Interaction between Residues of Different Organic Compounds on Platinum: A Mass Spectrometric Study

Elena Pastor, José L. Rodríguez, Candelaria M. Castro, and Sergio González

Departamento de Química Física, Universidad de La Laguna, 38071 Tenerife, Spain

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A consecutive absorption of formic acid and propargyl alcohol, as well as that of formic acid and ethanol on platinum in acid media were studied by on-line mass spectrometry (DEMS). Oxidation of the coadsorbed species remaining on the electrode surface after a flow-cell experiment yields only CO₂. Using H₁³COOH isotopically modified, the contribution of formic acid during the electro-oxidation of the coadsorbates can be distinguished from that of ethanol or propargyl alcohol residues. It is found that ethanol replaces formic acid residues, whereas the adsorption of propargyl alcohol is modified by the presence of formic acid on the surface. Formic acid cannot chemisorb on a platinum surface covered by propargyl alcohol residues, but reacts without replacement with platinum modified by ethanol residues.

Keywords: organic adlayers, mass spectrometry, isotopic labeling, adsorbate replacement

Introduction

The nature of the catalytic poisons formed during the successive adsorption of different organic compounds obviously depends strongly on the structure of the initial compound¹—⁶, and consequently, the electro-oxidation of these residues occurs in different potential regions, depending on the composition of the adlayer. The aim of the present work is to elucidate the processes taking place when a second compound reacts on a surface already modified by the presence of a first layer of organic residues. With this purpose, three simple molecules were chosen in order to study the interaction between their residues on platinum: formic acid (HCOOH)¹, ethanol (CH₃CH₂OH)³, and propargyl alcohol (HC≡CCH₂OH)⁴—⁶.

The above-mentioned compounds form different adsorbates on the Pt surface. Formic acid produces mainly CO₃ad¹, although COH₃ad species may also be present². CO₃ad oxidation occurs in the double layer region. In the case of ethanol, the residues are also mainly oxidized in the double layer region. However, a contribution in the platinum oxide region may be observed. Although CO₃ad is formed, most of the adsorbates contain the C-C chain (O-CH₂-CH₃, COCH₃ and =COCH₃)³. A maximum coverage of 0.85 is attained at an admission potential of E₃ad = 0.35 V for ethanol, and at E₃ad = 0.15-0.35 V for formic acid⁷. Adsorbates
from propargyl alcohol retain the C_3 structure, with only a very small amount of CO_{ad} being detected. Complete coverage was observed for E_{ad} > 0.15 V, oxidation of these species occurring at potentials in the platinum oxide region.

According to previous studies, the residues from formic acid, ethanol, and propargyl alcohol on platinum in acid media are different, and therefore, changes should be expected when one of these compounds reacts on platinum modified by the residues of one of the other compounds. Differential electrochemical mass spectrometry (DEMS) was selected as the appropriate technique for these studies.

**Experimental**

The solutions were prepared with Millipore-MilliQ water and analytical grade chemicals. 0.1 M HCOOH, CH_3CH_2OH and HC≡CCH_2OH were added to the supporting electrolyte (0.5 M H_2SO_4). Isotopically-labeled ^13C formic acid (Cambridge Isotope Laboratories, ^13C 99.5%) was employed without further purification. All experiments were performed at room temperature under argon atmosphere.

The electrochemical cell was a flow cell containing approx. 2 cm^3 solution. The working electrode was a platinum layer sputtered on a microporous PTFE membrane (Scimat 200/40/60). The real area, measured by H adsorption, varied between 4 and 20 cm^2. The electrode was activated by potential cycling at 0.10 V s\(^{-1}\) in the supporting electrolyte solution between the onset potentials for hydrogen and oxygen evolution. A platinum wire was the counter electrode, and a reversible hydrogen electrode (RHE) in the supporting electrolyte was used as the reference. The DEMS cell was directly attached to the vacuum chamber containing the mass spectrometer (Balzers QMG 112) with a Faraday cup detector. More details have been described elsewhere.

