ELECTROCHEMICAL BEHAVIOUR OF BENZOIC ACID ON PLATINUM AND GOLD ELECTRODES

F. Montilla, E. Morallón and J.L. Vázquez*

Departamento de Química Física. Universidad de Alicante. Apartado 99. 03080 Alicante.

SPAIN

Abstract

A voltammetric and spectroscopic study of the adsorption and oxidation of benzoic acid on platinum and gold electrodes has been carried out in acid medium. The oxidation of benzoic acid depends on the surface structure of the platinum electrode. Benzoic acid is adsorbed through the carboxylate group in a two-fold coordination at potential above 0.4V/RHE on platinum electrodes and above 0.5V/RHE on gold electrode. However, at lower potential it is adsorbed through the aromatic ring. The analysis of the potential dependent band centre frequencies and integrated band intensities indicates that lateral interactions between adsorbed benzoate anions are the responsible of the frequency shift observed with increasing potential. On platinum electrodes benzoic acid is reduced to cyclohexanecarboxylic acid at low potentials and is oxidised to CO₂, quinones and lactones, similarly to other aromatic compounds such as benzene. On gold electrodes, it is oxidised mainly to CO₂.

Keywords: Benzoic acid, platinum electrodes, gold electrodes, electrosorption, FTIR spectroscopy.

*e-mail: morallon@ua.es;

Telf: 34-965909590

Fax: 34-965903537

1. Introduction

The adsorption and reactivity at the electrode|electrolyte interface is a subject of general interest in Electrochemistry Surface Science. The electrosorption properties of benzoic acid on metallic surfaces have been quite well studied from a fundamental point-of-view and for its inhibitory effect on corrosion of iron and steel (1,2). This molecule can be adsorbed through two adsorption centres either the aromatic ring or the carboxylic group (3).

On polycrystalline platinum electrodes, the surface concentration of preadsorbed benzoic acid reaches a maximum at potential between 0.25-0.40V/RHE as could be observed by radiotracer and FTIR *in situ* techniques (4,4,5). At potentials more positive than 0.4V/SCE on platinum electrodes benzoic acid is oxidised to CO₂ as was checked by FTIR spectroscopy (5) and by Differential Electrochemical Mass Spectrometry (DEMS) (6). No products coming from the reduction of this compound can be detected with this later technique, which indicates that no volatile compounds are obtained during the cathodic reduction of benzoic acid, but cannot be discarded the formation of soluble non-volatile products such as cyclohexanecarboxylic acid (6).

Zelenay et al. (7) have shown that benzoic acid is adsorbed on gold electrodes in a wide range of potentials. When the potential of the working electrode goes to more positive values the surface concentration increase slowly up to 0.9V/RHE. At higher potentials, a sudden increment of benzoic acid surface concentration can be observed. It reaches a maximum at 1.2-1.3V/RHE. At potentials more positive than 1.3V the surface concentration of benzoic acid decreases because of the growing of the surface oxide of gold at those potentials that prevents the benzoic acid adsorption. The sudden increment of the surface concentration of the adsorbate has been related with a change in the adsorbate orientation from a planar adsorption through the aromatic ring to a perpendicular adsorption through the carboxylate group at more positive potentials (5,7-9).

The aim of this work is to study in acid media the adsorption and reactivity of benzoic acid on gold electrodes and platinum electrodes with different surface structure.

2. Experimental

The test solutions were 0.1M HClO_4 , 0.5M H_2SO_4 , prepared from Merck Suprapur concentrated acids. Benzoic acid was from Merck p.a. and the water employed for the preparation of the solutions was obtained from a Millipore-Milli-Q plus system. D_2O was from Aldrich chemicals, 99.9% atom %D. All potentials are referred to a reversible hydrogen electrode (RHE), which was immersed in the same test solution. Cyclic voltammograms were obtained at a constant sweep rate of 50 mV s^{-1} .

Platinum single crystal electrodes were prepared according to the method developed by Clavilier (10). The surfaces of the gold and platinum electrodes were thermally cleaned in an air + propane flame. The single crystal surface were cooled in an H_2 +Ar stream (11). Finally, a droplet of ultrapure water protected the surface of the electrodes.

