Revealing Structural Effects, Part II: The Influence of Molecular Structure on the Adsorption of Butanol Isomers on Platinum

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Abstract: The nature of the adsorbates formed when butanol isomers interact with platinum electrodes in a perchloric acid medium was investigated by the application of on-line differential electrochemical mass spectrometry (DEMS) and cyclic voltammetry. In this way, the reactivity of the residues remaining on the electrode surface after a flow-cell experiment was established for the different molecules. It was found that the four isomers form strongly adsorbed species on the electrode, which undergo both electro-oxidation and electroreduction, depending on the potential applied at the electrode. Oxidative stripping of the adsorbates produces CO_2 as the only oxidation product, whereas propane and the corresponding butane isomer are obtained on platinum in the hydrogen adsorption potential region. The yields of these hydrocarbons were found to depend strongly on the nature of the butanol isomer and on the adsorption potential. According to these results, it can be concluded that fragmentation of the butanol isomers occurs during adsorption and reduction reactions. C_4 alkene and acetyl species are proposed as the adsorbed intermediates in all cases.

Keywords: adsorption · electrochemistry · mass spectrometry · platinum · structural effects

Introduction

Geometric isomers exhibit different electroreactivity at metal electrodes, which is assumed to result from structural effects. This effect was found when considering the electrochemical reactions of butanol isomers on noble metal electrodes, particularly at platinum electrodes, both in acid and alkaline media.[1–7] Cyclic voltammetric data clearly established differences in the potential ranges and the distribution of voltammetric current peaks for the oxidation of different C_4-alcohols,[3–6] which were suggested to arise from the occurrence of adsorbed intermediates, the nature of which were very dependent on the molecular structure of the isomer.[4,5] Unfortunately, electrochemical techniques alone could not reveal the exact nature of those adspecies, and the effect of the molecular structure on the actual reaction mechanisms could not be established in these studies.

Recently, the electrochemical reactions of butanol isomers at platinum electrodes in acid aqueous solution have been studied on-line by differential electrochemical mass spectrometry (DEMS).[7] From the detection of the volatile products formed during electroreduction and electro-oxidation reactions, the similarities and the differences in the reactivity of these compounds were established and analyzed.[7]Electrochemical reactions were considered to result from the interaction of both adsorbed and dissolved alcohol species with the electrode. The oxidation of the dissolved alcohol produces partially oxidized compounds such as aldehydes and ketones. The number of hydrogen atoms present at the α-C atom appeared to be responsible for the different paths for a given isomer. Thus, the partial oxidation pathway does not take place for the tertiary alcohol, as no α-H atom is present in this molecule. The dehydration is proposed to occur for all isomers because in this pathway, only one H atom is necessary in the C atom adjacent to the α-C atom. These interpretations also explain the observations made by Li and Sun on the electro-oxidation of *n*-butanol on a platinum electrode in acid solutions from FTIRS data.[8]

On the other hand, the formation of adsorbed species was described to result from at least two different processes:

1) Electroadsorption of the butanol isomers by a dehydration process involving the OH group and one α-H atom.

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This reaction results in the formation of a C=C bond in the adsorbate that interacts with the metallic surface probably through its π system.

2) Dissociative chemisorption, in which the covalent bond between the C atom attached to the OH group and the rest of the chain was broken, with the production of strongly adsorbed C_1 species and a C_3 alkane.

All the residues formed in these two processes oxidize to CO_2 and a fraction of them can suffer electroreduction to form a C_4 alkane.

Further insight into the nature of the adsorbed intermediates formed during the interaction of butanol isomers with a platinum electrode in acid solution can be obtained by performing the DEMS studies in the absence of the bulk reaction. That is, by conducting adsorption experiments under potentiostatic control, followed by electrolyte exchange in an electrochemical flow cell. Accordingly, the present paper is devoted to complete the investigation reported in Part I with such experiments.[7] The main objective is to confirm the two pathways involving adspecies described above in the absence of the dissolved substances, thus allowing one to discriminate between bulk and adsorbate reactivities. Additionally, it should be possible to investigate the eventual occurrence of other reactions involving adsorbed intermediates, which could be masked by the reactions of the dissolved molecules when they were present in the solution.

Experimental Section

Electrodes: For the analysis of the desorption products, differential electrochemical mass spectrometry (DEMS) was used. The electrochemical cell was a small flow-cell directly attached to the vacuum chamber of the mass spectrometer, which allows the exchange of electrolyte keeping the electrodes under potential control since they are always covered by electrolyte (further details on the method have been described elsewhere).[9,10] The working electrode consisted of a porous metallic layer of platinum sputtered on a microporous PTFE membrane, which formed the interface between the electrochemical cell and the ion source of the mass spectrometer. The potential of the working electrode was determined against a reversible hydrogen electrode (RHE) in aqueous 0.1 M $HClO_4$, and a wire of platinum was used as the counter electrode.

Before each experiment, the working electrodes were activated in 0.1 M $HClO_4$ by applying repetitive potential cycles at 0.01 $V s^{-1}$ between 0.01 and 1.50 V until a reproducible voltammogram was obtained. The real area of the working electrode was measured through the voltammetric charge within the hydrogen potential range for platinum,[11] and varied between 19 and 20 cm^2.

Chemicals: Solutions were prepared with Millipore MilliQ® plus water (18.2 MΩ cm), and high purity chemicals (Fluka). The working electrolyte was 0.1 M $HClO_4$. The four butanol isomers considered were 1-butanol, isobutyl alcohol (2-methyl-1-propanol), *sec*-butyl alcohol (2-butanol), and *tert*-butyl alcohol (2-methyl-2-propanol). The butanol isomers were added to the supporting electrolyte to give a 0.2 M concentration. Solutions were carefully deaerated with 99.998 % argon. All measurements were performed at room temperature.

