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Preliminary Communication

ELECTROCHEMICAL BEHAVIOUR OF BENZALDEHYDE AT PLATINUM

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Abstract

The reactions of 5 mM benzaldehyde at platinum in 0.1 M $HClO_4$ were studied by means of differential electrochemical mass spectrometry (DEMS) combined with cyclic voltammetry. It was observed that this compound oxidises completely to CO_2 at $E > 0.60$ V vs. RHE (reference hydrogen electrode), but also produces toluene, benzene and cyclohexane in the potential region for hydrogen adsorption and H_2 evolution. No partial or total hydrogenation of toluene was observed. These results are compared and discussed with those previously obtained for benzyl alcohol and benzoic acid.

Keywords: Benzaldehyde; Benzyl alcohol; Benzoic acid; Platinum; Electrochemical mass spectrometry (DEMS)

Introduction

The electrochemical behaviour of benzyl alcohol [1-3] and benzoic acid [4] has been previously studied at platinum electrodes in acid media. The aim of this research was to establish the influence of the substituent in the aromatic ring on the reactivity of the aromatic compound. Both these molecules adsorb irreversibly at the platinum surface and oxidise to carbon dioxide. Applying the method of displacement with CO [1,2], it was established that benzyl alcohol adsorbs dissociatively producing benzene, but also suffers hydrogenolysis when the adsorption takes place in the hydrogen adsorption/desorption region of platinum, forming adsorbed toluene. The dissociation reaction produces adsorbed CO from the alcoholic group in addition to benzene from the aromatic ring. Partial and total hydrogenation compounds from benzene and toluene were detected simultaneously with the production of molecular hydrogen [2,3].

On the other hand, CO cannot displace benzoic acid and no hydrocarbons were detected from its reduction [4]. However, partial desorption of the adlayer was observed during the cathodic

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potential scan down to the onset of hydrogen evolution. This result was justified assuming that benzoic acid desorbs without further hydrogenation but is not volatile enough to be detected by DEMS.

The purpose of the present work is to complete the series of aromatic molecules (alcohol-aldehyde-acid) analysing the reactivity of benzaldehyde at platinum. As in references [1-4], Differential Electrochemical Mass Spectrometry (DEMS) was applied for the detection of gaseous and volatile compounds produced during the electrochemical reactions.

Experimental

Solutions were prepared from Millipore-MilliQ* water and analytical grade reagents. The working solution was 5 mM benzaldehyde in the supporting electrolyte (0.1 M $HClO_4$). All experiments were performed at room temperature under argon atmosphere.

The DEMS system consists of an electrochemical cell directly attached to a vacuum chamber containing the quadrupole mass spectrometer. The working electrode was a porous platinum layer deposited on a teflon membrane which interfaces the electrochemical cell and the vacuum components. The experimental set-up allows the simultaneous detection of mass spectrometric cyclic voltammograms (MSCVs) for selected mass to charge ratios (m/z) and the cyclic voltammograms (CVs) at a scan rate of $v = 0.01\ Vs^{-1}$. The electrochemical cell allows the solution exchange holding the potential control on the working electrode. More details about the technique and the experimental procedures have been given elsewhere [1,5].

The working electrodes were activated by potential cycling between the onset for hydrogen and oxygen evolution at $0.01\ Vs^{-1}$. The real area (18-20 cm^2) was estimated from the hydrogen adsorption region [6]. The counter electrode was a platinum wire, and the electrochemical cell was completed with a reversible hydrogen electrode prepared in the electrolyte solution (RHE). All potentials in the text refer to this electrode.

After electrode activation, the solution containing the organic compound is introduced in the cell under potential control in the double layer region of the platinum electrode, and three potential cycles were recorded. The second is shown in the figures. Three m/z ratios can be simultaneously detected.

Results and Discussion

The cyclic voltammogram for a platinum working electrode in a 5 mM benzaldehyde + 0.1 M $HClO_4$ solution is given in Figure 1A (solid line). For the sake of comparison, the CV in the base electrolyte is shown in the same figure (dashed line). A partial blockage of the surface is deduced from the current in the 0.05-0.40 V potential range. During the positive-going potential scan, an electrooxidation current develops at E > 0.60 V attaining a broad maximum at 1.31 V. In the reverse scan, the presence of an anodic contribution is confirmed comparing the curves in the presence (solid line) and in the absence (dashed line) of benzaldehyde in the solution.

In the potential ranges where the anodic currents are observed, only the mass signal for m/z = 44 displays a potential-dependent signal (Figure 1B). From this result, it could be concluded that CO_2 is the sole electrooxidation product from benzaldehyde (the signal for m/z = 44 corresponds to the radical cation $[CO_2]^{\bullet+}$). However, it was demonstrated that benzoic acid is not detected through DEMS [4], and therefore, its formation cannot be excluded in these experiments.

