

MULTIPLE ADSORBATE INTERACTIONS BETWEEN REDUCED CO₂ ADSORBATES AND EITHER ALLYL ALCOHOL OR PROPARGYL ALCOHOL RESIDUES ON PLATINUM IN 0.5 M SULPHURIC ACID

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(Received 11 July 1991; in revised form 27 August 1991)

Abstract—The interaction of propargyl alcohol and allyl alcohol with a platinum (Pt) electrode modified by the presence of reduced CO₂ adsorbates (r-CO₂) is studied through voltammetry and potentiostatic current transients by using a flow cell technique. The interaction between each alcohol and r-CO₂ is promoted at three constant potentials corresponding to different degrees of Pt surface coverage by H-atoms. For both alcohols the anodic stripping peaks and the charge balance are interpreted in terms of the formation of composed adsorbates. Based upon the probable r-CO₂ structure and H-bonding interactions between r-CO₂ and the alcohol molecules or their adsorbed residues, average alcohol residues/r-CO₂ molecular ratios are estimated.

Key words: reduced CO₂, allyl alcohol, propargyl alcohol, adsorbate interactions, anodic stripping.

INTRODUCTION

The formation of reduced carbon dioxide on platinum electrodes takes place when CO₂ dissolved in an acid electrolyte interacts with a Pt electrode covered by H-atoms[1, 2]. Depending on the adsorption conditions, the presence of two types of reduced CO₂ (r-CO₂) species can be inferred from the electrooxidation voltammograms. Both species can be electrodeposited within a potential range which lies close to the threshold potential of the O-atom electroadsorption reaction[3–5]. Similar conclusions concerning the number of r-CO₂ species can be derived from IRRAS and FTIRRAS data[6, 7].

As there is a relatively wide potential range where stable reduced CO₂-adsorbates can be formed on Pt, the possibility of promoting the formation of composed adsorbates through the addition of a foreign substance to the solution can be explored. The formation of composed adsorbates has been recently investigated on polycrystalline Pt electrode saturated with CO adsorbates interacting with unsaturated alcohol residues in acid solutions[8]. This type of process has been reported for CO-modified Pt electrodes with other simple organic molecules, and the composed adsorbates formed under these conditions have been described in terms of mixed adlattices involving lateral modifications and adsorbate reorganisations to approach defined structural situations[9].

The present paper refers to new interactions at constant potential in acid solution between reduced CO₂ adsorbates on Pt, and residues which result from the electroadsorption of either propargyl alcohol (PA) or allyl alcohol (AA). These results allow us to

advance limiting average stoichiometries for possible coadsorbates produced at different potentials.

EXPERIMENTAL

Runs were made in 0.5 M H₂SO₄ by using a 50 ml capacity flowing electrolyte electrochemical cell technique[10] with the usual arrangement of three electrodes. A polycrystalline (pc) Pt working electrode (0.23 cm² real surface area) was encased in a glass holder. The counter electrode was a Pt electrode (ca 1 cm² geometric area) mounted in a separate compartment. A Hg/Hg₂SO₄(s)/K₂SO₄(sat.)/0.5 M H₂SO₄ reference electrode (*mse*) (*E/V* (*nhe*) = 0.659) was employed. Potentials in the text are referred to the *mse* scale. The working electrode pretreatment consisted of a potential cycling in the –0.650 to 0.800 V range at 0.2 V s^{–1} in 0.5 M H₂SO₄.

The base electrolyte was prepared from 98% sulfuric acid (Merck p.a.) and Millipore-MilliQ*-water. The solutions of the different alcohols (PA and AA) were prepared from twice distilled p.a. chemicals. CO₂ was prepared from the reaction between 50% H₂SO₄ and NaHCO₃, and bubbled through the electrolyte solution under saturation. Runs were made at 25°C under either Ar or CO₂ atmosphere, depending on the stage of the experiment.

Each run consisted of the following steps. Firstly, the voltammetric behaviour of the H-atoms electroadsorption reactions were followed under potential cycling at 0.2 V s^{–1}. The stability of the cyclovoltammograms was taken as a purity test of the system following the criteria reported in the literature[11]. Then, the potential was set to *E*_{ad}(CO₂), the adsorption potential for CO₂. As the null current at this potential was reached, the solution was saturated

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with CO_2 to form the reduced CO_2 adsorbates. Subsequently, the solution was replaced by 0.5 M H_2SO_4 holding the value of $E_{\text{ad}}(\text{CO}_2)$. Afterwards, the potential was changed to $E_{\text{ad}}(\text{X})$, the adsorption potential for the unsaturated alcohol ($\text{X} = \text{PA}, \text{AA}$), and 2 ml of either 0.1 M PA or 0.1 M AA solution was added to produce the composed adsorbate. Simultaneously the current transient of the second electroadsorption process was recorded during 3 min, the time necessary to reach an adsorption-time-invariant anodic stripping voltammogram for the adsorbed residues. Occasionally, the adsorption of both substances was made at the same potential. From the current transients the total electroadsorption charge resulting from the addition of X was determined. Finally, after replacing the solution again by 0.5 M H_2SO_4 , the stripping voltammogram of the composed adsorbates was obtained at 0.2 V s^{-1} as indicated elsewhere[12]. The following adsorption potentials were chosen: $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ and -0.500 V ; $E_{\text{ad}}(\text{X}) = -0.650, -0.500$ and -0.250 V . At these potentials θ_{H} , the degree of surface coverage by H-atoms on Pt, is close to 1, 0.5 and 0, respectively.