A Nicolet Magna 850 spectrometer equipped with a liquid nitrogen-cooled MCT detector was employed for the in situ FT-IRRAS measurements. The spectroelectrochemical cell was made of glass and was provided with a prismatic CaF_2 window bevelled at 60° . Spectra were collected at 8 cm^{-1} resolution and are presented as $\Delta R/R$.

3. Results and discussion

Oxidation of benzoic acid on platinum electrodes

Figure 1 shows the voltammograms obtained for Pt(111), Pt(110) and Pt(100) electrodes in 0.5M H_2SO_4 + 1mM benzoic acid solution. Figure 1.a shows a strong blockade of the adsorption sites of the Pt(111) electrode at potentials lowers than 0.55V. In the negative scan, a sharp reduction peak appears at 0.07V, together with the corresponding anodic peak approximately at the same potential. The electric charge involved in each sharp peak is $80 \mu\text{C}$

cm⁻² and it could be associated to hydrogen adsorption-desorption processes. In the first scan to more positive potentials, two oxidation peaks appear at 1.05 and 1.35V. The first one is due to the oxidation of benzoic acid and the second corresponds to the simultaneous oxidation of the platinum surface and the benzoic acid. The reduction peak of the surface oxide can be observed in the reverse scan.

The behaviour of a Pt(110) electrode in a solution containing benzoic acid is showed in the figure 1.b. The adsorption processes at potentials lower than 0.5V of a Pt(110) electrode are strongly blocked by the presence of benzoic acid. The oxidation of benzoic acid starts at 0.8V, close to the oxidation of the platinum surface. The maximum of the oxidation peak appears at 1.4V. The reduction peak of the platinum oxide formed in the positive scan can be observed in the reverse scan. In the second and successive scans the intensity of this oxidation peak on the modified surface slightly decrease.

The voltammograms of the Pt(100) electrode in a 0.5M H₂SO₄ + 1 mM benzoic acid solution are shown in figure 1.c. Benzoic acid blocks the adsorption-desorption processes taking place at potentials between 0.06 and 0.5V for a Pt(100) surface. The oxidation of benzoic acid starts at potentials more positive than 0.9V close to the oxidation of the platinum surface reaching a strong oxidation peak at 1.48V. The reduction of the platinum surface can be observed in the reverse scan. The intensity of this oxidation peak decreases in the successive scans.

A similar behaviour has been obtained using perchloric acid solution with all the platinum electrodes.

Table 1 shows the values of current density, peak potential and oxidation charge of benzoic acid in 0.5M H₂SO₄ during the first scan up to 1.5V for the different platinum surfaces studied together with the results obtained with a polycrystalline platinum surface. The highest value of current density for the oxidation is obtained with the Pt(100) electrode. However the potential of the oxidation on this surface is higher than with other platinum single crystal

surfaces. Taking into account the values of oxidation charge and the potential of the peak the Pt(111) is the most electrocatalytic surface towards benzoic acid oxidation, meanwhile the surfaces Pt(100) and Pt(110) present a similar behaviour.

The nature of the species produced during the electrochemical experiments was determined by *in situ* FT-IR spectroscopy. Figure 2 shows the spectra obtained with *p*-polarised light for a polycrystalline platinum electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution. After the flame treatment, the electrode was immersed in the working solution at a controlled potential of 0.5V (reference spectrum, 200 interferograms). After this, the potential was shifted to lower values taking 200 interferograms at two sample potentials. At 0.3V (fig. 2.a) a positive band appears at 1387 cm⁻¹ that can be assigned to the symmetrical stretching vibration of the carboxylate group (12). The absence of this band in the spectrum collected under the same experimental conditions but with *s*-polarised light confirms its ascription to the vibrational modes of adsorbed species (spectrum not shown). Then, this band can be assigned to the symmetric OCO stretch of two-fold coordinated benzoate anions adsorbed on the platinum surface. To our knowledge, this band was not reported before by other author using platinum electrodes. Its positive character evidences the disappearance of adsorbed benzoate species at the sample potential. The evolution of this band with the potential will be discussed bellow.

