Investigation of the anodic acetoxylation of \( p \)-methylanisole (\( p \)-MA) in glacial acetic acid medium using graphite (sp\(^2\)) and BDD (sp\(^3\)) electrodes

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Abstract

The electrochemical investigation of carbon fiber (CF) and boron-doped diamond (BDD) ultramicroelectrodes (UME) in glacial acetic acid medium has shown that the overpotential for acetate oxidation is higher on BDD than on CF. Preparative electrolyses have revealed that the main anodic products correspond to the Kolbe reaction. Beside these products small amounts of methane and methyl acetate are formed in different amounts depending on electrode material. This difference has been attributed to the different adsorption properties of CF (sp\(^2\)) and BDD (sp\(^3\)). Electrochemical measurements of \( p \)-MA in glacial acetic acid media have shown that \( p \)-MA is firstly oxidized to the corresponding radical cation. This intermediate, formed at both CF and BDD electrode, can either be attacked by the AcO\(^-\) nucleophile leading to acetoxylated product or undergo dimerization ending up in polymeric material. The obtained results show clearly that on graphite acetoxylation is favored contrary to BDD where the dimerization step also takes place. Selectivity up to 93\% monoacetoxylated product can be achieved on graphite for more than 90\% conversion of \( p \)-MA using a bipolar capillary gap cell.

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1. Introduction

The anodic preparative acetoxylation of substituted aromatic compounds in glacial acetic acid has been investigated during the last decades using mainly graphite and platinum electrodes [1–6]. Nevertheless, electrochemical studies in this low polarity solvent are still rare, mainly due to problems related with the uncompensated resistance (\( R_u \)) during electrochemical measurements. In fact \( R_u \) is so large at a conventional electrode that the waves are broadened and shifted to point of invisibility. This difficulty can be overcome by the use of ultramicroelectrodes (UME) [7–10].

Synthetic boron-doped diamond (BDD) thin film electrodes are a recent type of electrode material that has been intensely investigated in aqueous media [11–15]. It has found applications in fields as wastewater treatment [12,16–18], preparation of powerful oxidants [19,20] and electroanalysis [21,22]. More recently, BDD has been used for electro-organic synthesis in organic solvents [23,24]. Typical examples are formation of dimers [25,26] and C–C bond cleavage [27]. These reactions can be carried out with high efficiency in methanol using BDD anode. A mechanism involving the anodic discharge of methanol to methoxyl radical has been proposed in order to explain the unique behavior of BDD anodes [23,27]. This
mechanism is similar to those proposed for the anodic oxidation in aqueous media where electrogenerated hydroxyl radicals are the active oxidation species [12].

This work is a comparative study between graphite and BDD for the electrochemical acetoxylation of \( p \)-methylanisole (\( p \)-MA) in a glacial acetic acid medium. The aim is to get a better understanding of the influence of the electrode material on the oxidation processes in glacial acetic acid. The system has been characterized electrochemically by steady-state linear voltammetry, chronopotentiometry and preparative electrolysis.

2. Experimental

Voltammetric and chronopotentiometric measurements have been carried out in a three-electrode cell with a platinum wire as counter electrode and an Ag/AgCl (3 M KCl) as a reference electrode. Two types of working electrodes (WE) were used, a carbon fiber (CF) disk ultramicroelectrode (UME) with a diameter of 7 \( \mu \)m and a boron-doped diamond (BDD) UME disk array. This latter was fabricated by Adamant Technologies SA, Switzerland, by covering the diamond layer (1000 ppm of boron doping level) with a Si\(_3\)N\(_4\) film, 0.5 \( \mu \)m in thickness. The patterning of the Si\(_3\)N\(_4\) layer was performed by a standard photolithographic technique through dry etching to form a hexagonal array of 473 microdiscs, 5 \( \mu \)m in diameter and separated by a distance of 150 \( \mu \)m. This large distance to size ratio avoids the interference of the diffusion field around the discs and ensures that each electrode of the array works individually. Such configuration has the advantage of a high overall current by keeping all features of a microelectrode. The electrodes were washed after each experiment in Milli-Q water, then acetone and finally glacial acetic acid for 2 min in an ultrasound bath, each step was done twice.