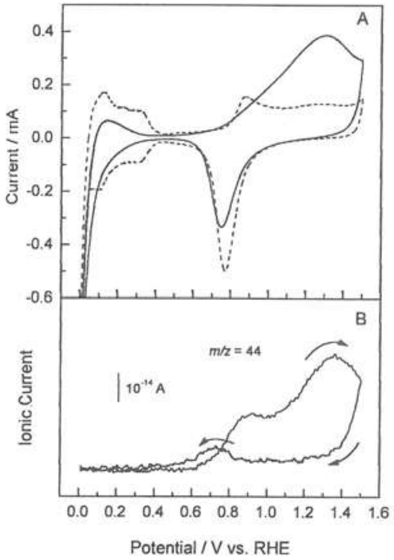

Figure 1. (A) CV for a Pt working electrode in 5 mM benzaldehyde + 0.1 M $HClO_4$. (B) MSCV for m/z = 44. (---) Base electrolyte. $v = 0.01\ Vs^{-1}$; area = 19.6 cm^2.

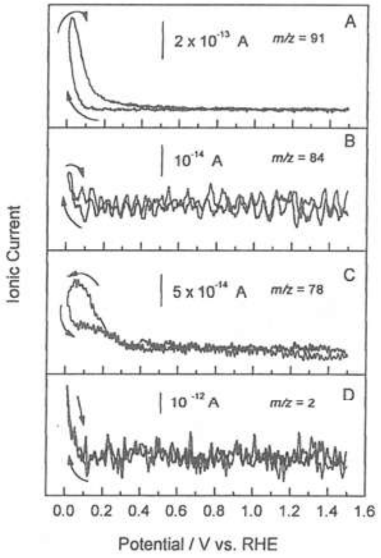

Figure 2. MSCVs for (A) $m/z = 91$ (toluene); (B) $m/z = 84$ (cyclohexane); (C) $m/z = 78$ (benzene) and (D) $m/z = 2$ (H_2). Same conditions as in Figure 1.

Three features are well established from the MSCV in Figure 1B: two in the positive-going scan centred at 0.90 and 1.35 V, and the third one in the negative sweep at 0.75 V. Only the contribution at 1.35 V was defined in the CV in Figure 1A.

The electroreduction products from benzaldehyde are summarised in Figure 2A-C. The signal for m/z = 91 describes the formation of toluene ($[C_6H_5CH_2]^+$), whereas those for m/z = 84 and 78 correspond to cyclohexane ($[C_6H_{12}]^{\bullet+}$) and benzene ($[C_6H_6]^{\bullet+}$), respectively. It should be noticed that these masses show different potential dependencies. Thus, the onset for the detection of benzene during the reverse run is observed at 0.40 V and the ion current attains a peak at 0.07 V (Figure 2C). The production of toluene (Figure 2A) and cyclohexane (Figure 2B) occurs at $E < 0.10$ V in the same potential region for hydrogen evolution (Figure 2D).

From these results it is made clear that benzaldehyde interacts with platinum, at least in part, dissociatively producing benzene ($m/z = 78$), which probably adsorbs at the platinum surface as in the case of benzyl alcohol [1,2]:

$$C_6H_5CHO \rightarrow (C_6H_6)_{ad} + R_{ad} \qquad (1)$$

$$(C_6H_6)_{ad} \leftrightarrows C_6H_6 \qquad (2)$$

The presence of a residue R_{ad} is assumed considering that no methane was detected. Evidence for the presence of both R_{ad} and adsorbed benzene molecules at the Pt surface can be achieved applying a flow-cell procedure in order to study the electrochemical behaviour of isolated adsorbed species. These studies will be discussed in a forthcoming publication.

Next, we consider the production of cyclohexane ($m/z = 84$). The onset for its formation (Figure 2B) coincides with the decrease of the benzene signal in the potential range for H_2 evolution. Accordingly, benzene can be regarded as being consumed through reaction with H_2 yielding cyclohexane:

$$C_6H_6 + 3\,H_2 \rightarrow C_6H_{12} \qquad (3)$$

Opposite to benzyl alcohol, partially hydrogenated hydrocarbons were not detected during electroreduction of benzaldehyde.

Finally, toluene is also detected from benzaldehyde at $E < 0.10$ V. In the case of benzyl alcohol, the onset potential for toluene was established at 0.20 V, i.e. at more positive potentials than the onset for the production of molecular hydrogen. Therefore, the formation of toluene from the alcohol was explained through the hydrogenolysis of the molecule by reaction with H_{ad} [1-3]. For benzaldehyde, interaction with molecular hydrogen is necessary:

$$C_6H_5CHO + 2\,H_2 \rightarrow C_6H_5CH_3 + H_2O \qquad (4)$$

Hydrogenation of the aromatic ring is not achieved for toluene. This fact suggests that toluene produced potentiodynamically does not adsorb and the main process in this potential region is the hidrogenation of bulk benzaldehyde molecules.

Final Comments

The experimental findings for benzoic acid, benzaldehyde and benzyl alcohol can be summarised as follows:

1. Benzoic acid oxidises to CO_2 but cannot be reduced. The absence of benzene suggests that the adsorption is not dissociative.
2. Benzaldehyde oxidises to CO_2. Fragmentation of the molecule takes place with the formation of benzene. Reduction by molecular hydrogen to toluene and cyclohexane is observed at $E < 0.10$ V for benzaldehyde and benzene, respectively.
3. Benzyl alcohol oxidises to CO_2. As for benzaldehyde, fragmentation of benzyl alcohol produces benzene. Toluene is formed by interaction with H_{ad}. Hydrogenation of benzene and toluene with H_2 yields the completely hydrogenated compounds (cyclohexane and methyl-cyclohexane), as well as partially hydrogenated hydrocarbons.

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