Electronic Supporting Information for

Catalytic Oxidative Cleavage of Catechol by a Non-Heme Iron(III) Complex as a Green Route to Dimethyl Adipate

Robin Jastrzebski, Bert M. Weckhuysen and Pieter C.A. Bruijnincx*

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands. E-Mail: p.c.a.bruijnincx@uu.nl

Contents

S1 Experimental Procedures .......................................................................................... 1
S2 Additional Catalysis Data ......................................................................................... 5
S3 UV-Vis Traces of Diluted Reaction Mixtures ............................................................ 5
S4 Spectral Data of µ-oxo,µ-carboxylato Dibridged Species ....................................... 8
S5 zTOCSY ¹H Spectrum of Reaction Mixture .............................................................. 11
S6 Analytical Data for Dimethyl Adipate ..................................................................... 12
References ................................................................................................................... 14

S1 Experimental Procedures

Physical Measurements. NMR spectra were recorded on a Varian spectrometer operating at 400 MHz (¹H) or 100 MHz (¹³C) in DMSO-d6 (unless mentioned otherwise) and referenced against the signal of the residual protio impurity of the solvent (2.50 ppm). UV-Vis-NIR spectra were recorded on a Varian Cary 50 spectrometer using a quartz cuvette with 10.00 mm path length or on a Varian Cary 60 spectrometer using a dip probe (10.00 mm path length) and corrected for absorption by the solvent. IR measurements were carried on a Bruker Tensor-27 Fourier transform spectrometer equipped with a deuterated triglycerine sulfate (DTGS) detector and ATR accessory (Pike Miracle, Pike Technologies) with a diamond crystal as the internal reflection element. GC-MS measurements were performed on a Shimadzu GC-2010 using a VF5-ms column, coupled to a Shimadzu GCMS-QP2010 mass spectrometer.

Chemicals. Tris(2-pyridylmethyl)amine¹ and [Fe₂(tpa)₂(µ-O)(µ-OAc)](ClO₄)₂.2H₂O² (12) were synthesised according to previously published procedures. Methanol (p.a. grade) was obtained from Merck and diethyl ether (p.a. grade) from Biosolve. All other chemicals were of reagent grade quality and were purchased from Sigma-Aldrich or Acros and used without further purification.

Catalytic Experiments. In typical catalytic experiment, a glass reactor with reflux condenser was charged with 100 mL methanol, 1.00 g (9.08 mmol) catechol and 1.00 g (5.37 mmol) of 1-dodecanol. Air was bubbled through the mixture through a glass frit at 170 mL/min and the reactor heated to 50 °C. Upon reaching reaction
temperature, stock solutions of iron(III) perchlorate nonahydrate (0.45 mmol), tris(2-pyridylmethyl)amine (0.45 mmol) and base (0.90 mmol) were injected, marking the start of the reaction. Samples were withdrawn during the reaction and reactions were run for 6 h. The withdrawn samples (1 mL) were diluted in 5 mL of 1 M HCl to dissociate the iron complexes and extracted 3 times with 5 mL diethyl ether. The combined organic layers were dried (MgSO₄), filtered and concentrated in vacuo. The residue was dissolved in DMSO-d6 and the products quantified as described below. Samples for UV-Vis spectroscopy (0.5 mL) were withdrawn, diluted in 9.5 mL of methanol and immediately measured.

**Identification of Reaction Products.** ¹H total correlation spectroscopy spectra with applied z-filter (zTOCSY) of selected samples were obtained (see figure S7 for a representative example). As zTOCSY gives cross-peaks for all ¹H peaks within the same spin system, this enabled grouping of peaks corresponding to a single muconate isomer and was used to identify the minor products. Based on ¹H NMR spectra of authentic samples and those previously reported in literature, assignments could be made for all products:

* cis,cis-muconic acid (3a) ¹H NMR: δ 5.99 (2H, dd, 8.2 Hz, 2.2 Hz), 7.72 (2H, dd, J = 8.2, 2.2 Hz).

(2Z,4Z)-6-methoxy-6-oxohexa-2,4-dienoic acid³⁴ (3b) ¹H NMR: δ 3.68 (3H, s), 6.04 (2H, d, J = 11.2 Hz), 6.73 (2H, m); GC-MS (EI+): m/z 156 (M⁺, 2%), 111 (M - COOH, 83), 97 (M - COOCH₃, 100).