At 0.02V (fig. 2.b) the spectrum shows the positive band around 1387 cm⁻¹ together with two negative bands at 2943 and 2863 cm⁻¹. These latter bands can be associated to the symmetric and asymmetric stretching vibration of C-H bonds of cycloalkanes (12) which indicates the reduction of the aromatic ring to cyclohexane as occurs with benzene (13-16). An additional negative band at 1730 cm⁻¹ can be observed. However, this spectral region can be interfered by the absorption of the solvent (water). Then, figure 2.c shows the spectrum collected at 0.05V (reference potential 0.5V, 1000 interferograms) using deuterated water. A positive band due to adsorbed benzoate anions at the sample potential can be observed at 1390 cm⁻¹. A negative band at 1690 appears, that is related to the stretching vibration of a

C=O group. This band can be due to the formation of cyclohexanecarboxylic acid by reduction of benzoic acid at the sample potential, which is obtained by cathodic reduction via the aromatic ring in a similar way than benzene or toluene reduction to the corresponding cyclohexane (15,17-19).

Figure 3 shows a series of spectra recorded with *p*-polarised light for a polycrystalline platinum electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution at different sample potentials (Reference potential 0.1V, 1000 interferograms). In these spectra the reference and sample spectra were collected alternately and then co-added. A negative band around 1380 cm⁻¹ appears at potentials more positive than 0.3V that was assigned before to the symmetrical stretching vibration of the carboxylate group. Figure 4.a shows the corresponding plot of the integrated band intensity as a function of the electrode potential. The intensity of this band grows with the potential reaching a maximum in intensity at 0.8V. Then, the surface concentration of the adsorbed benzoate anions increases for potentials above 0.3V and the maximum is reached at 0.8V. From these potential values, the intensity of this band decreases due to the oxidation of the adsorbate.

The band centre frequencies are plotted against the electrode potential in figure 4.b. Bellow 0.8V the band position shifts 34 V⁻¹ cm⁻¹ and above this potential, the band position follows the inverse tendency. Considering the orientation of benzoate anions (oxygen atoms oriented towards the metal) an increase of the electric field must result in an increase of the gap between the charges of the adsorbed dipole (electrochemical Stark effect) (7,20,21). Therefore as potential increase, the bond energy would decrease. However, bellow 0.8V, the shift of the band around 1380 cm⁻¹ follows the opposite trend. The positive shift of this band happens in the zone of potentials where increases the surface coverage of the adsorbed benzoate (see figure 4.b). Consequently, this behaviour suggests that the most important factor governing the frequency shift is the increasing of the lateral interaction between the adsorbed molecules. The absence of this band at potentials lower than 0.4V indicates that the orientation of

adsorbed benzoic acid changes at these potentials from perpendicular through the carboxylate group to parallel adsorption through the aromatic ring.

The products generated during the oxidation of benzoic acid with platinum electrodes have been also studied by FTIR spectroscopy. Figure 5 shows the spectra of a platinum electrode in a 0.1M HClO_4 + 1mM benzoic acid solution in water and deuterated water at higher potentials. Figure 5.a shows the spectrum at 1.0V (reference potential 0.5V) which shows a negative band at 2342 cm^{-1} corresponding to CO_2 in solution coming from the oxidation of benzoic acid. An additional negative band appears at 1659 cm^{-1} . A similar experiment was performed in deuterated water (figure 5.b), and a more evident negative band at 1665 cm^{-1} appears that can be assigned to the stretching vibration of C=O group, characteristic of *ortho* or *para*-quinones (12). Therefore at this potential benzoic acid is being oxidised to quinones and CO_2 .

Afterward, the potential was shifted to 1.5V in deuterated water (figure 5.c). Two additional negative bands at 1731 and 1356 cm^{-1} appear, which are very similar to those obtained in the oxidation of benzene in acidic medium at 1.4V with a polycrystalline platinum electrode (14). The former band can be assigned to the stretching vibration of C=O group. The second band at 1356 cm^{-1} is associated with the former, and is assigned to stretching vibration of C–O. These bands can be assigned to the formation at these potentials of α - β -unsaturated esters or to lactones coming from the oxidative cleavage of the aromatic ring.

Oxidation of benzoic acid on gold electrodes

Figure 6 shows the cyclic voltammogram of a polycrystalline gold electrode obtained in a 0.1M HClO_4 + 1 mM benzoic acid solution. In the zone of potential between 0.7-1.0V (magnification in figure 6) the presence of a redox couple due to adsorption-desorption of benzoic acid can be observed close to surface reconstruction of the different facets of the polycrystalline gold electrode (8,9). Comparing this voltammogram with that obtained in the

absence of organic compounds (dashed line in figure 6), it can be observed that the surface oxidation of the gold electrode is displaced towards more positive potentials and partially inhibited.