Experimental procedure: Butanol isomers were adsorbed on the platinum electrode at controlled adsorption potential values (E_{ad}), in the range $0.05 \leq E_{ad} \leq 0.70$ V, taken in 0.05 V steps. In this way, adsorption of the alcohols was produced at either a hydrogen-covered electrode or in the double-layer region. The reactivity of the adspecies formed in this way was subsequently investigated under either oxidation (anodic stripping) or reduction (cathodic stripping) conditions. The complete experimental procedure was as follows:

I) *Adsorption*: The electrode was activated in the base electrolyte. Then, the potential was stopped at E_{ad} during the anodic scan, and the electrolyte solution containing the corresponding butanol isomer was admitted in the flow cell.

II) *Elimination of bulk butanol isomer*: After an adsorption time of 3 min, the solution was completely replaced by pure base electrolyte under potential control at E_{ad}. To ensure a complete electrolyte replacement, about 10 times the volume needed to fill the electrochemical cell was allowed to flow through.

III) *Stripping of the adlayer*: After steps I and II, the residues were oxidized or reduced in the absence of residual alcohol, by the application of potential scans at a rate of 0.01 $V s^{-1}$, starting the potential scan in the positive- or negative direction, respectively. Simultaneously, cyclic voltammograms (CVs), and mass spectrometric cyclic voltammograms (MSCVs), at selected mass signal ratios (*m/z*), were recorded. Thus, electro-oxidation of the adsorbed residues was achieved during the application of a positive potential scan starting at E_{ad} and going up to 1.50 V, followed by potential reversal down to E_{ad}. Successive potential cycles were recorded until the CV of a "clean" platinum surface was obtained. Analogously, the adspecies were electroreduced when the potential was cycled from E_{ad} toward 0 V. The oxidation of the remaining species after reduction was monitored by the CVs and the MSCVs recorded from E_{ad} to 1.50 V.

The platinum surface and product assignment: Potential cycling of a platinum electrode in an aqueous electrolyte produces changes in the surface state of the metal. In this way, three potential regions are observed from inspection of the CV for a platinum surface in 0.1 M $HClO_4$, namely:

1) The "hydrogen region" (0.01–0.40 V): which is characterized by the presence of adsorbed hydrogen on the electrode surface. The features observed in the voltammetric curve correspond to the adsorption/desorption of hydrogen atoms bearing different energies. In this potential range the reduction processes prevail, because oxidation reactions are not expected to occur at potentials at which the surface is mainly covered with hydrogen. The formation of hydrocarbons from alcohols at platinum in the hydrogen region was established many years ago by chromatographic analysis.[12]
2) The "platinum oxide region": at $E > 0.75$ V the platinum oxide layer commences to be formed during the positive potential scan, which is subsequently electroreduced during the reverse sweep with the development of a peak centred at 0.77 V. The presence of oxygen at these potential values favors the formation of oxidation compounds.
3) The "double layer region": in this potential region (0.40–0.75 V during the positive run, narrower in the negative sweep), neither H_{ad} nor O_{ad} species are present at the surface.

Oxidation or reduction processes occur on platinum in different potential ranges, depending on whether oxygen (at $E > 0.75$ V) or hydrogen (at $E < 0.40$ V) is present at the metal surface. This fact must be considered together with the fragmentation patterns of different molecules to identify the products from the recorded mass spectrometric curves. In a previous publication from our group,[7] a careful identification of the products formed on platinum during the oxidation and the reduction of butanol isomers was presented. In this way, the signal for *m/z* 44 recorded during the anodic stripping experiments reported in this work could be attributed to the formation of CO_2, whereas the formation of C_4 and C_3 alkanes during cathodic stripping experiments was deduced from the MSCVs recorded for *m/z* 58 and *m/z* 44, respectively.

Results

The electrochemical behavior of the residues formed on platinum at different values of E_{ad} ranging from 0.05 to

0.70 V was investigated by cyclic voltammetry combined with electrochemical mass spectrometry.

Electro-oxidation of the adsorbed species formed from butanol isomers on platinum: Figures 1–4 show the typical CVs for the first positive potential scan and the corresponding MSCVs for CO_2 (*m/z* 44) production during oxidation of the adlayers formed from each butanol isomers at four adsorption potentials E_{ad}, two of them (namely 0.05 or 0.10, and 0.20 V) located in the hydrogen adsorption region of the platinum electrode, whereas the other two values (i.e., 0.50 and 0.70 V) are placed in its double-layer range. The dependence of CV and MSCV profiles on E_{ad} can be directly observed from the inspection of these figures.

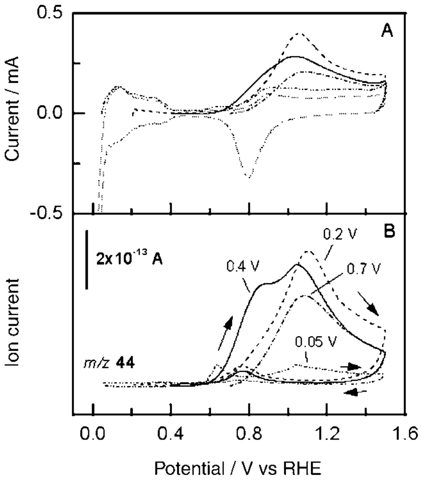


Figure 1. Direct electro-oxidation of the residues of 1-butanol formed at platinum in 0.1 M $HClO_4$ after adsorption at different E_{ad} values as indicated; $v = 0.01\ V s^{-1}$. A) CVs and B) MSCVs for CO_2 (*m/z* 44). (•••••) CV in pure supporting electrolyte.