RESULTS

Results from the blank are depicted in Fig. 1a-c for the sake of comparison. The anodic stripping voltammograms of r- CO_2 adsorbates (Fig. 1a) depend on $E_{\text{ad}}(\text{CO}_2)$. The value of $q_{\text{ox}}(\text{CO}_2)$, the r- CO_2 anodic

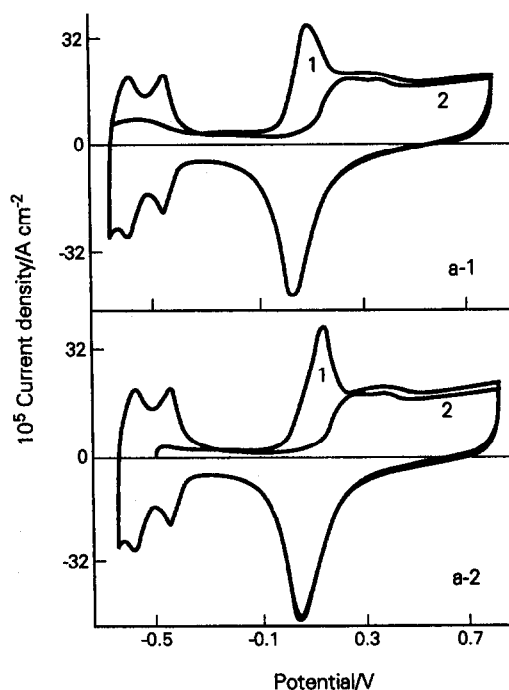


Fig. 1 (a).

stripping charge density, decreases only 20% when $E_{\text{ad}}(\text{CO}_2)$ is changed from -0.650 to -0.500 V

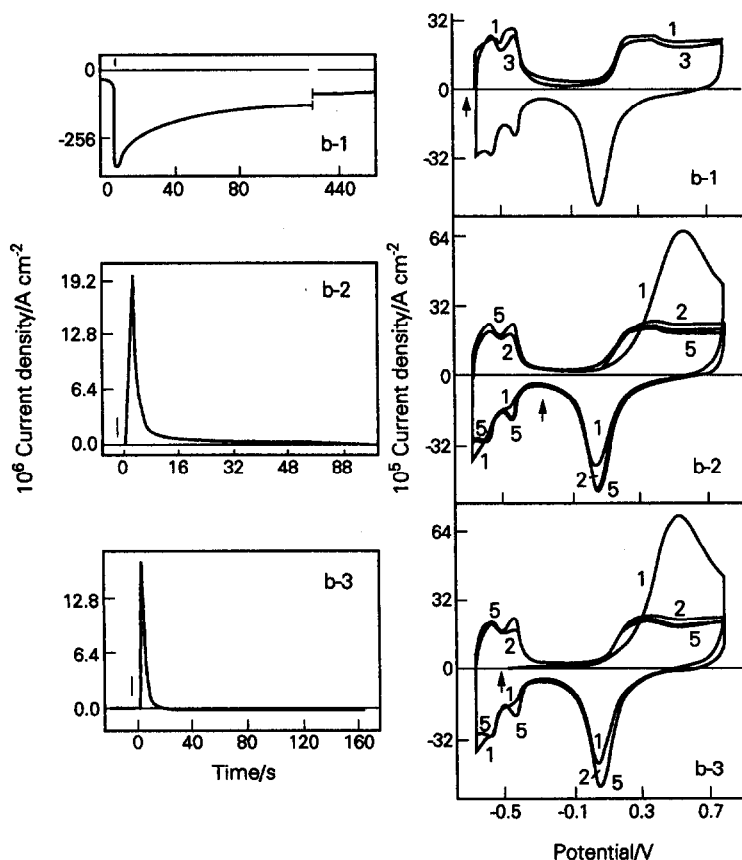


Fig. 1 (b).

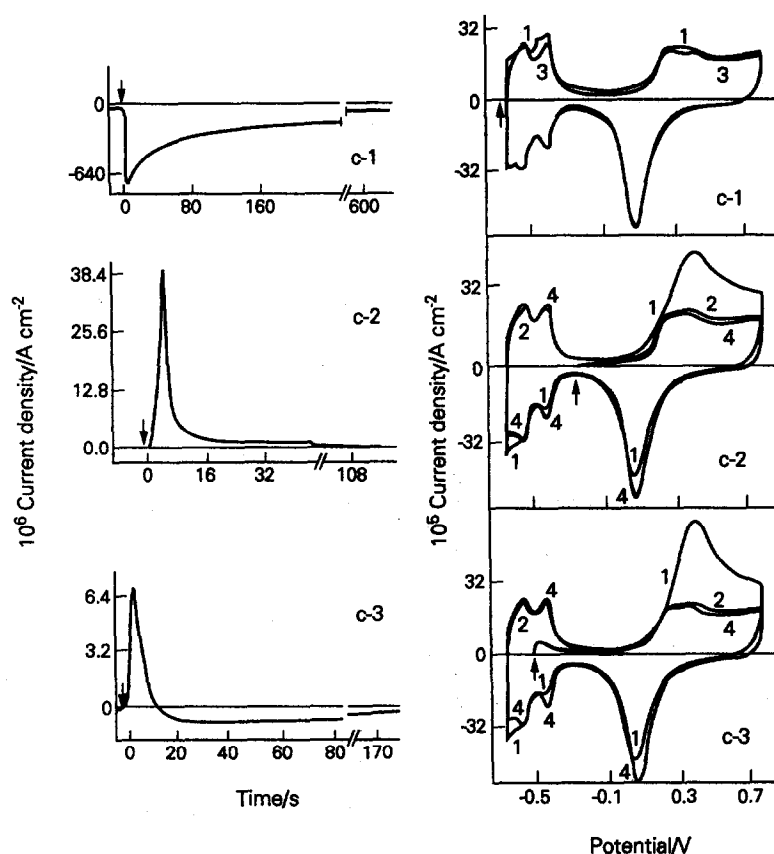


Fig. 1 (c).

