Reactivity of benzaldehyde at platinum in acid solution

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The electrochemical behavior of benzene (1,2), toluene (2), benzyl alcohol (2-4) and benzoic acid (5) has been previously studied at platinum electrodes in acid media. The aim of this research is to establish the influence of the substituent in the aromatic ring, on the reactivity of the aromatic compound. All these molecules adsorb irreversibly at the platinum surface and can be oxidized to carbon dioxide. Applying the method of displacement with CO (1,2), it was established that both benzene and toluene adsorb without dissociation, i.e. as the intact molecule. The production of cyclohexane and methyl-cyclohexane, respectively, confirms that total hydrogenation of these compounds occurs in the potential region for hydrogen evolution.

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

Finally, benzyl alcohol shows a different behavior. CO displacement experiments demonstrate that benzyl alcohol adsorbs dissociatively producing benzene, but also suffers hydrogenolysis when the adsorption takes place in the hydrogen adsorption/desorption region, forming adsorbed toluene. The dissociation reaction also produces adsorbed CO from the alcoholic group. Partial and total hydrogenation compounds from benzene and toluene were detected simultaneously with the production of molecular hydrogen.

The purpose of the present work is to complete the series of aromatic molecules (alcohol-aldehyde-acid) analyzing the reactivity of benzaldehyde. As in references (1-5), Differential Electrochemical Mass Spectrometry (DEMS) was applied for the detection of the gaseous and volatile compounds produced during the electrochemical reactions. This 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. Mass spectrometric cyclic voltammograms (MSCVs) for selected mass to charge ratios (m/z) were recorded in parallel to the cyclic voltammograms (CVs). The electrochemical cell allows a solution exchange holding the potential control on the working electrode. In this way, adsorbates can be isolated at the different adsorption potentials, and the reduction and oxidation of the adlayer performed independently from bulk contributions. More details about the technique and the experimental procedures have been given elsewhere (2,6).

Bulk studies in a 5 mM benzaldehyde solution prepared in the base electrolyte (0.1 M HClO4), have shown that total oxidation to carbon dioxide occurs for this molecule, as well as hydrogenolysis with the production of toluene. However, as a difference with benzyl alcohol, toluene is not formed during adsorption in the hydrogen region of platinum, but only simultaneously with the hydrogen evolution. Benzene is produced and its total hydrogenated hydrocarbon, cyclohexane, detected. Therefore, fragmentation of benzaldehyde is confirmed. Only benzene was displaced during adsorption of CO. Applying the flow cell procedure, adsorbates from benzaldeyde were isolated and its reduction and oxidation processes compared with those observed with the aldehyde present in the bulk of the solution.

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