

Article

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

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A absorção consecutiva do ácido fórmico e do álcool propargílico assim como a do ácido fórmico e o etanol sobre platina em meio ácido foram estudados por espectrometria de massa "online" (DEMS). A oxidação das espécies co-adsorvidas que permaneceram na superfície do eletrodo após um experimento em célula de fluxo resultou somente em CO<sub>2</sub>. Usando H<sup>13</sup>COOH isotopicamente modificado, a contribuição do ácido fórmico durante a eletro-oxidação dos co-adsorvatos pode ser distinguida daquelas do etanol ou de resíduos do álcool propargílico. Foi verificado que o etanol substitui os resíduos do ácido fórmico, enquanto que a absorção do álcool propargílico é modificada pela presença do ácido fórmico na superfície. O ácido fórmico não pode ser quimisorvido numa superfície de platina coberta por resíduos do álcool propargílico, mas reage sem haver substituição em platina modificada por resíduos de etanol.

The consecutive adsorption 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 CO<sub>2</sub>. Using isotopically labeled H<sup>13</sup>COOH, 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 compound<sup>1-6</sup>, 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)<sup>1,2</sup>, ethanol (CH<sub>3</sub>CH<sub>2</sub>OH)<sup>3</sup>, and propargyl alcohol (HC≡CCH<sub>2</sub>OH)<sup>4-6</sup>.

The above-mentioned compounds form different adsorbates on the Pt surface. Formic acid produces mainly CO<sub>ad</sub><sup>1</sup>, although COH<sub>ad</sub> species may also be present<sup>2</sup>. CO<sub>ad</sub> 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 CO<sub>ad</sub> is formed, most of the adsorbates contain the C-C chain (O-CH<sub>2</sub>-CH<sub>3</sub>, COCH<sub>3</sub>, and =COHCH<sub>3</sub>)<sup>3</sup>. A maximum coverage of 0.85 is attained at an admission potential of E<sub>ad</sub> = 0.35 V for ethanol, and at E<sub>ad</sub> = 0.15-0.35 V for formic acid<sup>7</sup>. Adsorbates

from propargyl alcohol retain the  $C_3$  structure, with only a very small amount of  $CO_{ad}$  being detected<sup>6</sup>. Complete coverage was observed for  $E_{ad} > 0.15$  V<sup>6,8</sup>, 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<sup>®</sup> water and analytical grade chemicals. 0.1 M HCOOH,  $CH_3CH_2OH$  and  $HC\equiv CCH_2OH$  were added to the supporting electrolyte (0.5 M  $H_2SO_4$ ). Isotopically-labeled  $^{13}C$  formic acid (Cambridge Isotope Laboratories,  $^{13}C$  99%, chemical purity 94.5%) 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<sup>3</sup> 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<sup>2</sup>. The electrode was activated by potential cycling at 0.10 V s<sup>-1</sup> 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<sup>7,8</sup>.

### Experimental procedure

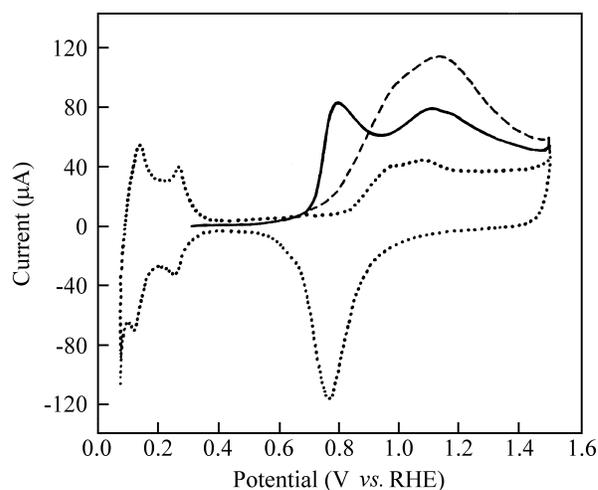
After activation of the electrode, the potential was set at the admission potential  $E_{ad} = 0.30$  or 0.35 V, the solution containing the first organic compound was introduced into the cell and the current transient was recorded for 3 min. The organic solution was then completely replaced by pure 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,  $Q_{t1}$  and  $Q_{t2}$ , 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<sup>-1</sup>. 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<sup>st</sup> HCOOH 2<sup>nd</sup> $HC\equiv CCH_2OH$ consecutive adsorption

A small anodic current transient of 6  $\mu C$  cm<sup>-2</sup> 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<sup>2</sup>) in 0.5 M  $H_2SO_4$  (first cycle after adsorption): (—) 1<sup>st</sup> HCOOH 2<sup>nd</sup>  $HC\equiv CCH_2OH$  and (---) 1<sup>st</sup>  $HC\equiv CCH_2OH$  2<sup>nd</sup> HCOOH; (.....) CV in pure supporting electrolyte.