Fig. 1. (a) First and second cyclic voltammograms for the anodic stripping of r-CO₂ at $v = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}} = -0.650 \text{ V}$ (a-1); $E_{\text{ad}} = -0.500 \text{ V}$ (a-2). (b) Cyclovoltammograms (1, 2, 5) corresponding to the anodic stripping of PA adsorbates at $v = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}} = -0.650 \text{ V}$ (b-1); $E_{\text{ad}} = -0.250 \text{ V}$ (b-2); $E_{\text{ad}} = -0.500 \text{ V}$ (b-3). (c) Cyclovoltammograms (1, 2, 4) corresponding to the anodic stripping of AA adsorbates at $v = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}} = -0.650 \text{ V}$ (c-1); $E_{\text{ad}} = -0.250 \text{ V}$ (c-2); $E_{\text{ad}} = -0.500 \text{ V}$ (c-3). The corresponding PA and AA electroadsorption current transients are also indicated.

(Table 1). The electroadsorption current transients and the anodic stripping voltammograms of the adsorbates produced on Pt from PA (Fig. 1b) and AA (Fig. 1c) at different $E_{\text{ad}}(\text{X})$ coincide with data recently published[13].

1. PA electroadsorption on Pt modified by r-CO₂

Firstly CO₂ was adsorbed at $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ ($\theta_{\text{H}} = 1$), for about 10 min to reach the r-CO₂ saturation coverage. The electroadsorption of PA

Table 1. Experimental charge density values and results from charge balance calculations

$E_{\text{ad}}(\text{CO}_2)/\text{V}$	$E_{\text{ad}}(\text{X})/\text{V}$	$q_{\text{ox}}(\text{CO}_2)/\text{mC cm}^{-2}$	$q_{\text{t}}(\text{X})/\text{mC cm}^{-2}$	$q_{\text{ox}}(\text{X})/\text{mC cm}^{-2}$	$q_{\text{t}}(\text{Y})/\text{mC cm}^{-2}$	$q_{\text{ox}}(\text{Y})/\text{mC cm}^{-2}$	n^*	$q_{\text{ox}}(\text{th})/\text{mC cm}^{-2}$	$\Delta q_{\text{ox}}(\text{X})/\text{mC cm}^{-2}$	$N(\text{X})^a$	$N(\text{X})^b$
X = PA											
-0.650	-0.650	0.21	-13.7	—	-2.23	0.48	—	—	0.27	0.28	0.33
-0.650	-0.500	0.21	0.09	1.05	0.01	0.64	—	—	0.43	0.44	0.51
-0.650	-0.250	0.21	0.18	0.95	0.04	0.63	4	0.44	0.42	0.44	0.51
-0.500	-0.650	0.18	-13.7	—	-2.80	0.46	—	—	0.28	0.33	0.39
-0.500	-0.500	0.18	0.09	1.05	0.05	0.65	—	—	0.47	0.56	0.66
-0.500	-0.250	0.18	0.18	0.95	0.07	0.69	2.6	0.53	0.51	0.60	0.70
X = AA											
-0.650	-0.650	0.21	-37.5	—	-21.4	0.21	—	—	—	—	—
-0.650	-0.500	0.21	0.05	0.70	-1.46	0.47	—	—	0.26	0.23	0.29
-0.650	-0.250	0.21	0.22	0.85	0.12	0.51	1.8	0.68	0.30	0.27	0.33
-0.500	-0.650	0.18	-37.5	—	-30.8	0.19	—	—	0.01	—	—
-0.500	-0.500	0.18	0.05	0.70	-0.85	0.45	—	—	0.27	0.28	0.35
-0.500	-0.250	0.18	0.22	0.85	0.11	0.55	1.9	0.63	0.37	0.38	0.47

^a $n(\text{PA}) = 14$; $n(\text{AA}) = 16$. ^b $n(\text{PA}) = 12$; $n(\text{AA}) = 13$.

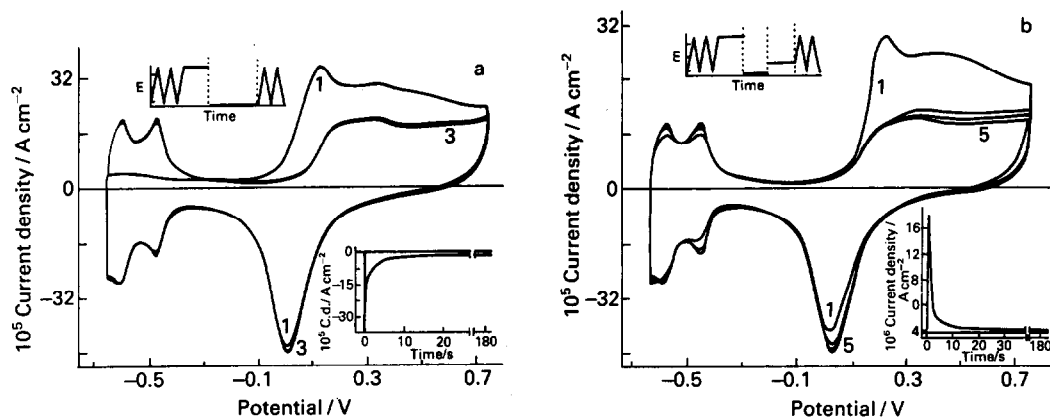


Fig. 2. (a) Cyclic voltammograms (1, 3) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{PA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$; $E_{\text{ad}}(\text{PA}) = -0.650 \text{ V}$. (b) Cyclic voltammograms (1, 5) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{PA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$; $E_{\text{ad}}(\text{PA}) = -0.250 \text{ V}$. The PA electroadsorption current transients and the potential routines are depicted in the insets.