The electrochemical behaviour of this compound on gold electrodes has been analysed by *in situ* FTIR spectroscopy. After the flame annealing, the gold electrode was immersed in a 0.1M HClO₄ + 1 mM benzoic acid solution at the reference potential of 0.3V/RHE (200 interferograms). Then, the potential was stepped towards more positive potentials. Figure 7.a shows a series of spectra recorded with *p*-polarised light at the potentials indicated in each spectrum. At potentials more positive than 0.7V a negative band around 1374 cm⁻¹ appears. This band can be assigned, as in the case of Pt electrodes, to the symmetrical stretching vibration of the carboxylate group. This band can be related to the adsorption of benzoic acid through the carboxylic group in perpendicular orientation to the electrode surface. At more positive potentials, the intensity of this band grows, reaching a maximum at 1.3V, after that, start to decrease (figure not shown) [5,7]. At the same time, the band centre is shifted to higher frequency values. At 1.3V, a negative band appears at 2342 cm⁻¹ due to the formation of CO₂ coming from the oxidation of benzoic acid. No bands related with the adsorbed benzoic acid can be observed at 1.7V.

Figure 7.b shows a similar experiments obtained in deuterated water. Both spectra were collected at the same sample potential of 1.3V, where the intensity of the bands is maximal, with *p*-polarised and *s*-polarised light, respectively. A positive band around 1680 cm⁻¹, in addition to the negative band related with the adsorbed carboxylate around 1380 cm⁻¹ can be observed. With *p*-polarised light the sharp negative band corresponding to symmetric stretching mode of carboxylate group at 1389 cm⁻¹ is clearly observed and this band does not appear with *s*-polarised light, indicating that this band corresponds to adsorbed species. The absence of the corresponding asymmetric stretching mode of this group is related with the adsorption geometry of benzoic acid (5). Two positive-going bands at 1689 and 1352 cm⁻¹ are

also observed and can be assigned to the stretching vibration of the carboxylic group (C=O stretching) and the O-H deformation vibration respectively, due to the decreasing of benzoic acid in the vicinity of the electrode due to its adsorption.

Figure 8 shows the band centre frequency around 1380 cm^{-1} with the potential. At potentials between 0.5 and 1.2V, the tuning rate for this band is $23\text{ V}^{-1}\text{ cm}^{-1}$. Since benzoic acid is adsorbed in a two-fold coordination, an increase in the potential should result in an increase of the separation of charge in the dipole and therefore a decrease of the C–O bonds energy. However, as in the case of platinum electrodes, the trend obtained in this zone of potentials is the opposite one. An increasing surface coverage of benzoate anions on the gold electrode is taking place in this region of potentials that may result in an increase of the lateral interaction between the adsorbed molecules. Therefore, the effect of lateral interaction prevails over the electric field in this zone of potentials. At potentials more positive than 1.3V the band intensity decreases due to the oxidative desorption of benzoic acid as confirmed by the appearance of a band at 2342 cm^{-1} , corresponding to CO_2 (Figure 7a).

Conclusions

The electrochemical behaviour of benzoic acid on platinum electrodes depends on the surface structure of the electrode. Benzoic acid blocks the adsorption states of polycrystalline platinum and Pt(hkl) at potentials less positive than 0.4V. The hydrogen adsorption-desorption processes on Pt(111) electrode are shifted to less positive potentials than 0.2V due to the adsorption of benzoic acid. During the oxidation of benzoic acid on this electrode, two oxidation peaks can be observed during the first voltammetric scan. Meanwhile with the other single crystal electrodes the oxidation of benzoic acid is produced in a single peak. The Pt(111) surface is the more active for the oxidation of benzoic acid, followed by Pt(100) and the less active is Pt(110).

Changes in the adsorption orientation of benzoic acid have been detected by *in situ* FTIR spectroscopy on polycrystalline platinum electrodes. At potentials less positive than 0.5V the reorientation of the organic compound passing from a perpendicular adsorption in a two-fold coordination through the carboxylate group to parallel adsorption (through the aromatic ring) can be observed. At potentials lower than 0.05V benzoic acid is reduced to the cyclohexane carboxylic acid.