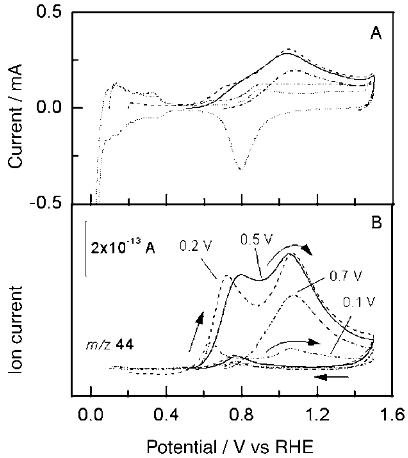


Figure 2. Direct electro-oxidation of the residues of isobutyl alcohol formed at platinum in 0.1 M $HClO_4$ after adsorption at different E_{ad} values as indicated; $v = 0.01\ V s^{-1}$. A) CVs and B) MSCVs for CO_2 (*m/z* 44). (•••••) CV in pure supporting electrolyte.

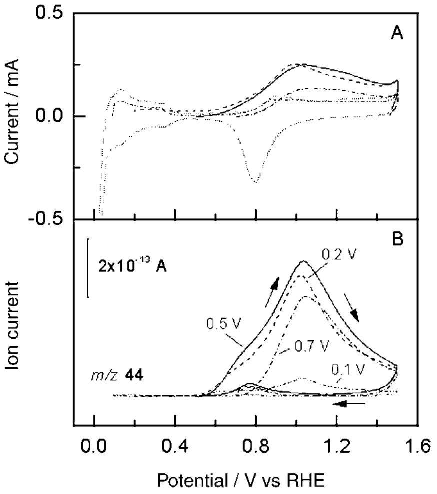


Figure 3. Direct electro-oxidation of the residues of *sec*-butyl alcohol formed at platinum in 0.1 M $HClO_4$ after adsorption at different E_{ad} values as indicated; $v = 0.01\ V s^{-1}$. A) CVs and B) MSCVs for CO_2 (*m/z* 44). (•••••) CV in pure supporting electrolyte.

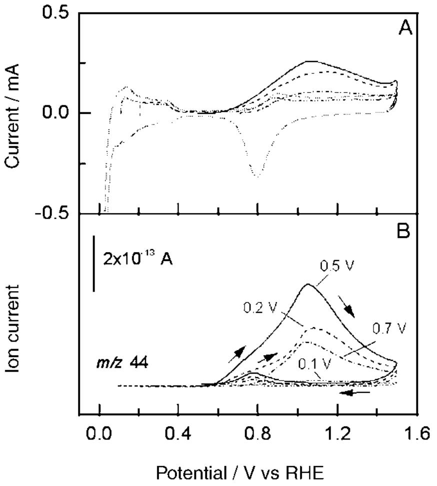


Figure 4. Direct electro-oxidation of the residues of *tert*-butyl alcohol formed at platinum in 0.1 M $HClO_4$ after adsorption at different E_{ad} values as indicated; $v = 0.01\ V s^{-1}$. A) CVs and B) MSCVs for CO_2 (*m/z* 44). (•••••) CV in pure supporting electrolyte.

Carbon dioxide is detected as the sole oxidation product of the adspecies formed from the butanol isomers in all the adsorption potential range, since no other species were detected by checking different *m/z* ratios. Thus, the formation of partially oxidized compounds (aldehydes or ketones), which were detected by DEMS when the 1-butanol, isobutyl alcohol, or *sec*-butyl alcohol were present in the bulk of the solution,[7] as followed by the signal *m/z* 72 ($[C_4H_8O]^{\cdot+}$), does not take place during the oxidation of the residues. That is, platinum is a good catalyst for the oxidation of organic compounds to CO_2 as it has been previously observed with DEMS and FTIR for the adsorbates formed from shorter chain alcohols on this metal.[13–17]

The mass signal for *m/z* 44 exhibits two contributions during the first positive potential scan centred around 0.75–0.82 and 1.03–1.10 V, respectively. They are resolved as two separate peaks for 1-butanol and isobutyl alcohol (see Figure 1B and Figure 2B), but are overlapped in the case of *sec*-butyl alcohol and *tert*-butyl alcohol (see Figure 3B and Figure 4B). The relative yield associated with these contributions depends on the adsorption potential and the butanol isomer. CO_2 is also formed in the negative scan at potentials below 0.95 V, that is, as soon as the electroreduction of platinum oxide has taken place, as indicated by the electroreduction peak centred at 0.80 V in the CVs depicted in Figure 1A–4A. Carbon dioxide is still formed in the following sweeps (not shown in the figure for the sake of simplicity), and three cycles are necessary to obtain a potential-independent signal for *m/z* 44.

Integration of the ion current signals during three potential cycles for each adsorption potential E_{ad} gives the total yields of carbon dioxide evolved during the electro-oxidation processes for the four butanol isomers, and these are plotted in Figure 5 (full circles, solid line) as a function of E_{ad}. These plots can be considered as the adsorption curves for each alcohol.

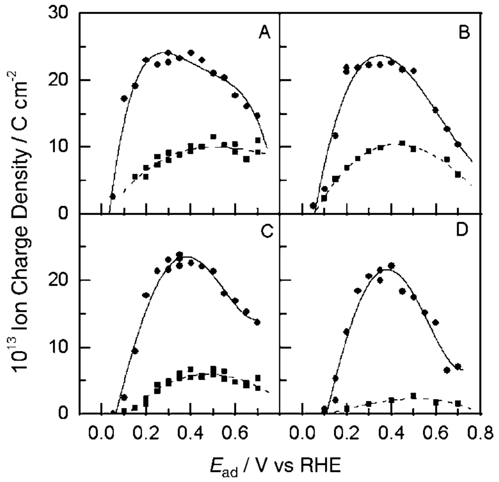


Figure 5. Ion charge densities for CO_2 (*m/z* 44) determined by integration of the MSCVs recorded during the oxidation of the residues as a function of E_{ad}: (●) direct electro-oxidation and (■) oxidation of the residues remaining on the surface after potential cycling in the hydrogen range of platinum. A) 1-butanol, B) isobutyl alcohol, C) *sec*-butyl alcohol, and D) *tert*-butyl alcohol.