**Experimental procedure**

After activation of the electrode, the potential was set at the admission potential E_{ad} = 0.30 or 0.35 V, the solution containing the first organic compound was introduced into the cell and the current transient was recorded for 3 min. The organic solution was then completely replaced by pure supporting electrolyte at E_{ad}. This procedure was repeated for the coadsorption of a second compound increasing the adsorption time to 10 min. The charge densities observed upon admission of each compound, Q_{11} and Q_{22}, were obtained by integration of the current transients. Finally, a forward potential scan starting at E_{ad} and going up to 1.50 V was performed at a scan rate of 0.01 V s\(^{-1}\). Successive cyclic voltammograms (CVs) and mass spectrometric cyclic voltammograms (MSCVs) for CO_{2} were simultaneously recorded between 0.05 and 1.50 V. The total charge density involved in the electro-oxidation process Q_{ox} was calculated by integrating the anodic currents in the CVs and subtracting the platinum oxide current. The integrated ion charge, Q_{i}, was obtained from the MSCVs.

**Results and Discussion**

\(^{1}\text{HCOOH} 2^\text{nd} \text{HC≡CCH}_2\text{OH} \text{consecutive adsorption}\)

A small anodic current transient of 6 μC cm\(^{-2}\) was obtained during the adsorption of propargyl alcohol at E_{ad} = 0.30 V on a platinum surface covered by formic acid residues (Table 1). The CV (solid line in Fig. 1) displays two contributions, at 0.78 V (in the double layer region) and at around 1.13 V (in the potential region of Pt oxide formation). In order to establish the differences between this

![Figure 1. CVs for the electro-oxidation of the coadsorbates formed at $E_{ad} = 0.30$ V on a porous Pt electrode (real area = 4 cm\(^2\)) in 0.5 M H\(_2\)SO\(_4\) (first cycle after adsorption): (---) \(^{1}\text{HCOOH} 2^\text{nd} \text{HC≡CCH}_2\text{OH and} (----) \(^{1}\text{H}_2\text{C≡CCH}_2\text{OH} 2^\text{nd} \text{HCOOH}; (-----) \text{CV in pure supporting electrolyte.}

### Table 1. Charge densities (Q) of the transients produced by admission at E_{ad} = 0.30 V of formic acid, propargyl alcohol, and the two compounds added successively (see text), and the anodic charge density (Q_{ox}) and peak potentials (E_{p1} and E_{p2}) obtained in a subsequent CV.

| Compound          | Q_{11} (μC cm\(^{-2}\)) | Q_{22} (μC cm\(^{-2}\)) | Q_{ox} (μC cm\(^{-2}\)) | E_{p1} (V) | E_{p2} (V) |
|-------------------|--------------------------|--------------------------|--------------------------|------------|------------|
| HCOOH             | 1500                     | —                        | 230                      | 0.76       | —          |
| HC≡CCH\(_2\)OH    | 40                       | —                        | 730                      | —          | 1.18       |
| \(^{1}\)HCOOH 2^\text{nd} \text{HC≡CCH}_2\text{OH} | 1500                     | 6                        | 520                      | 0.78       | 1.13       |
| \(^{1}\)HC≡CCH\(_2\)OH 2^\text{nd} HCOOH | 40                       | —                        | 730                      | —          | 1.18       |
adlayer and those obtained for each compound separately, the individual adsorption of formic acid and propargyl alcohol was performed at the same E_ad. Adsorption charges and peak potentials for the forward transition potential scan are summarized in Table 1.

The value of Q_{1} for the current transient at 0.30 V of pure formic acid on a "clean" platinum electrode, i.e., not covered with organic residues, is 1500 µC cm^{-2}, much higher than a 2e^{-} monolayer (~400 µC cm^{-2}), which means that at this E_ad, bulk oxidation of formic acid occurs simultaneous with the adsorption. During the first anodic stripping voltammogram, a peak at 0.76 V with a charge density of 230 µC cm^{-2} appears. In the case of pure propargyl alcohol, the anodic transient, also at 0.30 V, is much smaller (Q_{1} = 40 µC cm^{-2}), but Q_{ox} is significantly higher (730 µC cm^{-2}). The oxidation takes place in the platinum oxide region, producing a broad peak at 1.18 V.