at $E_{\text{ad}}(\text{PA}) = -0.650 \text{ V}$ produces an electroreduction current transient (Fig. 2a). The charge density for this process after 3 min becomes considerably smaller than that found for the blank (Fig. 1b). In contrast to Pt modified by CO adsorbates[8], the electroreduction of PA in the presence of $r\text{-CO}_2$ is not inhibited because H-atoms are available on Pt. The anodic stripping voltammogram resulting from $r\text{-CO}_2$ and PA residues differs from that depicted for $r\text{-CO}_2$ and PA residues (compare Figs 1a, 1b, and 2a). It shows firstly a small anodic current which is probably due to the electrodeposition of residual H-atoms and traces of molecular hydrogen in solution, followed by two partially overlapping anodic peaks (1 and 2) in -0.100 to 0.800 V range, peak 1 being higher than peak 2.

When PA is adsorbed at $E_{\text{ad}}(\text{PA}) = -0.250 \text{ V}$ (Fig. 2b), the electroadsorption current transient becomes definitely anodic comprising a limiting charge density value of *ca* 0.04 mC cm^{-2} . The anodic stripping voltammogram of the adsorbed residues presents also two anodic current peaks qualitatively

similar to those displayed in Fig. 2a, but in this case the initiation of the anodic processes takes place at potentials which are close to the O-electrodeposition threshold potential.

Results obtained by setting $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ and $E_{\text{ad}}(\text{PA}) = -0.500 \text{ V}$, differ also from the blank, as for the latter only an anodic PA electroadsorption current transient is observed. In this case the contribution of peak 1 is enhanced, its peak potential being intermediate between the peak potential values described previously.

When the $r\text{-CO}_2$ adsorbates are produced at $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$, *ie* below the $r\text{-CO}_2$ saturation coverage, and the PA electroadsorbed residues are formed at $E_{\text{ad}}(\text{PA}) = -0.650 \text{ V}$, the resulting electrochemical features are qualitatively comparable to those depicted in Fig. 2a.

On the other hand, when $E_{\text{ad}}(\text{PA}) = -0.250 \text{ V}$ (Fig. 3a), only an anodic electroadsorption current transient is observed, and the anodic stripping voltammogram shows that peak 2 results higher than peak 1.

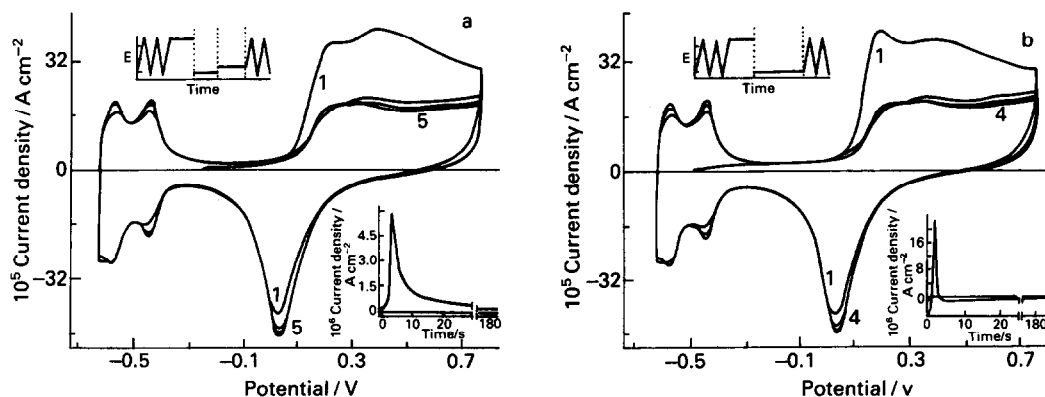


Fig. 3. (a) Cyclic voltammograms (1, 5) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{PA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$; $E_{\text{ad}}(\text{PA}) = -0.250 \text{ V}$. (b) Cyclic voltammograms (1, 4) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{PA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$; $E_{\text{ad}}(\text{PA}) = -0.500 \text{ V}$. The PA electroadsorption current transients and the potential routines are depicted in the insets.

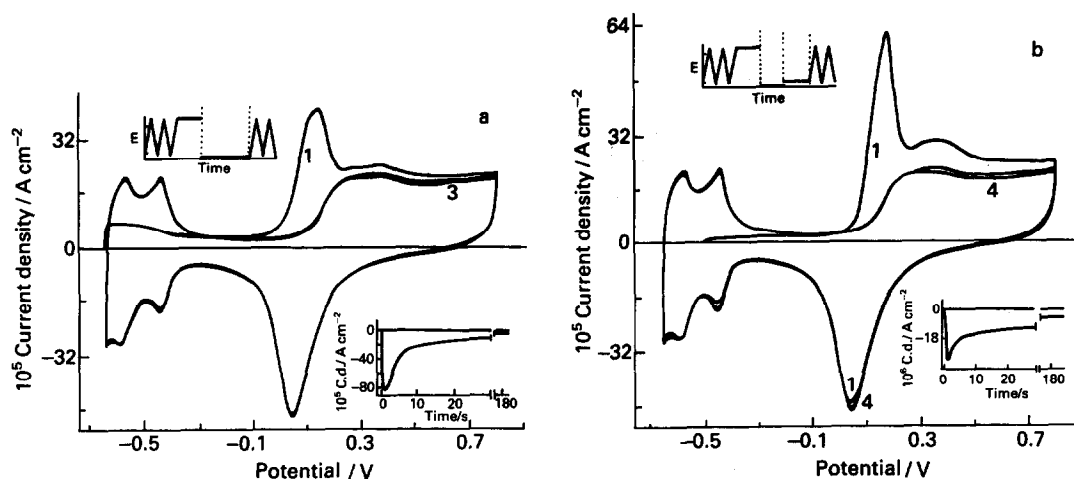


Fig. 4. (a) Cyclovoltammograms (1, 3) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{AA}$ adsorbates at $v = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$; $E_{\text{ad}}(\text{AA}) = -0.650 \text{ V}$. (b) Cyclovoltammograms (1, 4) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{AA}$ adsorbates at $v = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$; $E_{\text{ad}}(\text{AA}) = -0.500 \text{ V}$. The AA electroadsorption current transients and the potential routines are depicted in the insets.

