chemistry proceedings

Proceeding Paper

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

Lara Rouco [1], Sandra Fernández-Fariña [2], M. Isabel Fernández-García [1], Laura Rodríguez-Silva [1], M. Isabel Velo-Heleno [2] and Marcelino Maneiro [1],*

[1] Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain; lara.rouco.mendez@usc.es (L.R.); mislabel.fernandez.garcia@usc.es (M.I.F.-G.); laura.rodriguez@usc.es (L.R.-S.)

[2] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain; sandra.fernandez.farina@usc.es (S.F.-F.); mariaisabel.velo.heleno@usc.es (M.I.V.-H.)

* Correspondence: marcelino.maneiro@usc.es; Tel.: +34-982824106

† Presented at the 26th International Electronic Conference on Synthetic Organic Chemistry; Available online: https://ecsoc-26.sciforum.net.

Abstract: The electrochemical oxidation of HMF (5-hydroxymethylfurfural) to DMF (2,5-furandicarboxaldehyde) 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 synthetized and characterized by different analytical and spectroscopic techniques. Complex **1** behaves as an efficient catalyst for electrochemical oxidation of HMF to DMF. Conversion of HMF to DFF was performed under mild conditions. Oxidation of DFF to HMF with conversion rate of 75% was achieved at pH 8.5, using sodium chloride as electrolyte to increase the conductivity and to reduce power dissipation.

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

Citation: Rouco, L.; Fernández-Fariña, S.; Fernández-García, M.I.; Rodríguez-Silva, L.; Velo-Heleno, M.I.; Maneiro, M. Electrochemical Transformation of Bio-Derived Furans Using a Salen-Manganese Homogeneous Catalyst. *Chem. Proc.* **2022**, *4*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Julio A. Seijas

Published: 15 November 2022

1. Introduction

A sustainable model society requires a change from an economy based in fossil resources to the so-called bio-based economy, where most of the chemicals and materials are produced from renewable feedstocks like biomass [1]. Biomass arises as a major renewable carbon resource which can help reduce dependence on fossil raw 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 for market penetration of the sustainable biomass-based products. 5-hydroxymethylfurfural (HMF) is one of these most promising products, which has the potential to be converted to 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 is performed under mild conditions in saline media, following a procedure developed by us [3].

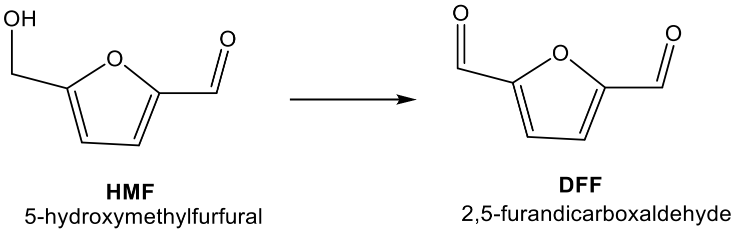

Figure 1. Conversion of HMF into DFF.

2. Materials and Methods

The salen-type ligand H_2L^1 was prepared by condensation of 3-ethoxy-2.hydroxybenzaldehyde and 1,2-diaminoethane, following a procedure already reported [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 the aromatic rings [5].

$[MnL^1(H_2O)(DCA)]$ **1** was prepared by addition of 0.17 g of $Mn(CH_3COO)_2$ to a methanolic solution of 0.25 g of H_2L^1. 0.06 g of sodium dicyanamide was added after thirty minutes of stirring the previous solution. 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 $C_{22}H_{24}MnN_5O_5$ (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 at the electrochemical cell. Phosphate buffer was added to mantain the solution at pH 8.25. In a typical experiment, 1% of **1** as catalyst is used and the cell was thermostatted at 40 °C. 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 remained catalyst was removed by filtration through silica gel. DFF was isolated by extraction with dichloromethane, dried and identified through ^1H NMR spectroscopy.

3. Results and Discussion

$[MnL^1(H_2O)(DCA)]$ **1** was obtained in high yield and its formulation was supported by 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.

X-ray crystallization studies revealed the structure of the complex, where the salen-type ligand is 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).

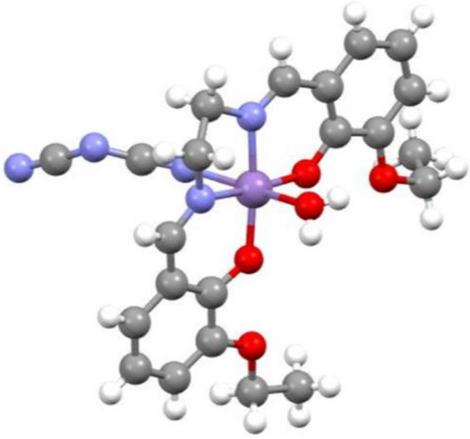

Figure 2. Crystal structure of **1**.