Preparative electrolyses have been conducted in a monopolar undivided small cell and in a bipolar undivided capillary gap cell.

The monopolar cell is of a filter press type (15 cm\(^3\)) without external recirculation and stirred using a magnetic bar. This cell is composed of two terminal elements made of stainless steel, used as supports for the working and the counter electrodes, and two central elements made of PTFE. The central elements of 1.5 cm thickness have a hole with a surface of 5 cm\(^2\).

The bipolar capillary gap cell is composed of five elements with an interelectrode gap of 1mm and each electrode element having a surface of 31.6 cm\(^2\) (Fig. 1). The electrolyte (1 l) is recirculated (200 l h\(^{-1}\)) using an external pump. The current bypass due to the bipolar reactor type has been measured by quantifying the volumetric hydrogen flow rate and was found to be about 15%.

Glacial acetic acid (Riedel-deHäen), anhydrous sodium acetate (Riedel-deHäen), acetic anhydride (Fluka) and \( p \)-MA (Fluka) were of highest purity and used as received.

The electrochemical measurements were done in glacial acetic acid containing 1 M sodium acetate + 0.1 M acetic anhydride (glacial acetic acid medium). The anhydride was added in order to guarantee operation under anhydrous conditions. In fact if accidentally moisture from the environment is introduced in the cell it reacts immediately with Ac\(_2\)O giving acetic acid.

The voltammetric and chronopotentiometric measurements were done using a computer-controlled Autolab PGstat12 with an ECD module.

The preparative electrolyses have been conducted under galvanostatic conditions (10 mA cm\(^{-2}\)) for a total charge passed of 2 Faradays per mole of substrate. The analysis and quantification of the reaction products formed in solution during the electrolysis was done using a gas chromatograph coupled with a mass spectrometer (GC–MS). A non-polar Supelco DB-5 column has been used. The detector was a flame ionization detector (FID) at a temperature of 250 °C. The temperature program applied for this analysis was 40 °C during 5 min and then a temperature ramp of 10 °C min up to 200 °C.

3. Results and discussion

3.1. Electrochemical measurements in glacial acetic acid medium

Fig. 2 shows steady-state linear voltamograms in glacial acetic acid medium (1 M CH\(_3\)COONa + 0.1 M Ac\(_2\)O in glacial acetic acid) using CF (curve A') and BDD (curve B') UME. It is seen that BDD has much higher overpotential for acetate oxidation than CF. This tendency is similar to that observed in aqueous media where BDD has much higher overpotential for water oxidation (O\(_2\) evolution) than conventional electrodes.
Preparative electrolysis under galvanostatic conditions (10 mA cm\(^{-2}\)) in glacial acetic acid medium (1 M CH\(_3\)COONa + 0.1 M Ac\(_2\)O in glacial acetic acid) revealed that the main products using both graphite and BDD electrodes are ethane and carbon dioxide corresponding to the Kolbe reaction

\[
2\text{CH}_3\text{COO}^- \rightarrow \text{C}_2\text{H}_6 + 2\text{CO}_2 + 2e^- \quad (1)
\]

Beside these products, methane and methyl acetate are produced in small amount during electrolysis. Table 1 shows the faradic current efficiencies of all four products. The relative error is ±3%, estimated on the basis of repeated measurements. The current efficiency of the side reactions varies between 0.1% and 2.3% depending on electrode material. Methane production is about twice more important on BDD electrode than on graphite, while methyl acetate is favored on the graphite electrode (about 14× higher).

The exact role of electrode material in the formation of these by products in the Kolbe reaction is not clear. However, the extent of interaction between the electrode surface and the reaction intermediates (acetoxy and methyl radical) should play an important role in the formation of these products (Eqs. (2) and (3)). It is expected that these radicals are much more strongly adsorbed on sp\(^3\) carbon (graphite electrode) than on sp\(^3\) (BDD) and consequently the surface reaction between these adsorbed radicals (Eq. (3)) is favored on graphite.