Finally, in runs made by setting $E_{\text{ad}}(\text{CO}_2) = E_{\text{ad}}(\text{PA}) = -0.500 \text{ V}$ (Fig. 3b) the electroadsorption current transients exhibit firstly a very small cathodic spike followed by an anodic current which reaches a peaked value, then decreases, becomes cathodic and tends slowly to zero. In this case the anodic stripping voltammogram becomes comparable to that resulting for $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ and $E_{\text{ad}}(\text{PA}) = -0.500 \text{ V}$, except that the peak 1 to peak 2 height ratio approaches 1.

In all these runs only a few cyclovoltammograms are required for cleaning the Pt electrode and recovering the voltammogram of the $\text{Pt}/0.5 \text{ M H}_2\text{SO}_4$ system.

2. AA electroadsorption on Pt modified by $r\text{-CO}_2$

When $E_{\text{ad}}(\text{CO}_2) = E_{\text{ad}}(\text{AA}) = -0.650 \text{ V}$ (Fig. 4a), the AA electroadsorption produces a large cathodic current transient involving a charge density which is one order of magnitude greater than that of plain AA. The corresponding anodic stripping charge remains, however, equal to that one in the blank (Table 1), although the potential range of the complex anodic stripping peak moves positively. It should be noted that the anodic stripping peak in the blank is somewhat distorted at its descending branch, whereas after the addition of AA a distortion can be seen at the ascending branch [compare Figs 1a and 4a].

Runs made at $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ and $E_{\text{ad}}(\text{AA}) = -0.250 \text{ V}$ show an anodic electroadsorption current involving a limiting charge density. The corresponding anodic stripping voltammogram shows firstly a sharp anodic peak at 0.170 V (peak 1) and another one at 0.370 V (peak 2) which partially overlaps peak 1.

Finally, when $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$ and $E_{\text{ad}}(\text{AA}) = -0.500 \text{ V}$ (Fig. 4b), the AA electroadsorption produces a cathodic current transient, in contrast to the anodic ones found for both AA and PA in the absence of $r\text{-CO}_2$. In this case the anodic stripping voltammogram exhibits peak 1 at 0.150 V

with a small distortion at its ascending branch, and peak 2 at 0.370 V , the former being higher than the latter.

Runs made at $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$ and $E_{\text{ad}}(\text{AA}) = -0.650 \text{ V}$ show a cathodic current transient related to AA electroadsorption, the corresponding charge density (Table 1) and the stripping voltammogram approaching those of the blanks. Conversely, when $E_{\text{ad}}(\text{AA}) = -0.250 \text{ V}$ (Fig. 5a) an anodic AA electroadsorption current transient is observed, and the subsequent anodic stripping voltammogram shows two peaks of nearly the same height located at 0.180 V (peak 1) and 0.390 V (peak 2), respectively. Finally, for $E_{\text{ad}}(\text{AA}) = -0.500 \text{ V}$ (Fig. 5b) the AA electroadsorption current transient is only cathodic, and the charge involved is smaller than that found for $E_{\text{ad}}(\text{CO}_2) = -0.650 \text{ V}$. The corresponding anodic stripping voltammogram is rather similar to that seen in Fig. 4b.

In all these experiments only a few cyclovoltammograms are also required to return to the voltammogram of the $\text{Pt}/0.5 \text{ M H}_2\text{SO}_4$ system.

3. Summary of results

The electroadsorption current transient and the anodic stripping voltammograms of the adsorbates produced from unsaturated alcohols (AA and PA) on a Pt electrode modified by the presence of $r\text{-CO}_2$ adsorbates are considerably dependent on $E_{\text{ad}}(\text{X})$. These results suggest specific interactions between $r\text{-CO}_2$ and the products formed from the unsaturated alcohol electroadsorption, and between the proper alcohol molecules with residual H-atoms on Pt.

Results from the different experiments are assembled in Tables 1 and 2. Table 1 displays the values of $E_{\text{ad}}(\text{CO}_2)$ and $E_{\text{ad}}(\text{X})$ [$\text{X} = \text{PA}, \text{AA}$] following the experimental sequence; the electroadsorption charge density, $q_{\text{e}}(\text{X})$, obtained from the current transients at different $E_{\text{ad}}(\text{X})$; the anodic stripping charge density, $q_{\text{ox}}(\text{X})$, obtained from the voltammograms at $v = 0.2 \text{ V s}^{-1}$; the electroadsorption charge