By FTIR, at potentials more positive than 0.4V, an increase of the surface coverage of benzoate anions adsorbed through the carboxylate group happens, reaching a maximum at 0.8V. At higher potentials (1.0V) benzoic acid is oxidised on polycrystalline platinum electrode to CO₂ and quinones. The cleavage of the aromatic ring at potentials more positive than 1.2V also yields lactones.

The electrochemical reactions of benzoic acid are quite similar to those of benzene in acidic medium.

Benzoic acid adsorbed on gold electrodes partially blocks the surface oxidation of this electrode. Reorientation phenomena of benzoic acid can also be observed by FTIR spectroscopy. Benzoic acid is mainly adsorbed parallel to the surface at potentials lower than 0.8V. At more positive potentials the sudden increase of the surface coverage is indicative of the adsorption of benzoic acid through the carboxylate group. Benzoic acid is oxidised on this electrode simultaneously with the oxide formation on the gold surface. Part of the benzoic acid is desorbed to the solution at potentials higher than 1.3V. It cannot be detected any intermediate product coming from the partial oxidation of the aromatic ring on this electrode like quinones or lactones.

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FIGURE CAPTIONS

Figure 1: Cyclic voltammograms for single crystal platinum electrodes in a 0.5M H₂SO₄ + 1mM benzoic acid solution. (— - — - —) Voltammograms obtained in the test solution in absence of benzoic acid.

a) Pt(111): (————) 1st scan, (— — —) 2nd scan.

b) Pt(110): (————) 1st scan, (— — —) 2nd scan, (-----) 5th scan.

c) Pt(110): (————) 1st scan, (— — —) 2nd scan, (-----) 5th scan.

Figure 2: FTIR spectra obtained with a polycrystalline platinum electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution. Reference potential 0.5V. *p*-polarised light. (a) Sample potential 0.3V, 200 interferograms (b) Sample potential 0.02V, 200 interferograms (c) FTIR spectra obtained in the similar conditions in deuterated water. Sample potential 0.05V. 1000 interferograms.

Figure 3: FTIR spectra obtained with a polycrystalline platinum electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution. Reference potential 0.1V. 1000 interferograms. *p*-polarised light. Sample potential indicated in each spectrum.

Figure 4: (a) Potential dependence of the integrated band intensity around 1380 cm⁻¹ for a polycrystalline platinum electrode. (b) Potential dependence of the band centre position for the band around 1380 cm⁻¹ for a polycrystalline platinum electrode.

Data taken from spectra of figure 3.

Figure 5: FTIR spectra obtained with a polycrystalline platinum electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution. Reference potential 0.5V. 500 interferograms. *p*-polarised light. (a) Sample potential 1.0V. In aqueous solution, (b) Sample potential 1.0V. In deuterated water. (c) FTIR spectra obtained in deuterated water. Sample potential 1.5V.

Figure 6: Steady-state cyclic voltammograms of a polycrystalline gold electrode. (— — — — —) 0.1M HClO₄ solution, (————) 0.1 M HClO₄ + 1mM benzoic acid solution.

Figure 7: (a) FTIR spectra obtained with a polycrystalline gold electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution. Reference potential 0.3V. 200 interferograms. *p*-polarised light. Sample potential indicated in each spectrum. (b) FTIR spectra obtained with a polycrystalline gold electrode in a 0.1M HClO₄ + 1 mM benzoic acid solution in deuterated water. Reference potential 0.3V. 1000 interferograms. Sample potential 1.3V. The spectrum marked with “p” was obtained with *p*-polarised light. The spectrum marked with “s” was obtained with *s*-polarised light.

Figure 8: Potential dependence of the band centre position for the band around 1380 cm⁻¹ for a polycrystalline gold electrode. Data taken from the spectra obtained in deuterated water.

TABLE CAPTIONS

Table 1: Peak potential, current density and electric charge obtained during the first voltammetric scan during the oxidation of benzoic acid in 0.5M H₂SO₄ solution for the different platinum surfaces studied.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1

	E	j	Q
	(V/RHE)	($\mu\text{A cm}^{-2}$)	($\mu\text{C cm}^{-2}$)
	1.05	75	661
Pt (111)	1.35	115	
Pt (110)	1.41	77	353
Pt (100)	1.48	118	328
Pt Polycrystalline	1.39	129	704