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^- & \rightarrow \text{CH}_4 + \text{CH}_3\text{COO}^+ \quad (2) \\
\text{CH}_3\text{COO}^- + \text{CH}_3\text{COO}^* & \rightarrow \text{CH}_3\text{COOCH}_3 \quad (3)
\end{align*}
\]

3.2. Electrochemical measurements in glacial acetic acid medium \(+ p\text{MA}\)

Steady-state linear voltammograms of 2 mM p-MA solution in the glacial acetic acid medium using CF and BDD UME are also shown in Fig. 2. p-MA is oxidized at potentials which are about 0.11 and 0.45 V less anodic than those required for the oxidation of acetate at graphite and BDD electrodes, respectively. Furthermore a shoulder corresponding to a current density of 0.8 mA cm\(^{-2}\) appears at about 1.7 U\(_{\text{NHE}}\) and 1.9 U\(_{\text{NHE}}\) at graphite and BDD, respectively. The process implicated in this shoulder is presumably related to the oxidation of p-MA to the corresponding radical-cation similarly to that observed in dry and wet acetonitrile [28].

It is worthwhile to mention that the voltammetric measurements obtained with CF electrodes are quite reproducible while the voltammetric curves obtained using BDD are hardly reproducible. In fact, fast electrode deactivation has been observed mainly due to deposition of polymeric material on the BDD surface.

In order to investigate this complex, time dependent system, the temporal evolution of potential at a fixed current density (10 mA cm\(^{-2}\)) after addition of p-MA to the glacial acetic acid medium using both CF and BDD electrodes (Fig. 3) has been followed as shown below.

This figure shows that using CF electrode the initial potential in the glacial acetic acid medium (1.95 U\(_{\text{NHE}}\)) corresponding to the Kolbe reaction, drops rapidly, after the addition of p-MA, to about 1.6 U\(_{\text{NHE}}\), and remains constant for a long period of time. At this potential p-MA is oxidized to the corresponding radical cation as has been shown in the voltammetric measurements (Fig. 2).

On BDD electrodes the situation is different, in fact after addition of p-MA, the potential initially slightly decreases then increases continuously. This increase in the potential is related to the deactivation of the BDD electrode by fouling due to polymer formation.

The first preparative electrolysis experiments have been conducted in the monopolar filter press type cell under galvanostatic oxidation (10 mA cm\(^{-2}\)) using a solution of 0.5 M p-MA in glacial acetic acid medium as electrolyte. The evolution of p-MA, its oxidation intermediates and products obtained using both CF and BDD electrodes are shown in Fig. 4. This figure shows that at CF electrolysis leads prevalently to monoaacetoxilation of p-MA (formation of anisyl acetate) observed until a specific charge of ~1 Faraday per mol p-MA, while at higher electrolysis charge diacetoxilation of p-MA occurs (Fig. 4a). On BDD, no diacetoxylated product was detected at any stage.

<table>
<thead>
<tr>
<th>Product</th>
<th>CF(_{\text{H}_6})</th>
<th>CO(_2)</th>
<th>CH(_4)</th>
<th>CH(_3\text{COOCH}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>97</td>
<td>97</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>BDD</td>
<td>98</td>
<td>98</td>
<td>2.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Relative error: ±3%.
of electrolysis. Up to a specific charge of \( \sim 0.25 \) Faraday per mol \( p\-MA \) (formation of monoacetoxylated product) the behavior is similar to that observed at CF, while beyond this charge the material balance is not closed. The miss is due to the formation of polymeric products deposited on the BDD surface (Fig. 4b).

The polymeric deposit on BDD surface (after a specific charge of 2 Faraday per mol \( p\-MA \)) has been characterized by SEM (Fig. 5) and FTIR (Fig. 6). The SEM images (Fig. 5) show that the film is consisted of clusters of about 20 \( \mu \)m covering partially the BDD surface. This may be related to the presence of high energy nucleation sites which favor the local growth of the polymeric material.