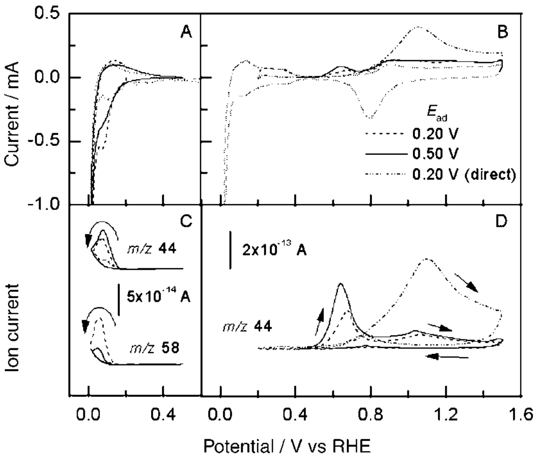


Figure 6. A) First CVs during the electroreduction of the residues of 1-butanol formed at platinum in 0.1 M $HClO_4$ at different E_{ad} values as indicated. B) Corresponding MSCVs for propane (*m/z* 44) and 1-butane (*m/z* 58) in the hydrogen region. C) First CV for the oxidation of the residues remaining on the surface after A and B. D) Corresponding MSCVs for CO_2 (*m/z* 44). CV and MSCV for the direct electro-oxidation of the adsorbates formed at $E_{ad}=0.20$ V are also plotted (dotted-dashed line). $v=0.01$ V s^{-1}.

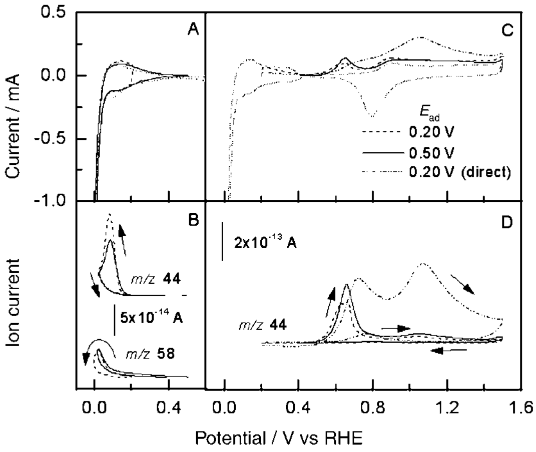


Figure 7. A) First CVs during the electroreduction of the residues of isobutyl alcohol formed at platinum in 0.1 M $HClO_4$ at different E_{ad} values as indicated. B) Corresponding MSCVs for propane (*m/z* 44) and isobutane (*m/z* 58) in the hydrogen region. C) First CVs for the oxidation of the residues remaining on the surface after A and B. D) Corresponding MSCVs for CO_2 (*m/z* 44). CV and MSCV for the direct electro-oxidation of the adsorbates formed at $E_{ad}=0.20$ V are also plotted (dotted-dashed line). $v=0.01$ V s^{-1}.

Electroreduction of the adsorbed species formed from butanol isomers on platinum: The reduction of the adsorbates was accomplished through consecutive potential cycles in the hydrogen adsorption region, and it occurred at potentials below 0.20 V. Four potential cycles between E_{ad} and 0.01 V were performed after adsorption and electrolyte replacement. The typical CVs measured during the first potential scan for the residues produced at two E_{ad} (0.20 and 0.50 V) are given in Figures 6A–9A for the different butanol isomers. Partial removal of the adsorbates is produced, especially during the first potential cycle as deduced from the additional cathodic current in the negative scan in these figures. Analogously, the first MSCV presents the highest mass intensity, which decays drastically during the following potential scans (not shown). The cathodic current is more noticeable for 1-butanol (Figure 6A).

The formation of C_3 and C_4 alkanes was detected during the reduction of the adsorbates (Figure 6B–9B), which are followed through the mass signals for *m/z* 44 ($[C_3H_8]^{\cdot +}$) and

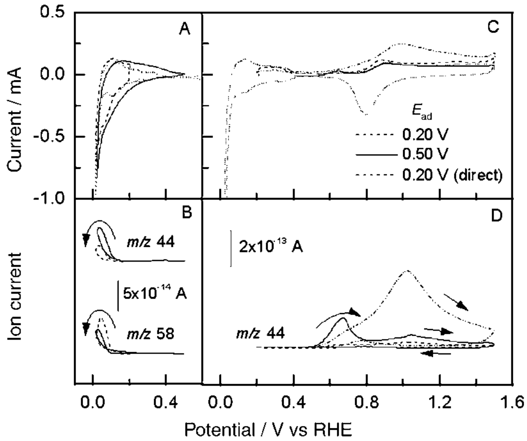


Figure 8. A) First CVs during the electroreduction of the residues of *sec*-butyl alcohol formed at platinum in 0.1 M $HClO_4$ at different E_{ad} values as indicated. B) Corresponding MSCVs for propane (*m/z* 44) and *n*-butane (*m/z* 58) in the hydrogen region. C) First CVs for the oxidation of the residues remaining on the surface after A and B. D) Corresponding MSCVs for CO_2 (*m/z* 44). CV and MSCV for the direct electro-oxidation of the adsorbates formed at $E_{ad}=0.20$ V are also plotted (dotted-dashed line). $v=0.01$ V s^{-1}.

