of a carboxilic acid.[24] Thus, it seems plausible to consider that BA is partially oxidized to benzoate at 0.40 V:

$$C_6H_5CH_2OH + Pd + H_2O \rightarrow (C_6H_5COO)Pd + 5H^+ + 5e^-$$
$$(5)$$
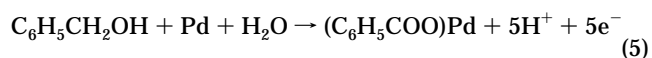
As observed for other week acids, the electrode potential has an effect on the dissociation equilibrium of week acids, the dissociation being favored at more positive potentials.[25]

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It is therefore thinkable that at 0.05 V benzoate anions associate to form benzoic acid as shown in the spectrum of Figure 7A. Benzoic acid formed at 0.05 V seems to be less strongly adsorbed than the corresponding anion and is eliminated from the surface. Therefore, a spectrum taken after returning the potential to 0.40 V (Figure 7B) shows that benzoate species are not recovered again. Benzoic acid molecules in the bulk are probably not enough to reestablish the original coverage.

Finally, other two positive bands in the spectra are due to uncompensated water (1640 cm^{-1}) and to ClO_4^- ions (1110 cm^{-1}).

4. Conclusions

The combined application of electrochemical and in-situ spectroscopic techniques to the investigation of the interaction of BA with a Pd electrode reveals several parallel pathways during the adsorption processes, depending on the presence or not of adsorbed hydrogen. When the latter is present, the adsorption process has basically a character of a chemical reaction of BA with (H)Pd. Toluene and benzene are produced during adsorption in the (H)Pd region. In part, these species become adsorbed on the surface and can be entirely displaced in the presence of a CO-saturated solution. When benzene is formed, the C_1 residue from the BA molecule produces adsorbed CO. For a low hydrogen coverage, e.g. at 0.40 V, or well above the (H)Pd region, BA molecules are strongly adsorbed in a nondissociative process. At these potentials, partial oxidation of BA produces benzoate anions.

During a positive potential scan, benzene desorbs as the Pd oxide region is reached. Other adsorbed residues oxidize to CO_2 at potentials depending on their molecular complexity. Thus, for C_1 species oxidation is complete in the positive-going part of the potential cycle. Aromatic adsorbates require higher potentials and several cycles for complete elimination.

Electroreduction at 0.05 V of nondissociatively adsorbed BA molecules produces benzene and methanol. On the other hand, toluene formed on the surface from BA at E_{ad} = 0.20 V desorbs during potential cycling in the hydrogen region.