The FTIR spectrum (Fig. 6) reveals the presence of \( p\-MA \) units in the polymer, evidenced by C–H stretch and bend as well as C–C stretch lines characteristic for aromatic rings. Furthermore, the presence of a relatively strong ester stretch is an indication that the polymer is acetoxylated to some extent.

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Fig. 3. Chronopotentiometric responses to the addition of 2 mM \( p\-MA \) at zero time to glacial acetic acid medium (\( \text{CH}_3\text{COOH} + 1 \text{ M CH}_3\text{COONa} + 0.1 \text{ M Ac}_2\text{O} \)). (a) Graphite anode; (b) BDD anode; \( j = 10 \text{ mA cm}^2 \); \( T = 298 \text{ K} \).

Fig. 4. Preparative electrolysis in the monopolar electrolyzer of 0.5 M \( p\-MA \) in the glacial acetic acid medium (\( \text{CH}_3\text{COOH} + 1 \text{ M CH}_3\text{COONa} + 0.1 \text{ M Ac}_2\text{O} \)) at 10 mA cm\(^{-2}\) and \( T = 313 \text{ K} \), using: (a) graphite anode, (b) BDD anode. 1: \( p\-MA \), 2: anisyl acetate, 3: anisyl diacetate, 4: missing monomer equivalent.

Fig. 5. SEM images at different magnifications of the polymeric film formed on BDD electrode during preparative electrolysis of \( p\-MA \) in the glacial acetic acid medium (\( \text{CH}_3\text{COOH} + 1 \text{ M CH}_3\text{COONa} + 0.1 \text{ M Ac}_2\text{O} \)).
In the second series of preparative electrolysis experiments, the acetoxylation of \( p \)-MA has been conducted in the bipolar capillary gap cell (Fig. 1) using graphite electrodes (Fig. 7). This figure shows that the monoacetoxylated product (anisyl acetate) is formed with high selectivity (>93%) even for conversion of \( p \)-MA over 90%. Only small amounts of diacetoxylated product (anisyl diacetate) are formed (<4%). This difference observed between the two investigated cells is probably related with the involved hydrodynamic conditions. It is well-known that product distribution in preparative electrolysis may depend strongly on scaling-up, because concentration profiles, current densities and reaction times change when passing from micro- to macroscale electrolysis [29]. In the present case, the high recirculation rate of the electrolyte through the capillary gap cell allows increasing efficiently the mass transfer coefficient and consequently avoids the segregation of the monoacetoxylated product close to the anode surface.

The obtained results show clearly that on graphite acetoxylation is favored, contrary to BDD where the dimerization step also takes place. Similar behavior has been found during oxidation of \( p \)-tert-butyltoluene in methanol [23]. In fact preparative electrolysis using both graphite and BDD electrodes have shown that BDD favor the formation of dimeric products. This behavior of BDD has been attributed to a mechanism based on the non-catalytic character of BDD electrode and the presence of active functionalities on graphite anode [23]. Deposition of polymeric material are also favored on BDD during the anodic oxidation of \( p \)-MA in acetonitrile [28]. Furthermore deposition of polymeric material on BDD is initiated on the high energy sites that are favorable to nucleation and initiation of polymeric clusters [28,30].

4. Conclusion

The electrochemical measurements in glacial acetic acid medium have shown that the overpotential for acetate oxidation is higher on boron-doped diamond (BDD) than on carbon fiber (CF) electrode. Preparative electrolysis in this medium have revealed the formation of small amounts of methane and methyl acetate beside the Kolbe reaction products and the extent of these side products depends on the electrode material. This difference has been attributed to the different adsorption properties of CF and BDD electrodes.

Electrochemical measurements of \( p \)-MA in glacial acetic acid media have shown that selectivity up to 93% monoacetoxylated product can be achieved on graphite for more than 90% conversion of \( p \)-MA using a bipolar capillary gap cell. The situation is different on BDD electrode where a low selectivity is obtained due mainly to the formation of polymeric compounds.

Although graphite electrode remains superior to BDD for acetoxylation due mainly to passivation of the latter, the present results revealed higher dimerization and methylation rates on BDD. The results emphasize the importance of the choice of electrode material depending on the desired product.

References