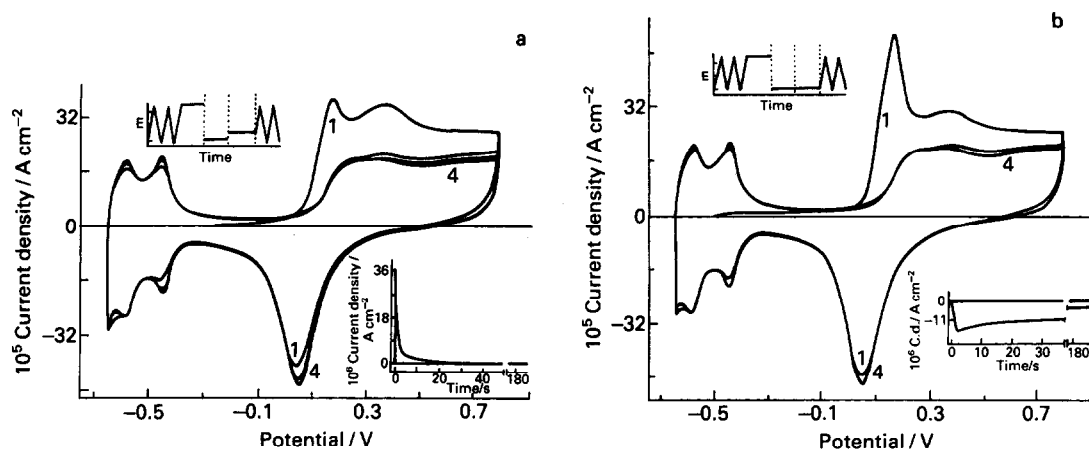


Fig. 5. (a) Cyclovoltammograms (1, 4) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{AA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$; $E_{\text{ad}}(\text{AA}) = -0.250 \text{ V}$. (b) Cyclovoltammograms (1, 4) corresponding to the anodic stripping of the composed $r\text{-CO}_2 + \text{AA}$ adsorbates at $\nu = 0.2 \text{ V s}^{-1}$; $E_{\text{ad}}(\text{CO}_2) = -0.500 \text{ V}$; $E_{\text{ad}}(\text{AA}) = -0.500 \text{ V}$. The AA electroadsorption current transients and the potential routines are depicted in the insets.

density, $q_i(Y)$ [$Y = r\text{-CO}_2 + X$] resulting from the current transients at $E_{\text{ad}}(\text{CO}_2)$ and $E_{\text{ad}}(X)$; and the anodic stripping charge density, $q_{\text{ox}}(Y)$, determined at $\nu = 0.2 \text{ V s}^{-1}$. These magnitudes can be derived from the experimental data. The rest of the symbols are explained further on in the discussion.

The anodic stripping voltammetric peak potentials (peaks 1 and 2) are given in Table 2.

DISCUSSION

Results previously reported for Pt electrodes modified by CO adsorbates interacting with PA and AA electroadsorbed residues[8], show that the anodic stripping charge density resulting from the composed adsorbed residues was practically the sum of the anodic stripping charge densities of the blanks. This simple charge addition rule is not directly applicable to the present results. Then, to explain the present data it is convenient to consider firstly the electrochemical behaviour of $r\text{-CO}_2$ on Pt, and to continue with the composed systems resulting from the interactions between $r\text{-CO}_2$ and the unsaturated alcohols.

This procedure makes possible to estimate average stoichiometries and probable structures of the composed adsorbates.

1. Behaviour of reduced CO_2 adsorbates

Radiochemical[14, 15] and EMIRS[16] investigations of the $r\text{-CO}_2$ adsorbates favour a CO_2 -clathrate-type structure for $r\text{-CO}_2$ [14, 15] approaching the $\{\text{Pt}\}(\text{H}_3\text{CO}_2 \cdot \text{H}_2\text{O})_{\text{ad}}$ stoichiometry[3]. Accordingly, the $r\text{-CO}_2$ structure can be described as a H-bonding ensemble mainly consisting of CO_2 , H-atoms and H_2O molecules at Pt sites. Then, the resulting molecular configuration would approach the structure of H-bonded compounds like either $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ yielding infinite chain like HCO_3^- ions held together by Na^+ ions or $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ producing finite groups as dimers carboxylic acids[17]. However, in contrast to bulk compounds, the structure of $r\text{-CO}_2$ on Pt likely implies an asymmetric potential dependent, probably flickering structure. This type of structure can explain the dependence of the electrochemical behaviour of $r\text{-CO}_2$ on the electrolyte composition[4, 5], and allows us to understand the formation of a number of electroreduction products

Table 2. Potentials of the anodic stripping peaks

$E_{\text{ad}}(\text{CO}_2)/\text{V}$	$E_{\text{ad}}(X)/\text{V}$	$E_p(\text{CO}_2)/\text{V}$	$E_p(X)/\text{V}$	$E_p(1)/\text{V}$	$E_p(2)/\text{V}$
X = PA					
-0.650	-0.650	0.080	—	0.130	0.350
-0.650	-0.500	0.080	0.530	0.170	0.380
-0.650	-0.250	0.080	0.570	0.220	0.440
-0.500	-0.650	0.120	—	0.130	0.350
-0.500	-0.500	0.120	0.530	0.170	0.380
-0.500	-0.250	0.120	0.570	0.230	0.430
X = AA					
-0.650	-0.650	0.080	—	0.110	—
-0.650	-0.500	0.080	0.370	0.150	0.370
-0.650	-0.250	0.080	0.380	0.170	0.370
-0.500	-0.650	0.120	—	0.120	—
-0.500	-0.500	0.120	0.370	0.150	0.370
-0.500	-0.250	0.120	0.380	0.180	0.390

from unsaturated alcohols, and the appearance of distinguishable adsorbates at different $E_{ad}(X)$ [18].

The multiplicity of voltammetric peaks related to the electrooxidation of r-CO₂ on Pt in acid has been interpreted through a complex reaction mechanism which includes an interconversion of two types of r-CO₂ species [5].

The r-CO₂ saturation electroadsorption charge density at $E_{ad} = -0.650$ V ($\theta_H = 1$) is only 20% greater than that obtained at $E_{ad} = -0.500$ V ($\theta_H = 0.5$). This is consistent with the fact that the initial CO₂ electroadsorption involves the participation of strongly bound H-atoms [3]. However, the fact that after reaching about 20% saturation coverage, the amount of r-CO₂ further increases, would indicate a redistribution of the electronic charge between Pt(H) and r-CO₂ leading to potential and environmental interaction dependent adsorbate structures [5]. This fact also reflects on the redistribution of the residual H-atom electrodesorption peaks in the anodic stripping voltammogram (Fig. 1a). These changes can explain why in the presence of r-CO₂ the H-atom electroadsorption processes are not completely inhibited as it occurs in the presence of CO.