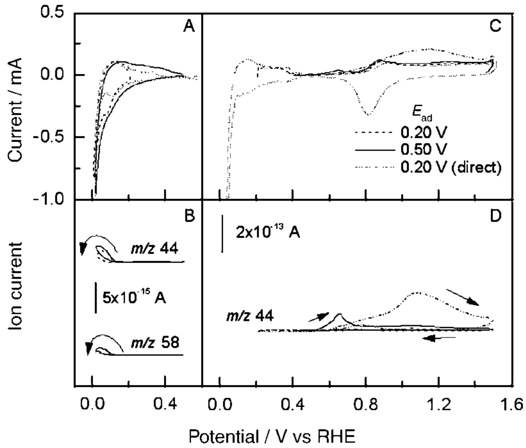


Figure 9. A) First CVs during the electroreduction of the residues of *tert*-butyl alcohol formed at platinum in 0.1 M $HClO_4$ at different E_{ad} values as indicated. B) Corresponding MSCVs for propane (*m/z* 44) and isobutane (*m/z* 58) in the hydrogen region. C) First CVs for the oxidation of the residues remaining on the surface after A and B. D) Corresponding MSCVs for CO_2 (*m/z* 44). CV and MSCV for the direct electro-oxidation of the adsorbates formed at $E_{ad}=0.20$ V are also plotted (dotted-dashed line). $v=0.01$ V s^{-1}.

for *m/z* 58 ($[C_4H_{10}]^{\bullet+}$), respectively. The first mass signal can be assigned to the formation of propane for all the butanol isomers. It must be observed that the same *m/z* value was related to the production of CO_2 for $E>0.40$ V. However, considering the state of the platinum surface, which is covered by H_{ad} at $E<0.20$ V, no oxidation to CO_2 but to a reduction product instead has to be responsible for the contribution to this mass signal in this potential range. Accordingly, the signal for *m/z* 58 is assigned to 1-butane in the case of the residues from 1-butanol and *sec*-butyl alcohol, or to isobutane in the case of isobutyl alcohol and *tert*-butyl alcohol. The onsets for the production of these alkanes correlate well with the initiation of the reduction current in the corresponding CVs.

In general, the signal for the C_4 hydrocarbon (*m/z* 58) shows a steady increase for $E<0.10$ V and presents the maximum value near the cathodic potential limit. The production of this alkane diminishes during the subsequent anodic scan. Conversely, the potential dependence displayed by propane (*m/z* 44) for 1-butanol and isobutyl alcohol shows a pronounced increase during the cathodic scan for $E<0.20$ V, attaining a maximum at 0.10 V, just at the potential where H_2 evolution starts. During the remainder of the cathodic scan and subsequent anodic sweep, the mass current continuously decreases. As a difference to the primary alcohols, in the case of *sec*- and *tert*-butyl alcohol adsorbates, the signals for the production of propane (*m/z* 44) closely follows that of isobutane (*m/z* 58).

The integrated ion charges for *m/z* 58 and *m/z* 44 as a function of the adsorption potential are given in Figure 10. It should be noted that, for the sake of comparison, the integrated values for *m/z* 58 measured for the residues from isobutyl alcohol and *tert*-butyl alcohol are multiplied by a factor of 5 because isobutane presents a fragmentation for this signal about five times lower than that for 1-butane.[18,19]

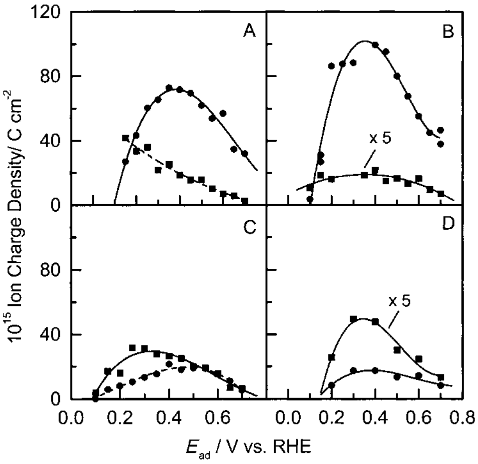


Figure 10. Ion charge densities for (●) C_3 alkanes (*m/z* 44) (■) and C_4 alkanes (*m/z* 58) determined by integration of the curves obtained for these *m/z* values during the electroreduction of the residues as a function of E_{ad}. A) 1-butanol, B) isobutyl alcohol, C) *sec*-butyl alcohol, and D) *tert*-butyl alcohol.

After reduction of the adsorbates, the CVs (Figures 6C–9C) and MSCVs for CO_2 (*m/z* 44) (Figures 6D–9D) were also recorded to monitor the oxidation of the organic residue not desorbed during cycling in the hydrogen region. The corresponding CVs and MSCVs for CO_2 production obtained during the direct electro-oxidation of the adsorbates formed at $E_{ad}=0.20$ V are plotted for comparison in Figures 6C–9C and Figures 6D–9D, respectively. Some differences are observed when comparing the currents recorded after the electroreduction process with those for the direct oxidation of the adsorbates. That is, the onset for the oxidation of the residues to CO_2 is shifted to less positive potentials, with a peak clearly displayed around 0.55 V. The second contribution appears in practically the same potential range to that in the case of the direct oxidation. These current responses resemble those obtained for the adsorbates formed in the hydrogen adsorption region (see Figures 1–4 for $E_{ad} = 0.07$ or 0.10 V).

The total yields of CO_2 during the subsequent oxidation of the non-electroreduced residues was again determined from the integration of the ion-current signals for the ratio *m/z* 44 measured during three potential cycles, and these are also plotted in Figure 5 (full squares, dashed line) for the four butanol isomers at the different E_{ad} values tested. It can be noted that the total amounts of CO_2 evolved from the electrode at all the E_{ad} values are now much smaller (50–90 % depending on the isomer and E_{ad}) than those obtained for the direct oxidation of the residues formed at these potentials.