**Table 1.** Charge densities ( $Q_t$ ) 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	$Q_{t1}$ ( $\mu C$ cm <sup>-2</sup> )	$Q_{t2}$ ( $\mu C$ cm <sup>-2</sup> )	$Q_{ox}$ ( $\mu C$ cm <sup>-2</sup> )	$E_{p1}$ (V)	$E_{p2}$ (V)
HCOOH	1500	—	230	0.76	—
$HC\equiv CCH_2OH$	40	—	730	—	1.18
1 <sup>st</sup> HCOOH 2 <sup>nd</sup> $HC\equiv CCH_2OH$	1500	6	520	0.78	1.13
1 <sup>st</sup> $HC\equiv CCH_2OH$ 2 <sup>nd</sup> HCOOH	40	—	730	—	1.18

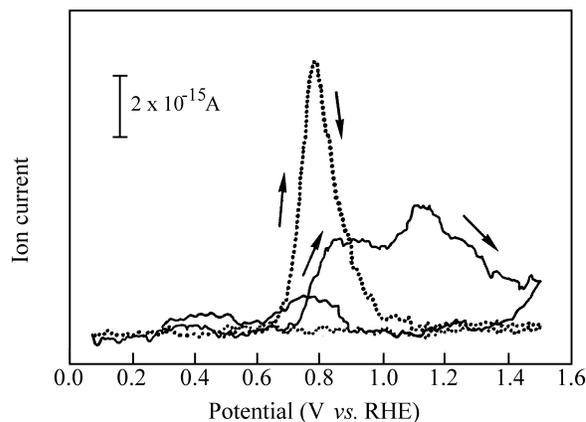
adlayer and those obtained for each compound separately, the individual adsorption of formic acid and propargyl alcohol was performed at the same  $E_{ad}$ . Adsorption charges and peak potentials for the first forward potential scan are summarized in Table 1.

The value of  $Q_{I1}$  for the current transient at 0.30 V of pure formic acid on a "clean" platinum surface, *i.e.* not covered with organic residues, is  $1500 \mu\text{C cm}^{-2}$ , much higher than a  $2e^-$  monolayer ( $\sim 400 \mu\text{C cm}^{-2}$ ), 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  $230 \mu\text{C cm}^{-2}$  appears. In the case of pure propargyl alcohol, the anodic transient, also at 0.30 V, is much smaller ( $Q_{I1} = 40 \mu\text{C cm}^{-2}$ ), but  $Q_{ox}$  is significantly higher ( $730 \mu\text{C cm}^{-2}$ )<sup>6,7</sup>. The oxidation takes place in the platinum oxide region, producing a broad peak at 1.18 V<sup>6,7</sup>.

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  $Q_{ox} = 520 \mu\text{C cm}^{-2}$  obtained from the 1<sup>st</sup> HCOOH 2<sup>nd</sup> HC≡CCHOH coadsorption process with  $Q_{ox}$  for formic acid (see Table 1), the charge density increases by  $290 \mu\text{C cm}^{-2}$ . In previous research, a maximum coverage of 0.85 was established for pure formic acid residues at  $E_{ad} = 0.30 \text{ V}$ , 15% of the surface remaining free. Then an excess of only  $730 \times 0.15 = 110 \mu\text{C cm}^{-2}$  should be expected if there is no replacement of formic acid adspecies by propargyl alcohol residues. Since the experimental value is  $290 \mu\text{C cm}^{-2}$ , 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  $\text{H}^{13}\text{COOH}$  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  $m/z = 44$  ( $[\text{C}^{12}\text{CO}_2]^+$ ) related

to the production of  $\text{CO}_2$  from propargyl alcohol (solid line), and  $m/z = 45$  ( $[\text{C}^{13}\text{CO}_2]^+$ ) corresponding to formic acid residue oxidation to  $\text{CO}_2$  (dotted line) in a 1<sup>st</sup>  $\text{H}^{13}\text{COOH}$  2<sup>nd</sup>  $\text{HC}\equiv\text{CCH}_2\text{OH}$  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,  $Q_I$  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,  $Q_{I2} = 6 \mu\text{C cm}^{-2}$ , is only 15% of the anodic transient of  $40 \mu\text{C cm}^{-2}$  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 1<sup>st</sup>  $\text{H}^{13}\text{COOH}$  2<sup>nd</sup>  $\text{HC}\equiv\text{CCH}_2\text{OH}$  formed at  $E_{ad} = 0.30 \text{ V}$  on a porous Pt electrode (real area =  $4 \text{ cm}^2$ ) in  $0.5 \text{ M H}_2\text{SO}_4$  (first cycle after adsorption): (—) ion current for  $m/z = 44$  and (.....) ion current for  $m/z =$

**Table 2.** Integrated  $\text{CO}_2$  mass signals from MSCVs obtained during the electro-oxidation of  $\text{H}^{13}\text{COOH}$  and  $\text{HC}\equiv\text{CCH}_2\text{OH}$  residues and corresponding coadsorbates ( $E_{ad} = 0.30 \text{ V}$ ).

