Selective Anodic Oxidation of 5-Hydroxymethylfurfural

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A selective electrochemical oxidation of 5-hydroxymethylfurfural to 2,5-furandicarbaldehyde was performed. Yields were various depending on the time of the reaction and on the kind of salt used as a supporting electrolyte.

A wide variety of heterocyclic aromatic compounds, among them furans, are the subject of study of electrochemical reactions. As a part of our program of functionalization of 2,5-disubstituted furan derivatives, the present paper describes the selective anodic oxidation of 5-hydroxymethylfurfural (1) to furan-2,5-dicarbaldehyde (2). The dialdehyde 2 is a compound of interest in polymer and macrocyclic chemistry; many routes to its synthesis have been reported. For example: from 2,5-bis(hydroxymethyl)furan, furan-2,5-dicarbonitrile, and 5-hydroxymethylfurfural.

Primary alcohols are easily oxidized electrochemically to carboxylic acids; however, it is much more difficult to obtain aldehydes. Benzyl type aldehydes were reported to be formed in pyridine or in water/tert-butyl alcohol mixture at a platinum electrode. Schäfer et al. reported the electrooxidation of various alcohols to the corresponding aldehydes at a nickel oxide hydroxide electrode in a biphasic system to a mixture of aldehyde and carboxylic acid. Here, we describe the selective electrooxidation of 5-hydroxymethylfurfural (1) to the corresponding dialdehyde 2 at a platinum anode in a biphasic system.

\[
\text{HO} \quad \text{CHO} \quad \text{HO} \quad \text{CHO} \quad \text{H}_2\text{O} / \text{O}_2 \text{C}_2
\]

Scheme 1

The constant current electrolysis was carried out at a current density of 8 mA cm\(^{-2}\) in a biphasic system of an aqueous solution of an inorganic salt and dichloromethane in a divided cell at room temperature. Yields vary depending on the salt used as a supporting electrolyte and the time of the reaction. Results are shown in the Table.

Constant potential coulometry was performed at 0.800 V vs SCE. Initially the reaction was terminated after passage of 2 F mol\(^{-1}\) and the conversion rate did not exceed 50%; secondly, the electrolysis was conducted until 5 F mol\(^{-1}\) had passed through the solution. This improved the conversion rate, but it shows that the current efficiency is not high.

The selectivity of this reaction is very remarkable. The only product is the dialdehyde 2 and no trace of the corresponding furan-2,5-dicarboxylic acid was found (as confirmed by UV studies of the aqueous layer of the product mixture showing the absence of a band at \(\lambda_{\text{max}} = 265 \text{ nm}\), which is characteristic for this compound). UV studies of the aqueous layer of the product mixture pointed out that no other product is formed. Only the evidence for the presence of unreacted 1 is visible (\(\lambda_{\text{max}} = 329 \text{ nm}\), \(\epsilon_{\text{max}} = 14600\)). Its concentration diminished during the course of the reaction and after the passage of 5 F mol\(^{-1}\) was six times less (runs 3 and 4) or four times less (runs 1 and 2). Hence, a recovery of about 20% and 25%, respectively, of 1 was detected in the aqueous layer. While only product 2 accompanied by 5% of the unreacted 1 was detected by \(^1\text{H}\) NMR in the organic layer of the product mixture, the selectivity of the reaction is 100%. The presence of the corresponding furan-2,5-dicarboxylic acid could be expected as reported by van Bekkum in the platinum catalyzed oxidation of 5-hydroxymethylfurfural (1), as well as Bover et al. in the electrochemical oxidation of benzyl alcohol. As these authors noted, the reaction stops at the aldehyde stage in non-aqueous media, but if water is present, the aldehyde is hydrated to a geminal diol, which is subsequently oxidized to an acid as shown in Scheme 2.

\[
\text{RCH(OH)CH}_2 \text{OH} \quad \text{H}_2\text{O} \quad \text{H}_2\text{O} \quad \text{RCH(OH)CH}_2 \text{O} \quad \text{RCONH}_2
\]

Scheme 2

Actually, the described reaction takes place in the aqueous layer. To explain the phenomenon, we performed a similar oxidation of 1 in an aqueous basic solution, without an organic solvent layer. The only product was furan-2,5-dicarboxylic acid. Considering the above result, we believe that the biphasic system seems to play a key role, as the product 2 is poorly soluble in water and easily soluble in dichloromethane. An organic layer is practically some kind of a "trap", which captures the dialdehyde 2. In this way, the product 2 is protected from the possible subsequent oxidation to diacid.

Table. Electrooxidation of HMF in Biphasic System

<table>
<thead>
<tr>
<th>Run</th>
<th>Supporting</th>
<th>Concentration (%)</th>
<th>Yield (%) ( \text{after 3 h} )</th>
<th>Yield (%) ( \text{after 7 h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AcOH</td>
<td>10</td>
<td>32</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
<td>NaH(_2)PO(_4)</td>
<td>10</td>
<td>32</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>Na(_3)HPO(_4)</td>
<td>10</td>
<td>40</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>NaHCO(_3)</td>
<td>10</td>
<td>38</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Na(_2)CO(_3)</td>
<td>5</td>
<td>5(^b)</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>NaOH</td>
<td>5</td>
<td>7(^b)</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>NaOH</td>
<td>1</td>
<td>10(^b)</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Yields of isolated product.

\(^b\) Determined by \(^1\text{H}\) NMR spectroscopy.
The electrolysis was performed on ZUE UNITEM 5351M DC power supply in a divided, H-shaped cell with fritted glass as a divider. A platinum net of a geometric surface 12.5 cm\(^2\) was used as an anode. It was configured for reaction on one face. A platinum rod was used as the cathode. Saturated calomel electrode was used as the reference electrode.

All spectra were recorded on SPECORD 75 (IR), Bruker 200 Gemini (\(^1\)H NMR 200 MHz) and SPECORD (UV-Vis) spectrometers.

**Furan-2,5-dicarboxaldehyde (2):**

In the anodic compartment of the cell were placed 5-hydroxymethylfurfural (1; 0.63 g, 5 mmol), the supporting electrolyte (Table, 90 mL) and CH\(_4\)Cl\(_2\) (10 mL). In the cathodic compartment was placed a solution of the supporting electrolyte (Table, 50 mL). Electrosynthesis at a current density 6 mA cm\(^{-2}\) was carried out for a given time (Table). Then the anolyte was separated, an aqueous solution was extracted with CH\(_2\)Cl\(_2\) (3 x 20 mL) and the combined organic layers were dried (MgSO\(_4\)) and evaporated. The residue was recrystallized from CCl\(_4\) to give a product 2 as white crystals; mp 108 - 109°C (lit.\(^2\) mp 109 - 110°C).

IR (KBr): \(v = 2920\) (CHO), 1690 (C=O), 1580, 1520, 1410 cm\(^{-1}\) (C=C, furan).

\(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.35\) (s, 2 H, H-3,4), 9.85 (s, 2 H, CHO).

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