Discussion

Preliminary considerations: All the four butanol isomers are found to adsorb irreversibly at platinum electrodes, in both the double layer and the hydrogen potential ranges of this metal. The stripping of the residues was performed through both electro-oxidation and electroreduction, and the yields of their products were determined by DEMS. The results obtained allow us to make the following remarks:

1) The adlayer of the four butanol isomers formed at platinum is electro-oxidized at $E > 0.50$ V to CO_2 (*m/z* 44, $[CO_2]^{\cdot+}$) as the sole oxidation product (see Figures 1–4). Three potential cycles up to 1.50 V are necessary to complete the stripping of the adsorbates. This result suggests that oxidation occurs through a stepwise mechanism involving the gradual rupture of the C–C chain. Most of the molecule is oxidized during the first potential excursion, but some portion needs further potential scans to be completely desorbed as CO_2.
2) Three different contributions can be detected in the first MSCVs for *m/z* 44 during the oxidative desorption of the residues (see Figures 1B–4B). That is, there are two different potential ranges for the formation of CO_2 during the positive potential scan, which are observed in the double layer ($0.50\,V < E < 0.90\,V$) and in the platinum oxide ($E > 0.90$ V) regions. CO_2 is also formed in the negative potential scan when the Pt oxide layer is reduced.
3) The relative yield associated with these oxidation contributions depends on the adsorption potential and on the nature of the alcohol. CO_2 formation in the $0.50\,V < E < 0.90\,V$ potential range is more pronounced for the two primary alcohols (see Figures 1B and 2B for 1-butanol and isobutyl alcohol, respectively). As this potential range corresponds to that for the oxidation of adsorbed CO (see below), it is concluded that the fragmentation of the C_4 initial chain into C_1 and C_3 species is favored for these alcohols. This process is also favored as the potential is set at more negative values.
4) The amount of residues formed at platinum can be determined as a function of the adsorption potential through the integration of the ion current signals measured for the *m/z* 44 signal (Figure 5). These plots represent the adsorption curve for each butanol. It is observed that, except for *tert*-butyl alcohol, butanol isomers display a maximum value of about $24 \times 10^{-13}\,C\,cm^{-2}$ in the potential range 0.20–0.50 V. In the case of *tert*-butyl alcohol, though a similar maximum value is attained, the potential region in which it occurs is narrower (namely, 0.35–0.40 V). From these results, a common initial intermediate with a similar structure seems to be involved for the four isomers.
5) C_3 (propane, *m/z* 44, $[C_3H_8]^{\cdot+}$) and C_4 (butane or isobutane, *m/z* 58, $[C_4H_{10}]^{\cdot+}$) hydrocarbons are detected from the electroreduction of the adsorbates. These compounds are formed at $E < 0.20$ V during the application of repetitive potential cycling in the range between E_{ad} and 0 V (see Figures 6A, B–9A, B).
6) The relative yields of propane and either butane or isobutane depend on E_{ad} and on the nature of the alcohol. The potential dependences for the production of these hydrocarbons are depicted in Figure 10.
7) The highest C_3/C_4 ratios are observed for 1-butanol and isobutyl alcohol, rather than for *tert*-butyl alcohol. Accordingly, the fragmentation is favored for the primary alcohols, and then, CO_{ad} species are probably formed from primary butanols, as previously assumed.
8) The residues remaining at the electrode after the electroreduction process also oxidize to CO_2 (see Figures 6C, D–9C, D). The coverage of the surface by the adspecies diminishes as a result of the reductive stripping process, and the decrease amounts to 60 % for 1-butanol and isobutyl alcohol, 80 % for *sec*-butyl alcohol, and 90 % for *tert*-butyl alcohol (see Figure 5). This diminution is related with the production of C_3 and C_4 hydrocarbons during the reduction.
9) The electro-oxidation of the residues mentioned in point 8) mainly displays the feature occurring in the $0.50\,V < E < 0.90\,V$ potential range, whereas that occurring at $E > 0.90$ V in the corresponding MSCVs for the direct oxidation has greatly decreased and contributes very little to the total CO_2 yields (see Figures 6D–9D). The voltammetric and mass responses are similar to those obtained for the same butanol adsorbed at $E_{ad} = 0.07$ or 0.10 V. Therefore, during reduction of the adsorbate in the H_{ad} potential region or during adsorption at these low potentials, "CO-like" species (see below), which oxidizes in the 0.50–0.90 potential range, are formed.

Revision of the adsorption and electrochemical reactions of shorter chain alcohols at Pt in acidic solutions: Complementary information could be obtained from the consideration of the adsorption and electrochemical reactions of C_2 and C_3 alcohols on Pt electrodes in acid solution, which have been the object of thorough investigation in our group.[14–18] On the basis of those studies, conclusions regarding the reactivity of the alcohol group and the influence of the hydrocarbon chain were extracted from the comparison of their electrochemical responses under oxidation and reduction conditions. The compounds studied were, namely, ethanol,[13] 1-propanol,[14] isopropyl alcohol,[15] allyl alcohol (2-propen-1-ol),[16] and propargyl alcohol (2-propyn-1-ol).[17] Thus, both primary and secondary saturated alcohols, as well as unsaturated primary C_3 alcohols, have been investigated. The electro-oxidation and the electroreduction products detected from adsorbate experiments on platinum with these alcohols are summarized in Table 1. In the cases where more than one product was obtained simultaneously, the yield ratios of the products are also given.