Compound	$Q_I$ (a.u.) <sup>#</sup> $m/z = 44$ (from $\text{HC}\equiv\text{CCH}_2\text{OH}$ )	$Q_I$ (a.u.) <sup>#</sup> $m/z = 45$ (from $\text{HCOOH}$ )
$\text{H}^{13}\text{COOH}$	—	15.1
$\text{HC}\equiv\text{CCH}_2\text{OH}$	18.2	—
1 <sup>st</sup> $\text{H}^{13}\text{COOH}$ 2 <sup>nd</sup> $\text{HC}\equiv\text{CCH}_2\text{OH}$	9.7	14.0
1 <sup>st</sup> $\text{HC}\equiv\text{CCH}_2\text{OH}$ 2 <sup>nd</sup> $\text{H}^{13}\text{COOH}$	18.2	—

<sup>#</sup> (a.u.) = arbitrary units.

of different adsorbates<sup>6</sup>. The value of  $Q_{t2}$  obtained in the successive adsorption experiment agrees with the dissociative adsorption of propargyl alcohol on one Pt site, producing Pt-CHOH-C≡CH and Pt-C≡C-CH<sub>2</sub>OH<sup>7</sup>.

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<sup>7</sup>.

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<sup>st</sup> HC≡CCH<sub>2</sub>OH 2<sup>nd</sup> HCOOH consecutive adsorption*

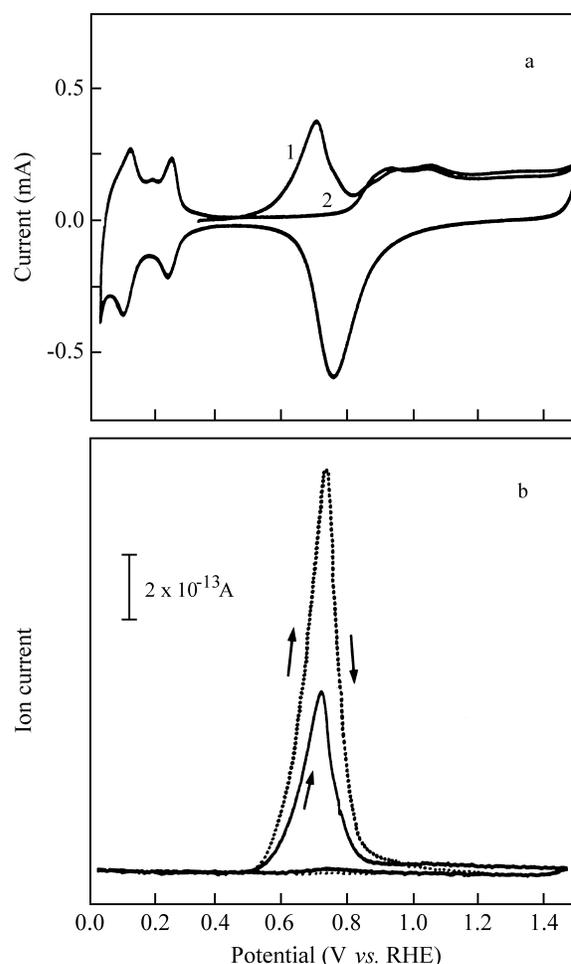
The absence of formic acid adsorption at  $E_{ad} = 0.30$  V on a platinum electrode covered by propargyl alcohol residues can be seen in the CV in Fig. 1 (dashed line), which coincides with that obtained for propargyl alcohol residues<sup>6,7</sup>. No current transient is observed upon the admission 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<sup>7</sup>, 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<sup>st</sup> HCOOH 2<sup>nd</sup> CH<sub>3</sub>CH<sub>2</sub>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  $Q_{t2} = 95 \mu\text{C cm}^{-2}$  (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  $265 \mu\text{C cm}^{-2}$  (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<sup>3</sup> which is not present in the case of formic acid adsorbates<sup>7</sup>. The  $Q_{t1}$  for pure formic acid and ethanol processes are  $7180$  and  $460 \mu\text{C cm}^{-2}$ , whereas  $Q_{ox}$  is  $205 \mu\text{C cm}^{-2}$  for formic acid adsorbates and  $300 \mu\text{C cm}^{-2}$  for ethanol. The value of  $Q_{ox}$  for the 1<sup>st</sup> HCOOH 2<sup>nd</sup> CH<sub>3</sub>CH<sub>2</sub>OH



**Figure 3.** Electro-oxidation of 1<sup>st</sup> H<sup>13</sup>COOH 2<sup>nd</sup> CH<sub>3</sub>CH<sub>2</sub>OH residues coadsorbed at  $E_{ad} = 0.35$  V on a porous Pt electrode (real area =  $15 \text{ cm}^2$ ) in  $0.5 \text{ M H}_2\text{SO}_4$ : (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

**Table 3.** Charge densities ( $Q_i$ ) 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 ( $E_{p1}$  and  $E_{p2}$ ) obtained in a subsequent CV.

