Electrochemical Transformation of Bio-Derived Furans Using a Salen-Manganese Homogeneous Catalyst ‡

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Abstract: The electrochemical oxidation of HMF (5-hydroxymethylfurfural) to DMF (2,5-furandicarbonylaldehyde) catalysed by a salen-manganese homogeneous catalyst is reported. DMF is a versatile precursor in the synthesis of functional polymers, pharmaceuticals, antifungal agents, and furan-urea resins. A manganese(III)-Schiff base complex 1 was synthesised and characterized by different analytical and spectroscopic techniques. Complex 1 behaved as an efficient catalyst of the electrochemical oxidation of HMF to DMF. The conversion of HMF to DFF was performed under mild conditions. The oxidation of DFF to HMF with a conversion rate of 75% was achieved at pH 8.5, using sodium chloride as the electrolyte to increase the conductivity and to reduce the power dissipation.

Keywords: furan; manganese; catalyst; salen; Schiff base; electrochemistry

1. Introduction

A sustainable society requires a change from an economy based on fossil resources to the so-called bio-based economy, in which most chemicals and materials are produced from renewable feedstocks, such as biomass [1]. Biomass is a major renewable carbon resource, which can help to reduce the dependence on raw fossil materials [2]. The development of new catalysts for the transformation of biomass-derived compounds into valued-added chemicals and liquid fuels is highly desirable to overcome the key challenges facing the market penetration of sustainable biomass-based products. One of the most promising products in this regard is 5-hydroxymethylfurfural (HMF), which has the potential to be converted into a variety of useful intermediates for polymers and many other fine chemicals.

In this communication, we report the effective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxaldehyde (DFF) catalysed by a new manganese(III)-Schiff base complex (Figure 1). The electrocatalysis was performed under mild conditions in saline media, following a procedure developed by us [3].

![Figure 1. Conversion of HMF into DFF.](https://example.com/figure1.png)
2. Materials and Methods

The salen-type ligand H$_2$L$^1$ was prepared by condensation of 3-ethoxy-2-hydroxybenzaldehyde and 1,2-diaminoethane, following a procedure reported previously [4]. The Schiff base has been already characterized by different techniques [4]. Schiff bases are considered very versatile ligands; their basic character or steric properties can be tuned choosing the appropriate substituents on aromatic rings [5].

The [MnL$^1$(H$_2$O)(DCA)] 1 was prepared by addition of 0.17 g of Mn(CH$_3$COO)$_2$ to a methanolic solution of 0.25 g of H$_2$L$^1$. A total of 0.06 g of sodium dicyanamide was added after stirring the previous solution for thirty minutes. The mixture was heated for 10 additional minutes and then concentrated by slow evaporation at room temperature. The product was obtained as brownish crystals suitable for X-ray-diffraction studies. Yield: 60%. Anal. Calcd. For C$_{22}$H$_{24}$MnN$_5$O$_5$ (493.4): C, 53.5; H, 4.8; N, 14.2. Found: C, 52.9; H, 4.8; N, 14.0%. ES/MS (m/z): 409 [MnL$^1$]$^+$. IR (KBr, cm$^{-1}$): ν(C≡N) 2266 (m), ν(C-O) 1248 (s), ν(C=N) 1618 (vs), ν(O-H) 3422 (m).

Oxidations of HMF to DFF were made under mild conditions in saline media [3]. Sodium chloride was used as supporting electrolyte to increase the conductivity and to reduce power dissipation in the electrochemical cell. Phosphate buffer was added to maintain the solution at pH 8.25. In a typical experiment, a total of 1% of 1 as catalyst was used and the cell was thermostatted at 40 °C. The HMF was added and the preset current was applied using an Iso-Tech DC power supply at a fixed potential for 2 h. After electrochemical reaction, the remaining catalyst was removed by filtration through silica gel. DFF was isolated by extraction with dichloromethane, dried and identified through $^1$H NMR spectroscopy.

3. Results and Discussion

The [MnL$^1$(H$_2$O)(DCA)] 1 was obtained in a high yield and its formulation was supported by an elemental analysis, electrospray mass spectrometry and IR spectroscopy. The formation of the coordination compound was confirmed by the shift of the IR imine band of the free Schiff-base ligand upon coordination to the metal ion.

The X-ray crystallisation studies revealed the structure of the complex, in which the salen-type ligand was tightly bound to the manganese ion through the ONNO donor set, occupying the equatorial positions of a distorted octahedron. The coordination sphere of the metal is completed by an axial water molecule and a dicyanamide ligand (see Figure 2).

![Figure 2. Crystal structure of 1.](image_url)

An electrochemical procedure was employed for the oxidation of HMF to DFF. We previously reported that this type of complex is able to catalyse the oxidation of veratryl alcohol (VA), a lignin-model compound, to veratrylaldehyde using a similar procedure [3]. The catalysis takes place under mild conditions at 40 °C, in saline media, under atmospheric pressure and with an alkaline medium of pH 8.25 buffered with phosphate buffer. Previous
studies using a similar procedure, veratryl alcohol as the substrate and different catalyst analogs have shown that a significant improvement in catalytic efficiency can be achieved when the experiments are carried out at 40 °C rather than at room temperature, but this efficiency did not show a relevant increase at higher temperatures [3].

The design of the electrochemical catalysis featured hypochlorite as the prevalent oxidizing agent in the media. At basic pH, the electric current induces the oxidation of chloride into hypochlorite; at this alkaline pH, chlorine undergoes a disproportionation reaction and produces chloride and hypochlorite. In this way, during catalysis, the presence of chlorine and the formation of other undesirable chlorinated derivatives are avoided [6].

Complex 1 behaves as an efficient catalyst in the oxidation of HMF to DFF, with a conversion rate of 75%, calculated after the isolation of the product and identification by $^1$H NMR. The electrochemical experiment in the absence of the catalyst limits the conversion of HMF to DFF to 15–20%, which enhances the catalytic effect of 1 in the electrochemical process.

The product obtained, DFF, is a platform molecule, which can act as a versatile precursor in the functional synthesis of polymers, pharmaceutical derivatives, antifungal agents, and furan-urea resins [7,8].

4. Conclusions

In this work, a novel electrochemical approach to selectively oxidizing HMF to DFF was reported. This DFF is a platform molecule, which can be used in the manufacturing of functional polymers. The manganese(III)-salen complex (1) was obtained and characterized, and subsequently used as a catalyst in the electrochemical process, obtaining a conversion of 75% in the transformation of HMF into DFF, in which hypochlorite is the oxidizing agent generated in situ.

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