Table 1. Electro-oxidation and electroreduction products from a series of alcohols at platinum in acid media, detected by on-line differential electrochemical mass spectrometry (DEMS) from adsorbate experiments.[13–17]

Alcohol	Oxidation products	Reduction products
ethanol	CO_2	ethane, methane ratio 1:6
n-propanol	CO_2	propane, ethane ratio 1:3.5
2-propanol	CO_2	propane
allyl alcohol	CO_2	propane, propene, ethane ratio 1:1:1
propargyl alcohol	CO_2	propane, propene, propyne, ethane ratio 10:12:2:1

Though different products were detected during the cathodic stripping of the adsorbates formed at platinum from the different organic compounds, they all form CO_2 as the only oxidation product. But even in this case, differences were found for each alcohol as for the potential range for CO_2 formation and the number of oxidation cycles necessary to achieve complete electro-oxidation. Thus, the residues formed from ethanol were almost completely stripped in one cycle up to 1.50 V, and the small rest of adsorbate that remained at the surface was oxidized during the reverse scan, after the reduction of the Pt oxide. In this case, oxidation mainly took place in the potential region where "CO-like" adsorbates are oxidized (namely 0.60–0.80 V).[20] For 1-propanol, at least two oxidation cycles were needed for complete electro-oxidation, and the main contribution to the CO_2 signal was found at more positive potentials. This effect was even more dramatic for the adsorbates from 2-propanol as their oxidation occurred around 1.04 V, and no "CO-like" species were observed. Intermediate situations were encountered for the two unsaturated C_3 alcohols considered, which exhibited varying fractions of CO_2 formed in the 0.60–0.80 V region as compared to the mass signal located at more positive potentials.

When the electroreduction is considered, a great diversity in the composition of the products, as well as in their yields, is observed. In general, hydrocarbons with the same number of C atoms as the original molecule or containing one less were detected for all cases, with the exception of 2-propanol, which forms propane as the only reduction product. This is a strong indication that cleavage of the hydrocarbon chain mainly occurs for the primary alcohols, that is, for those compounds that contain a hydrogen atom linked to the carbon atom bearing the OH group. This correlates well with the absence of "CO-like" adsorbates for 2-propanol. In the case of the unsaturated alcohols, the different extent of hydrogenation of the organic chain resulted in the production of mixtures of C_3 hydrocarbons during the electroreduction of the adsorbates.

These results indicate that at platinum electrodes, the reactive center for the saturated alcohols is the α-C atom. Adsorption can occur as at least one H atom at the α-C atom is lost, and the residue is then directly linked to a site at the platinum surface through this α-C atom. In this way, the C_n chain is retained. In addition to this process, a fraction of the residues formed from primary alcohols result from the cleavage of the hydrocarbon chain, which is responsible for the formation of "CO-like" and C_{n-1} species. The necessary condition for this reaction to take place is the presence of the OH group at the extreme of the carbon chain. The extent of cleavage as compared to the adsorption of the complete hydrocarbon chain depends on the length of the chain; it amounts to 86 % for ethanol, 78 % for 1-propanol, 33 % for allyl alcohol, and 4 % for propargyl alcohol.

In the case of allyl and propargyl alcohols, electrochemical reactivity is influenced by the existence of another reaction center in addition to the α-C atom, which is the unsaturated C–C bond. Accordingly, residues are formed after the abstraction of either the vinyl or the acetylenic hydrogen atoms for allyl or propargyl alcohols, respectively. Thus, the alcohol group is not directly involved in the adsorption process, as the interaction between the Pt site and the organic compound is established through the unsaturated C–C bond. The subsequent hydrogenolysis of the C–O bond in the residues produces propene or propyne, respectively. Finally, an additional pathway is observed during the adsorption of propargyl alcohol, which is due to the rupture of the triple bond. The adspecies formed in this reaction is electroreduced to propylene.

Reactions of adsorbed butanol isomers at platinum electrodes: In our previous study,[7] the electrochemical behavior of butanol isomers at platinum electrodes in acidic medium, when present in the bulk solution, was explained by considering six different reaction pathways (for details, see Part I),[7] namely:

Reaction 1: Complete oxidation: It results in the formation of CO_2 during the oxidation of the four butanol isomers.

Reaction 2: Partial oxidation: During the oxidation of the primary and the secondary butanol isomers, compounds containing a carbonyl group (i.e. aldehydes and ketones) are also obtained. *tert*-butyl alcohol does not exhibit this reaction.

Reaction 3: Dehydration: It leads to the formation of strongly adsorbed intermediates containing a C=C bond. This reaction takes places for the four isomers since they all contain a H-atom at the carbon adjacent to the α-C atom.

Reaction 4: Hydrogenation: Hydrogen is added to the C=C bond in the adsorbates formed through reaction pathway (3), and leads to the corresponding C_4 alkanes.

Reaction 5: Fragmentation: Alternatively, the C_4 chain in the adsorbates can be broken with the formation of C_3 and C_1 species.

Reaction 6: Hydrogenolysis: C_4 alkanes are also formed by a direct reaction between the alcohol molecules in the bulk of the solution and the hydrogen adsorbed on the electrode.

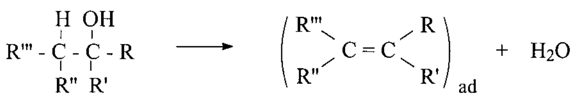
The formation of irreversibly adsorbed species was proposed before.[7] The results obtained in this work allow us to unambiguously establish which of the preceding reaction pathways involve the participation of these residues. Thus, it is possible to conclude that:

1) The sole *oxidation* product for the adsorbed species is CO_2, which is formed through reaction 1 at $E > 0.50$ V, as shown by the potential dependence of the mass response for *m/z* 44 [Eq. (1)].Partial oxidation (reaction 2)

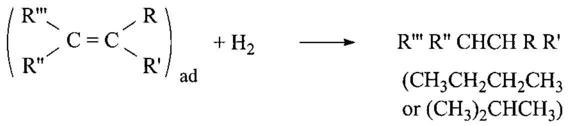
$$\text{Adsorbate} + x\,H_2O \rightarrow x'CO_2 + x''H^+ + x''e^- \qquad (1)$$

does not occur for the adsorbates in any case.