According to the above results for the individual adsorption of formic acid and propargyl alcohol, the peak at around 0.80 V in the CV for the stripping of the coadsorbed layer (Fig. 1 - solid line) seems to correspond to the oxidation of formic acid residues, whereas the anodic peak at 1.13 V could be assigned to propargyl alcohol residues. Comparing the value of Q_{ox} = 520 µC cm^{-2} obtained from the 1st HCOOH 2nd HC≡CCHOH coadsorption process with Q_{ox} for formic acid (see Table 1), the charge density increases by 290 µC cm^{-2}. In previous research, a maximum coverage of 0.85 was established for pure formic acid residues at E_ad = 0.30 V, 15% of the surface remaining free. Then an excess of only 730 x 0.15 /110 µC cm^{-2} should be expected if there is no replacement of formic acid adspecies by propargyl alcohol residues. Since the experimental value is 290 µC cm^{-2}, it seems that there is a replacement of formic acid residues by propargyl alcohol. However, cyclic voltammetry cannot provide clear proof of this replacement.

The DEMS technique using isotopically labeled H^{13}COOH makes it possible to distinguish each contribution in the coadsorbed layer, providing unquestionable evidence of whether the replacement reactions occur or not. Fig. 2 displays the MSCVs for m/z = 44 ([^{13}CO_{2}]^{+}) related to the production of CO_{2} from propargyl alcohol (solid line), and m/z = 45 ([^{13}CO_{2}]^{+}) corresponding to formic acid residue oxidation to CO_{2} (dotted line) in a 1st H^{13}COOH 2nd HC≡CCHOH experiment. The results from this experiment, from a similar one but with reverse adsorption order, and from the two pure compounds are shown in Table 2. The ion charge of the m/z = 45 signal for the oxidation of formic acid species in the coadsorbate (14.0 a.u.) in the experiment of Fig. 2 is similar to that for the adsorption of pure formic acid (15.1 a.u.), the difference being within experimental error. Thus, it is clear that no replacement of formic acid residues by propargyl alcohol occurs. On the contrary, Q_{1} for the m/z = 44 signal from propargyl alcohol oxidation in the coadsorbate (9.8 a.u.) is about 50% of the ion charge for the oxidation of pure propargyl alcohol residues. However, the charge density corresponding to the anodic admission transient for propargyl alcohol in the experiment of Fig. 2, Q_{2} = 6 µC cm^{-2}, is only 15% of the anodic transient of 40 µC cm^{-2} for the admission of pure propargyl alcohol (Table 1). As no replacement of formic acid residues is observed, a modification in the composition of the adsorbed layer of propargyl alcohol possibly occurs, especially since it has been shown that propargyl alcohol residues are a mixture

![Figure 2. MSCVs for the electro-oxidation of the coadsorbate 1st HCOOH 2nd HC≡CCHOH formed at E_ad = 0.30 V on a porous Pt electrode (real area = 4 cm^{2}) in 0.5 M H_{2}SO_{4} (first cycle after adsorption): (-----) ion current for m/z = 44 and (........) ion current for m/z =](image)

**Table 2.** Integrated CO_{2} mass signals from MSCVs obtained during the electro-oxidation of H^{13}COOH and HC≡CCHOH residues and corresponding coadsorbates (E_ad = 0.30 V).

| Compound | Q_{1} (a.u.)^{8} m/z = 44 (from HC≡CCHOH) | Q_{1} (a.u.)^{8} m/z = 45 (from HCOOH) |
|----------|----------------------------------------|----------------------------------------|
| H^{13}COOH | --- | 15.1 |
| HC≡CCHOH | 18.2 | --- |
| 1st H^{13}COOH 2nd HC≡CCHOH | 9.7 | 14.0 |
| 1st HC≡CCHOH 2nd H^{13}COOH | 18.2 | --- |

^{8} (a.u.) = arbitrary units.
of different adsorbates. The value of \( Q_2 \) obtained in the successive adsorption experiment agrees with the dissociative adsorption of propargyl alcohol on one Pt site, producing \( \text{Pt-CHOH-\equiv CH} \) and \( \text{Pt-\equiv C-CH}_2\text{OH} \).

It should be mentioned that propargyl alcohol residues oxidize not only at potentials in the Pt oxide region, but also in the double layer region in a first peak at around 0.80 V (see MSCV in Fig. 2 - solid line). A similar MSCV was observed for pure propargyl alcohol adsorbed at \( E_{ad} = 0.05 \) V. Thus, propargyl alcohol seems to adsorb in the same way on a Pt surface covered by H or formic acid residues.