2. Influence of r-CO₂ on PA and AA electroreduction

The electroreduction of PA and AA in acids yields a number of species with the predominance of different saturated hydrocarbons [19] and minor amounts of the corresponding saturated alcohols. The latter can be voltammetrically detected particularly at the initial stages of the electroreduction process [13].

In the presence of r-CO₂ the rate of electroreduction of both alcohols at -0.650 V is considerably diminished, as seen from the corresponding cathodic current transients. For PA this effect becomes relatively greater than for AA. Otherwise, in contrast to AA (Table 1) the anodic stripping charge for PA exceeds that of the blank. However, in both cases the potential of the anodic current peaks are positively shifted as compared to the blank, and in the case of AA the peaks are slightly distorted. The preceding description depends somewhat on the amount of r-CO₂.

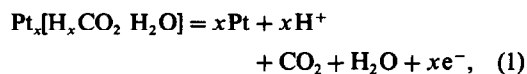
The results obtained for PA and AA electroadsorption at $E_{ad} = -0.650$ V on Pt under r-CO₂ saturation coverage, suggest that the partial inhibition of PA and AA electroreduction reactions may be due partly to a decrease of θ_H , and partly to the formation of new adsorbates acting progressively as poisons for the electroreduction reactions themselves. It appears that the first effect predominates for AA, whereas the second one becomes the most relevant for PA.

3. Formation of composed adsorbates

When the r-CO₂ covered Pt interacts with either PA or AA diluted solution there is a certain E_{ad} value for each alcohol which is related to the appearance of an excess of anodic stripping charge with respect to the r-CO₂ blank. Under these circumstances, the anodic electroadsorption current transients for PA at $E_{ad} > -0.500$ V, becomes comparatively smaller than that expected from the blanks. These results suggest that the interaction between PA and r-CO₂ likely involves adsorbed PA molecules rather than electroadsorbed residues.

The situation appears to be somewhat different for AA, since the addition of the latter at $E_{ad} = -0.500$ V, in the presence of r-CO₂ produces a cathodic current transient in contrast to the anodic current transient which results in the absence of r-CO₂. This difference becomes even more remarkable as the amount of r-CO₂ on Pt is increased. In this case, unlike the situation already described in sub-section 2, there is an apparent enhancement of the AA electroreduction process. On the other hand, the fact that at $E_{ad} = -0.250$ V, the AA electroadsorption charge density on r-CO₂ covered Pt is about one half the value resulting for the blank, points out that the presence of r-CO₂ favours a molecular adsorption of AA rather than the formation of electroadsorbed residues.

The preceding analysis allows us to estimate at least the limiting average PA/r-CO₂ and AA/r-CO₂ molecular ratios for the composed adsorbates produced between r-CO₂ and PA, and r-CO₂ and AA. For this purpose let us consider that under r-CO₂ saturation coverage the charge involved in the proper electrooxidation of r-CO₂ approaches the H-atom monolayer charge. Then, the number of electrons per r-CO₂ species should depend on both the stoichiometry of the r-CO₂ adsorbates and the overall electrooxidation reaction. In this case, let us put forward the reaction in the following way [3, 5]:



by taking $x = 3$ as the most probable value.

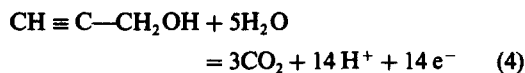
On the other hand, for the composed adsorbate $\Delta q_{ox}(X)$, the fraction of the anodic stripping charge associated with X, is given by

$$\Delta q_{ox}(X) = q_{ox}(Y) - q_{ox}(\text{r-CO}_2). \quad (2)$$

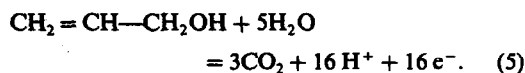
In these cases, one considers that CO₂ and H⁺ are the only products of the anodic stripping reactions [1, 3]. Analogously, the number of adsorbed residues related to each X molecule can be obtained by dividing $\Delta q_{ox}(X)$ by $n(X)$, the number of electrons entering the electrooxidation of each X-adsorbate. Then, $N(X)$, the number of adsorbed residues resulting from X per r-CO₂ adsorbate can be defined by the ratio

$$N(X) = \frac{x \Delta q_{ox}(X)}{n(X) q_{ox}(\text{CO}_2)}. \quad (3)$$

In the electroadsorption of X the value of $n(X)$ changes according to the stoichiometry of the adsorbed residue in the following way. When, the adsorbed residues is the X molecule itself, one has either



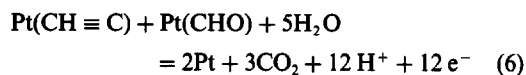
or



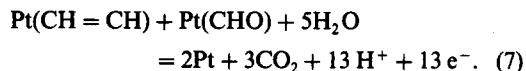
Accordingly, $n(X) = n(\text{PA}) = 14$, and $n(X) = n(\text{AA}) = 16$. For a preset value of X and further assuming

that there is no displacement of r-CO₂ caused through the electroadsorption of X, those figures provide limiting PA/r-CO₂ and AA/r-CO₂ molecular ratios for the coadsorbed species.

On the other hand, one can also assume that the electroadsorption of X as well as the corresponding stripping processes are represented by the same stoichiometric reactions already proposed for the blanks, either[13]



or



Then, $n(\text{X}) = n(\text{PA}) = 12$, and $n(\text{X}) = n(\text{AA}) = 13$. Therefore, in the absence of competitive adsorption these figures provide another limiting PA/r-CO₂ and AA/r-CO₂ molecular ratios for the coadsorbates.