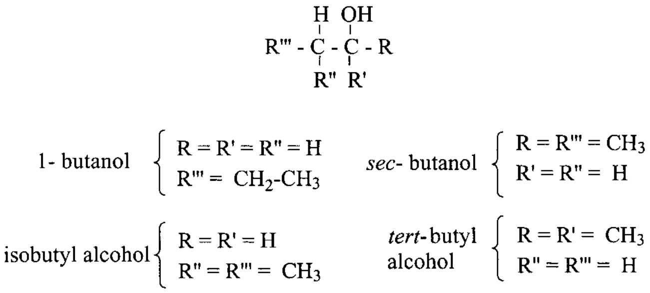
2) The intensity of the signal for *m/z* 58 at $E < 0.20$ V is lower for the isolated adsorbates than for the molecules in the bulk solution, especially in the case of 1-butanol and isobutyl alcohol. This can be explained by considering that adsorption involves a *dehydration* reaction (reaction 3) with the formation of alkene species [Eq. (2)], which undergoes *hydrogenation* (reaction 4) in the H_2 evolution region giving the corresponding butane isomer [Eq. (3)].A common nomenclature for butanol isomers is used (Scheme 1).



$$R'''\text{-}\underset{R''}{\overset{H}{C}}\text{-}\underset{R'}{\overset{OH}{C}}\text{-}R \longrightarrow \left(\begin{matrix}R''' & & R\\ & C=C & \\ R'' & & R'\end{matrix}\right)_{ad} + H_2O \qquad (2)$$

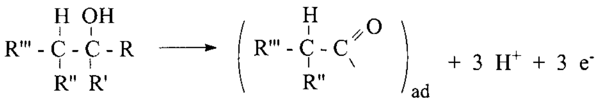


$$\left(\begin{matrix}R''' & & R\\ & C=C & \\ R'' & & R'\end{matrix}\right)_{ad} + H_2 \longrightarrow \begin{matrix}R'''\,R''\,CHCH\,R\,R'\\ (CH_3CH_2CH_2CH_3\\ \text{or } (CH_3)_2CHCH_3)\end{matrix} \qquad (3)$$

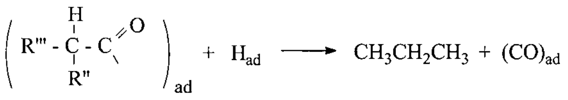


Scheme 1.

3) All butanol isomers undergo *fragmentation* (reaction 5) during their adsorption at platinum, thus accounting for the formation of propane (*m/z* 44 at $E < 0.20$ V). In addition to the adsorption potential, the extent of this reaction depends strongly on the structure of the alcohol, and it is favoured for the primary butanol isomers. For these alcohols, acetyl adsorbed species can be formed [Eq. (4)], which suffers the fragmentation by interaction with H_{ad} [Eq. (5)].For secondary and tertiary butanol isomers, the formation of these adsorbates should involve an isomerization process, probably through the alkene intermediate, which hinders the reaction. As the intensities measured for the production of propane from adsorbed species are similar to those determined when the molecule is present in the bulk solution, it is concluded that the reaction has to proceed through adsorbed species.



$$R'''\text{-}\underset{R''}{\overset{H}{C}}\text{-}\underset{R'}{\overset{OH}{C}}\text{-}R \longrightarrow \left(R'''\text{-}\underset{R''}{\overset{H}{C}}\text{-}C{\overset{\displaystyle O}{\lessdot}}\right)_{ad} + 3\,H^+ + 3\,e^- \qquad (4)$$



$$\left(R'''\text{-}\underset{R''}{\overset{H}{C}}\text{-}C{\overset{\displaystyle O}{\lessdot}}\right)_{ad} + H_{ad} \longrightarrow CH_3CH_2CH_3 + (CO)_{ad} \qquad (5)$$

4) *Fragmentation* is favored for primary butanol isomers, and therefore, this reaction competes with the *dehydration* process thus decreasing the ratio of butane formed from the corresponding adsorbed species. The formation of the C_4 alkane during the hydrogenolysis of the alcohol molecules in the bulk solution is responsible for the higher intensities measured for butane formation.[7]

Conclusion

The formation of strongly adsorbed residues from the four butanol isomers at Pt with poisoning effects, which were considered in our previous publication concerning the electrochemical reactions of butanol isomers,[7] has been confirmed. The extent of adsorption is observed to depend on both the nature of the butanol isomer and the applied potential. All the alcohols show the highest coverages in the 0.25–0.50 V potential range with a decrease for $E_{ad} > 0.50$ V.

The α-C atom is the reactive center in the molecules. The electroadsorption process has been interpreted as the dehydration of the molecule at the CH-C_αOH group and the adsorbate is then bound to Pt surface through the C=C_α bond formed. This reaction explains why primary and secondary butanol isomers exhibit the highest adsorption rates, but also applies to the adsorption of *tert*-butyl alcohol molecules.

Primary alcohols predominantly undergo cleavage of the C_α–C bond during adsorption, thus producing CO-like species and propane. The yields of the C_3 alkane resulting from the electroreduction of these adsorbates in the hydrogen region of Pt are very similar for both 1-butanol and isobutyl alcohol at most E_{ad} values, and give C_3 to C_4 alkane ratios of around 2.5:1. This may indicate that the main effect concerning the rupture of the C–C bond arises from the presence of the OH group at the extreme of the C–C chain. In this case, the formation of acetyl intermediates accounts for the experimental results. The C_3 alkane/C_4 alkane ratio is almost 1:1 for *sec*-butyl alcohol and very small for *tert*-butyl alcohol. Thus, cleavage is a major effect for the primary alcohols but hardly occurs for *tert*-butyl alcohol.

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