(2Z,4Z)-6-(2-hydroxyphenoxy)-6-oxohexa-2,4-dienoic acid (3c) ¹H NMR: δ 6.08 (1H, d, J = 11.5 Hz), 6.32 (1H, d, J = 11.6 Hz), 6.75-7.10 (4H, m), 7.72 (1H), 7.91 (1H, t, J = 11.6 Hz), 8.25 (1H, ddd, J = 11.6, 11.7, 1.1 Hz), 9.78 (1H, s); GC-MS (EI+): m/z 234 (M⁺, 7%), 125 (M - C₆H₄O₂, 29), 110 (M - C₃H₅O₃, 100), 83 (M - C₆H₃O₃, 54).

6-oxo-6-(piperidin-1-yl)hexa-2,4-dienoic acid (3d) ¹H NMR: δ 1.47 (2H, m), 1.58 (4H, m), 3.48 (4H, m), 5.83 (1H, dt, J = 11.4, 1.3 Hz), 6.50 (1H, dt, J = 11.5, 1.1 Hz), 7.05 (1H, td, J = 11.6, 1.1 Hz), 7.46 (1H, td, 11.7, 1.1 Hz).

* cis,trans-muconic acid (4a) ¹H NMR: δ 5.99 (1H, dd, J = 8.0, 2.4 Hz), 6.20 (1H, d, J = 15.5 Hz), 6.81 (1H, t, J = 11.6 Hz), 8.20 (1H, ddd, J = 15.5, 11.6, 1.1 Hz); GC-MS: m/z 156 (M⁺, 2%), 111 (M - COOH, 83), 97 (M - COOCH₃, 100).

(2Z,4E)-6-methoxy-6-oxohexa-2,4-dienoic acid⁵ (4b) ¹H NMR: δ 3.71 (3H, s), 6.01 (1H, d, J = 11.3 Hz), 6.31 (1H, d, J = 15.6 Hz), 6.82 (1H, t, J = 11.6 Hz), 8.25 (1H, ddd, J = 15.6, 11.7, 1.1 Hz); GC-MS (EI+): m/z 234 (M⁺, 2%), 111 (M - COOH, 83), 97 (M - COOCH₃, 100).

(2Z,4E)-6-(2-hydroxyphenoxy)-6-oxohexa-2,4-dienoic acid (4c) ¹H NMR: δ 6.08 (1H, d, J = 8.9 Hz), 6.54 (1H, d, 15.4 Hz), 6.75-7.10 (m, 5H), 8.39 (1H, ddd, J = 15.3, 11.5, 0.8 Hz), 9.74 (s, 1H); GC-MS (EI+): m/z 234 (M⁺, 2%), 125 (M - C₆H₃O₂, 38), 110 (M - C₆H₄O₃, 100).

methyl 2-(5-oxo-2,5-dihydrofuran-2-yl)acetate⁶ (5b) ¹H NMR: δ 2.62 (1H, dd, J = 16.5, 8.3 Hz), 2.96 (1H, dd, J = 16.5, 4.7 Hz), 5.41 (1H, m), 6.25 (1H, ddd, J = 5.8, 2.0 Hz), 7.75 (1H, s).
2-hydroxyphenyl 2-(5-oxo-2,5-dihydrofuran-2-yl)acetate (5c) \(^1\)H NMR: \(\delta\) 2.94 (1H, dd, J = 16.7, 8.0 Hz), 3.21 (1H, dd, J = 16.7, 5.0 Hz), 5.52 (1H, m), 6.30 (dd, J = 5.7, 2.0 Hz), 6.76 - 7.12 (4H, m), 7.86 (1H, dd, J = 5.7, 1.5 Hz), 9.69 (1H, s).

* The multiplicity and coupling constants of these peaks were determined from the \(^1\)H zTOCSY spectra, which were of limited resolution (4.7 Hz).

**Scheme S1** All products observed in the catalytic dioxygenation of catechol using an iron(III) tris(2-pyridylmethyl)amine catalyst.

**Product Quantification.** Recorded \(^1\)H NMR spectra were processed using MestreNova 7.1.2. Phase and baseline corrections were applied and characteristic muconic acid peaks were integrated and the integrals normalised to the 1-dodecanol triplet at 0.85 ppm. The response factor of catechol to 1-dodecanol was experimentally determined to be 0.979, whereas the response factor for muconic acid was determined to be 0.968. The latter value was used for all muconate isomers. The overlapping peaks of 4a and 4b at 8.25 ppm were deconvoluted using MestraNova’s GSD algorithm. The strongly overlapping peaks at 5.98 and 7.72 ppm could not be deconvoluted in this manner. To determine the contribution of 3a to the 5.98 ppm peak, the known integral of 4a was subtracted. To determine the contribution of 3b to the 7.72 ppm peak, the known integrals of 3a and 3c were subtracted.