Results from these calculations are assembled in Table 1. Accordingly, the average stoichiometry of the r-CO₂-PA-adsorbate can be represented as [(r-CO₂)₃(PA-residues)] at low $E_{\text{ad}}(\text{PA})$, and [(r-CO₂)₃(PA-residues)₂] at high $E_{\text{ad}}(\text{PA})$, whereas the average stoichiometry for the r-CO₂-AA-adsorbate results [(r-CO₂)₄(AA-residues)] at low $E_{\text{ad}}(\text{AA})$ and [(r-CO₂)₅(AA-residues)₂] at high $E_{\text{ad}}(\text{AA})$. Therefore, the composed adsorbates formed between r-CO₂ and the unsaturated alcohol residues on pc Pt can be described, in principle, as coadsorbates approaching limiting potential dependent stoichiometries.

Data assembled in Table 1 allow description of other features of the coadsorption phenomena involving r-CO₂ and products resulting from X electroadsorption. Thus, if one assumes that the electrochemical reactions of the composed adsorbates are not much different to those taking place for the separate adsorbates, the value of n^* which represents the X electroadsorption to coadsorbate electroadsorption charge ratio, permits to estimate $q_{\text{ox}}(\text{th})$, the hypothetical anodic stripping charge of the composed adsorbate. Thus, for AA taking $n^* = 2$, the values of $q_{\text{ox}}(\text{th})$ always exceed the experimental ones, whereas for PA, taking $2.6 < n^* < 4$, the opposite result is obtained.

The fact that in the present cases the charge addition rule is not obeyed can be attributed to specific chemical interactions; the interactions between PA and r-CO₂ being stronger than those involving AA and r-CO₂. This conclusion is consistent with the chemical reactivity of these unsaturated alcohols. It is known that PA is able to produce dimers and polymers at metal surfaces[20]. Then, PA dimer formation can take place on the r-CO₂ covered Pt electrode, a fact which can explain the relatively large value of $q_{\text{ox}}(\text{Y})$ resulting in this case.

Finally, in the presence of r-CO₂, the reactivity of PA in the hydrogen evolution reaction (HER) potential range is considerably enhanced, and correspondingly, the electroadsorption charge is diminished as expected for a facile PA electroreduction promoted by H-atoms.

4. Possible interactions involving the complex adsorbates

The interaction of r-CO₂ with unsaturated alcohols should involve a predominant participation of H-bonding. This type of interaction is well known for substances with -CH₂OH functional groups either in the presence or in the absence of water[16, 17]. Therefore, one should expect that the basic clathrate-type structure of r-CO₂ largely remains for the composed adsorbates. In this case, the entire adsorbed layer can be thought of as consisting of two types of domains, namely r-CO₂ + X-residues and r-CO₂ domains, including lateral interactions among domains. This description is consistent with the fact that the anodic stripping voltammograms of the composed adsorbates exhibit a first anodic peak (peak 1) resembling that of r-CO₂, and a second one (peak 2) approaching the anodic stripping peak of the X-residues. Nevertheless, it should be noted that for PA + r-CO₂ composed adsorbates peaks 1 and 2 are displaced with respect to those ones in the blanks, the former positively and the latter negatively. These potential shifts depend on $E_{\text{ad}}(\text{X})$ and operate in the direction of increasing peak overlapping, in agreement with a relatively strong interaction between the adsorbates domains.

Otherwise, for AA + r-CO₂ composed adsorbates peak 1 is also shifted positively, but the potential of peak 2 remains practically constant, although the difference between the potentials of peaks 1 and 2 decreases as $E_{\text{ad}}(\text{AA})$ increases. Certainly, for AA the overall effect is considerably smaller than for PA, as one should expect from the different chemical reactivity of these unsaturated alcohols.

In conclusion, the presence of either PA or AA residues on the r-CO₂ covered Pt electrodes also delays the initiation of the voltammetric electro-oxidation processes. From the structural standpoint the anodic stripping voltammograms are consistent with an adsorbate adlattice probably consisting of two domains, one in which the alcohol residues interact directly with r-CO₂ adsorbates, and a second domain where r-CO₂ adsorbates keep to some extent their own characteristics although the global properties of domains become interdependent. Then, in the present case, the composed adsorbates can be probably described as mixed adlattices involving lateral modifications and adsorbate ensemble reorganisation, approaching the structural situations which were advanced a few years ago for other adsorbates on Pt electrodes[9].

CONCLUSIONS

The adsorption of unsaturated alcohols (AA, PA) dissolved in 0.5 M H₂SO₄ on a polycrystalline Pt electrode modified by the presence of r-CO₂ adsorbates produces a potentiostatic current transient, which is either anodic or cathodic depending on the adsorption potential. The anodic stripping charge of the anodic residues is greater than that expected from the adsorption/electroadsorption of the independent substances. The anodic stripping voltammograms are also different from those corresponding to the blanks.

According to these results specific coadsorption interactions between r-CO₂ and AA-electroadsorbed residues, and r-CO₂ and PA-electroadsorbed residues have been considered. For both alcohols the anodic stripping peaks and the charge balance were interpreted through the formation of composed adsorbates. Based upon the probable r-CO₂ structure and H-bonding interactions between r-CO₂ and the alcohol molecules or their electroadsorbed residues, average alcohol residue/r-CO₂ molecular ratios have been estimated.

Acknowledgements—Financial support for this work by the Gobierno de Canarias (Dirección General de Universidades e Investigación) under research contract No. 21/31.07.89 is gratefully acknowledged.

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