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 <sub>3</sub> CH <sub>2</sub> OH	460	—	300
1 <sup>st</sup> HCOOH 2 <sup>nd</sup> CH <sub>3</sub> CH <sub>2</sub> OH	7180	95	265
1 <sup>st</sup> CH <sub>3</sub> CH <sub>2</sub> OH 2 <sup>nd</sup> HCOOH	460	2950	320

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  $\text{H}^{13}\text{COOH}$  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  $\text{CO}_2$  from ethanol and 12.4 a.u. for  $\text{CO}_2$  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  $Q_1 = 16.0$  a.u. is measured, a replace-

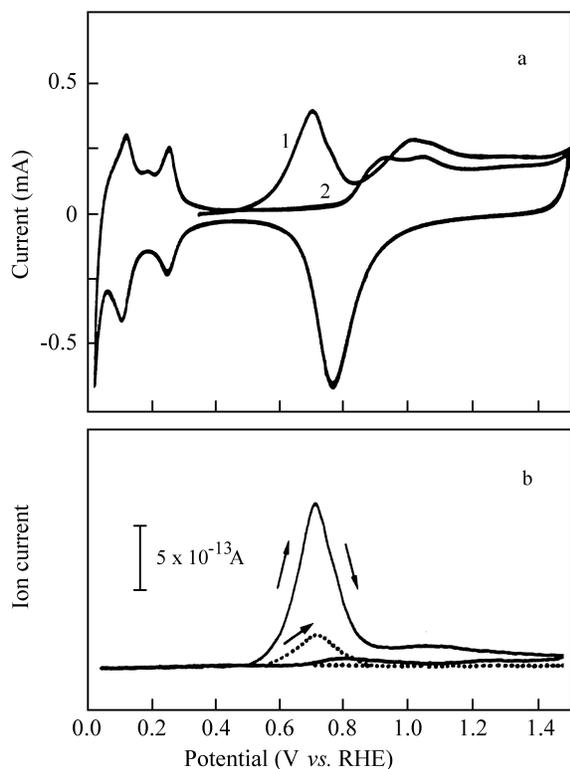
ment of about 25% of formic acid residues by ethanol is established.

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

The anodic current transient of  $2950 \mu\text{C cm}^{-2}$  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  $1^{\text{st}}\text{CH}_3\text{CH}_2\text{OH}$   $2^{\text{nd}}\text{HCOOH}$  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<sup>3</sup>. 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 ( $16.0 \times 0.15 = 2.4$ ). In the same way, the ion charge for  $m/z = 44$ ,  $Q_1 = 19.8$  a.u., obtained for the contribution of ethanol in the coadsorbate (solid line in Fig. 4b) coincides with the value of  $Q_1 = 21.2$  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 coadlayer. 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.



**Figure 4.** Electro-oxidation of  $1^{\text{st}}\text{CH}_3\text{CH}_2\text{OH}$   $2^{\text{nd}}\text{H}^{13}\text{COOH}$  residues coadsorbed at  $E_{\text{ad}} = 0.35$  V on a porous Pt electrode (real area =  $15 \text{ cm}^2$ ) in  $0.5 \text{ M H}_2\text{SO}_4$ : (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

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

Compound	$Q_1$ (a.u.) <sup>#</sup> $m/z = 44$ (from $\text{CH}_3\text{CH}_2\text{OH}$ )	$Q_1$ (a.u.) <sup>#</sup> $m/z = 45$ (from $\text{HCOOH}$ )
$\text{H}^{13}\text{COOH}$	—	16.0
$\text{CH}_3\text{CH}_2\text{OH}$	21.2	—
$1^{\text{st}}\text{H}^{13}\text{COOH}$ $2^{\text{nd}}\text{CH}_3\text{CH}_2\text{OH}$	6.2	12.4
$1^{\text{st}}\text{CH}_3\text{CH}_2\text{OH}$ $2^{\text{nd}}\text{H}^{13}\text{COOH}$	19.8	2.1

<sup>#</sup> (a.u.) = arbitrary units.

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