It should be mentioned that formic acid residues oxidize not only at potentials in the Pt oxide region, but also in the double layer region in a first peak at around 0.80 V (see MSCV in Fig. 2 - solid line). A similar MSCV was observed for pure propargyl alcohol adsorbed at \( E_{ad} = 0.05 \) V. Thus, propargyl alcohol seems to adsorb in the same way on a Pt surface covered by H or formic acid residues.

Comparing the MSCVs in Fig. 2 with those from the oxidation of the residues formed from pure propargyl alcohol and formic acid, it can be concluded that both compounds form domains that maintain their individual characteristics.

### 1\(^{st}\) HCOOH 2\(^{nd}\) CH\(_3\)CH\(_2\)OH consecutive adsorption

The absence of formic acid adsorption at \( E_{ad} = 0.30 \) V on a platinum electrode covered by propargyl alcohol residues can be seen in the CV in Fig. 1 (dashed line), which coincides with that obtained for propargyl alcohol residues. No current transient is observed upon the admission of formic acid, and the charge \( Q_{ox} \) for the oxidation of propargyl alcohol residues is the same as for pure propargyl alcohol (Table 1). No potential-dependent mass signal for \( m/z = 45 \) was observed, which shows the absence of formic acid residues. These experiments confirm that the reactivity of formic acid on platinum is completely inhibited by propargyl alcohol residues.

### 1\(^{st}\) HCOOH 2\(^{nd}\) CH\(_3\)CH\(_2\)OH consecutive adsorption

For this study, \( E_{ad} \) was set at 0.35 V, because at this potential the maximum coverage for the individual adsorption of ethanol was observed. The anodic current transient during the adsorption of ethanol on a platinum surface modified by formic acid residues has a charge of \( Q_2 = 95 \) \( \mu \)C cm\(^{-2} \) (Table 3). Figure 3a shows the first and second CVs for the oxidation of the residues. During the first forward scan, an oxidation peak appears at about 0.70 V, involving a charge density of 265 \( \mu \)C cm\(^{-2} \) (Table 3).

Both ethanol and formic acid mainly oxidize in the same potential region, i.e. before the onset of platinum oxide formation, and therefore, the peak potential cannot give any information on the nature of the coadsorbed layer. It should be mentioned that ethanol also shows a small contribution in the PtO region during the oxidation of its residues which is not present in the case of formic acid adsorbates. The \( Q_{ox} \) for pure formic acid and ethanol processes are 7180 and 460 \( \mu \)C cm\(^{-2} \), whereas \( Q_{ox} \) is 205 \( \mu \)C cm\(^{-2} \) for formic acid adsorbates and 300 \( \mu \)C cm\(^{-2} \) for ethanol. The value of \( Q_{ox} \) for the 1\(^{st}\) HCOOH 2\(^{nd}\) CH\(_3\)CH\(_2\)OH

| Compound                  | \( Q_{t1} (\mu \text{C cm}^{-2}) \) | \( Q_{t2} (\mu \text{C cm}^{-2}) \) | \( Q_{ox} (\mu \text{C cm}^{-2}) \) |
|---------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| HCOOH                     | 7180                              | —                                 | 205                               |
| CH\(_3\)CH\(_2\)OH         | 460                               | —                                 | 300                               |
| 1\(^{st}\) HCOOH 2\(^{nd}\) CH\(_3\)CH\(_2\)OH | 7180                              | 95                                | 265                               |
| 1\(^{st}\) CH\(_3\)CH\(_2\)OH 2\(^{nd}\) HCOOH | 460                               | 2950                              | 320                               |

**Figure 3.** Electro-oxidation of 1\(^{st}\) H\(^{13}\)COOH 2\(^{nd}\) CH\(_3\)CH\(_2\)OH residues coadsorbed at \( E_{ad} = 0.35 \) V on a porous Pt electrode (real area = 15 cm\(^2\)) in 0.5 M H\(_2\)SO\(_4\): (a) the CVs for the first and second potential cycle after adsorption starting with a forward scan; (b) the MSCVs for \( m/z = 44 \) (—) and \( m/z = 45 \) (-----) for the first potential cycle after

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**Table 3.** Charge densities \( (Q) \) of the transients produced by admission at \( E_{ad} = 0.30 \) V of formic acid, ethanol, and the two compounds added successively (see text), and the anodic charge density \( (Q_{ox}) \) and peak potentials \( (E_{p1} \text{ and } E_{p2}) \) obtained in a subsequent CV.
coadsorption experiment lies between those obtained for the individual adsorption of formic acid and ethanol. No more information can be obtained from the CVs.