An electrochemical procedure has been employed for the oxidations of HMF to DFF. We have previously reported that this type of complexes is able to catalyze 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, saline media, atmospheric pressure and at alkaline medium of pH 8.25 buffered with phosphate buffer. Previous studies using a similar procedure, veratryl alcohol as substrate and different catalyst analogs have shown that a significant improvement in catalysis efficiency can be achieved when the experiments were carried out at 40 °C rather than room temperature, but this efficiency did not show relevant increase at higher temperatures [3].

The design of the electrochemical catalysis is done to use hypochlorite as the prevalent oxidizing agent in the media. At basic pH the electric current induces the oxidation of chloride into hypochlorite; at such alkaline pH chlorine undergoes a disproportionation reaction to give 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 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%, a fact that 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 oxidize HMF to DFF is reported. DFF is a platform molecule which can be used in functional polymer manufacture. The manganese(III)-salen complex (**1**) has been 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 in situ generated oxidizing agent.

Author Contributions: Conceptualization, L.R. and M. M.; methodology, L.R., L.R.-S. and M.M.; validation, M.I.F.-G., L.R.-S. and M.M.; formal analysis, L.R., S.F.-F. and L.R.-S.; investigation, L.R., S. F.-F. and M.I.V.-H.; data curation, M.I.F.-G., L.R.-S. and M.M.; writing—original draft preparation, L.R. and M.M.; writing—review and editing, L.R., M.I.F.-G., L.R.-S. and M.M.; supervision, M. I.F.-G., L.R.-S. and M.M.; project administration, M.M.; funding acquisition, M.I.F.-G. and M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Xunta de Galicia (*Convenio de Colaboración entre a Xunta de Galicia e a Universidade de Santiago de Compostela polo que se regula o Campus de Especialización "Campus Terra*), Ministerio de Ciencia, Innovación y Universidades (Project PID2021-127531NB-I00; AEI/10.13039/501100011033/FEDER, UE), and European FUR4Sustain COST Action (CA 18220).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhu, Y.; Romain, C.; Willians, C.K. Sustainable polymers from renewable resources. *Nature* **2016**, *540*, 354–362. https://doi.org/10.1038/nature21001.
2. Aljammal, N.; Jabbour, C.; Thybaut, J.W.; Demeestere, K.; Verpoort, F.; Heynderickx, P.M. Metal-organic frameworks as catalysts for sugar conversion into platform chemicals: State-of-the-art and prospects. *Coord. Chem. Rev.* **2019**, *401*, 213064. https://doi.org/10.1016/j.ccr.2019.213064.
3. Rouco, L.; Fernández-García, M.I.; González-Riopedre, G.; Tyryshkin, A.M.; Maneiro, M. Electrochemical conversion of the lignin model veratryl alcohol to veratryl aldehyde using manganese (III)-Schiff base homogeneous catalysts. *Appl. Sci.* **2019**, *9*, 3430. https://doi.org/10.3390/app9163430.
4. Vázquez-Fernández, M.Á.; Bermejo, M.R.; Fernández-García, M.I.; González-Riopedre, G.; Rodríguez-Doutón, M.J.; Maneiro, M. Influence of the geometry around the manganese ion on the peroxidase and catalase activities of Mn (III)–Schiff base complexes. *J. Inorg. Biochem*. **2011**, *105*, 1538–1547. https://doi.org/10.1016/j.jinorgbio.2011.09.002.
5. Gupta, K.C.; Kumar-Sutar, A. Catalytic activities of Schiff base transition complexes. *Coord. Chem. Rev*. **2008**, *252*, 1420–1450. https://doi.org/10.1016/j.ccr.2007.09.005.
6. Szpyrkowicz, L.; Juzzolino, C.; Kaul, S.N.; Daniele, S.; de Faveri, M.D. Electrochemical oxidation of dyeing baths bearing disperse dyes. *Indus. Eng. Chem. Res.* **2000**, 39, 3241–3248. https://doi.org/10.1021/ie9908480.
7. Han, X.; Geng, L.; Guo, Y.; Jia, R.; Liu, X.; Yongguang, Z.; Wang, Y. Base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over a Pt/C-O-Mg catalyst. *Green Chem*. **2016**, *18*, 1597–1604. https://doi.org/10.1039/C5GC02114F.
8. Dai, J. Synthesis of 2,5-diformylfuran from renewable carbohydrates and its applications: A review. *Green Energy Environ.* **2021**, 6, 22–32. https://doi.org/10.1016/j.gee.2020.06.013.