The MSCVs for the mass signals m/z = 45 of H$^{13}$COOH oxidation (dotted line) and m/z = 44 for ethanol residues (solid line) recorded simultaneously with the CV for the stripping of the coadsorbate are given in Fig. 3b. The integrated ion currents are 6.2 a.u. for CO$_2$ from ethanol and 12.4 a.u. for CO$_2$ from formic acid (Table 4). The signal related to ethanol is much higher than 15% of the value of 21.2 obtained with pure ethanol. Since for the adsorption of formic acid a value of Q$_I$ = 16.0 a.u. is measured, a replacement of about 25% of formic acid residues by ethanol is established.

$^{1}$CH$_3$CH$_2$OH  2$^{nd}$ HCOOH consecutive adsorption

The anodic current transient of 2950 µC cm$^{-2}$ obtained at 0.35 V for formic acid on a platinum surface poisoned by ethanol residues suggests that bulk oxidation of formic acid takes place at this modified electrode. The CVs for the first and second potential cycles after the coadsorption of $^{1}$CH$_3$CH$_2$OH 2$^{nd}$ HCOOH are shown in Fig. 4a. Two potential regions for the oxidation of the adsorbates are distinguished: the first between 0.50 and 0.90 V with an anodic peak at 0.70 V, and the second for E > 0.90 V as a broad peak. These CVs are similar to those for the adsorption experiment with ethanol$^3$. Thus, it can be established that the oxidation of ethanol predominates, but the presence of formic acid residues cannot be disregarded. The MSCVs in Fig. 4b demonstrate that a small amount of formic acid is coadsorbed (dotted line), involving an ion charge for m/z = 45 of 2.1 a.u., in reasonable agreement with the adsorption of formic acid on 15% of free Pt sites after ethanol adsorption (16.0 x 0.15 = 2.4). In the same way, the ion charge for m/z = 44, Q$_I$ = 19.8 a.u., obtained for the contribution of ethanol in the coadsorbate (solid line in Fig. 4b) coincides with the value of Q$_I$ = 21.2 a.u. for pure ethanol within experimental error. Thus, it is concluded that no replacement takes place, formic acid only adsorbing on the free sites of the Pt surface.

**Concluding Remarks**

The application of DEMS using isotopically labeled compounds to study multicomponent systems makes it possible to distinguish the contributions of the different compounds in the coadsorbate. Thus, the nature of the interaction between the chemisorbates of each compound can be established. No replacement occurs during the adsorption of propargyl alcohol on a platinum surface covered by formic acid residues, in opposition to the case of ethanol. The reactivity of formic acid with a platinum surface is inhibited by propargyl alcohol residues, whereas it can react without replacement on the free platinum sites of the surface modified by the ethanol adsorbed layer.

**Table 4.** Integrated CO$_2$ mass signals from MSCVs during the electro-oxidation of H$^{13}$COOH and CH$_3$CH$_2$OH residues, and corresponding coadsorbates (E$_{ad}$ = 0.35 V).

| Compound                  | Q$_I$ (a.u.)$^\#$ m/z = 44 (from CH$_3$CH$_2$OH) | Q$_I$ (a.u.)$^\#$ m/z = 45 (from HCOOH) |
|---------------------------|-----------------------------------------------|----------------------------------------|
| H$^{13}$COOH              | ---                                           | 16.0                                   |
| CH$_3$CH$_2$OH            | 21.2                                          | ---                                    |
| $^{1}$H$^{13}$COOH 2$^{nd}$CH$_3$CH$_2$OH | 6.2                                           | 12.4                                   |
| $^{1}$CH$_3$CH$_2$OH 2$^{nd}$H$^{13}$COOH | 19.8                                          | 2.1                                    |

$^\#$(a.u.) = arbitrary units.
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