**Stoichiometric Experiment.** Iron(III) perchlorate nonahydrate (496 mg, 0.96 mmol), tris(2-pyridylmethyl)amine (297 mg, 1.02 mmol), piperidine (173 mg, 2.02 mmol) and catechol (110 mg, 1.00 mmol) were dissolved in 30 mL of methanol. The intensely purple solution was exposed to an atmosphere of pure oxygen and allowed to stir gently for 16 h at room temperature. The formed precipitate was removed by filtration and washed with a small amount of methanol to obtain 194 mg of a brown microcrystalline solid. UV-Vis-NIR, NMR and ATR-IR spectra are shown in figures S4-S6.
Spectrophotometric Titration of 12 With Catechol. To a stirred solution of [Fe$_2$(tpa)$_2$(µ-O)(µ-OAc)](ClO$_4$)$_3$.2H$_2$O (5 mL, 0.20 mM) in acetonitrile was added 20 µL of 50 mM piperidine solution in acetonitrile at room temperature. Catechol solution (50 mM) was added in steps of 10 µL. UV-Vis-NIR spectra of the solution were recorded between additions.

Hydrogenation/Transesterification of Isolated Product Mixture. A glass reactor with reflux condenser was charged with 100 mL methanol and 1.15 g (10.4 mmol) catechol and heated to 50 °C while bubbling air through the reaction mixture through a glass frit at 170 mL/min. Upon reaching reaction temperature, stock solutions of iron(III) perchlorate nonahydrate (0.14 mmol), tris(2-pyridylmethyl)amine (0.16 mmol) and piperidine (0.34 mmol) were added. After 24 hours, the reaction mixture was concentrated in vacuo and the resulting dark oil partitioned over 100 mL 1M HCl and 75 mL diethyl ether. The organic layer was separated and the aqueous layer extracted twice with diethyl ether (75 mL). The combined organic layers were dried over MgSO$_4$, filtered and concentrated in vacuo to obtain 1.53 g of dark yellow oil, which solidified upon standing. The solid was dissolved in 50 mL of methanol and 5% wt Pd/C (55 mg) and p-toluenesulfonic acid monohydrate (195 mg, 1.03 mmol) were added. The mixture was heated to 50 °C under stirring and exposed to a H$_2$ atmosphere for 24 h. Afterwards, Pd/C was removed by centrifugation and filtration over a 0.4 µm PTFE filter. Pd/C was again extracted with 50 mL of methanol, centrifuged and filtered, after which the combined methanol solutions were concentrated in vacuo. The resulting oil was dissolved in 100 mL diethyl ether, which was subsequently washed with 100 mL saturated aqueous NaHCO$_3$, 100 mL 0.1 M NaOH solution and brine. The ethereal layer was dried (MgSO$_4$), filtered and concentrated in vacuo to obtain dimethyl adipate (1.00 g, 5.74 mmol, 55%) as very pale yellow oil. $^1$H NMR (CDCl$_3$): δ 1.61 (4H, m), 2.27 (4H, m), 3.61 (6H, s); $^{13}$C NMR (CDCl$_3$): δ 24.38, 33.66, 51.52, 173.72; GC-MS (EI+): m/z 143 (M$^+$ - OCH$_3$, 59%), 114 (94), 111 (79), 101 (73), 59 (100), 55 (73).

Hydrogenation/Transesterification of Crude Reaction Mixture. A glass reactor with reflux condenser was charged with 100 mL methanol and 1.02 g (9.23 mmol) catechol and heated to 50 °C while bubbling air through the reaction mixture through a glass frit at 170 mL/min. Upon reaching reaction temperature, stock solutions of iron(III) perchlorate nonahydrate (0.17 mmol), tris(2-pyridylmethyl)amine (0.20 mmol) and piperidine (0.36 mmol) were added. After 24 hours, the reaction mixture was transferred to a Schlenk flask and 5% wt Pd/C (50 mg) and p-toluenesulfonic acid monohydrate (180 mg, 0.95 mmol) were added. The mixture was heated to 50 °C under stirring and exposed to a H$_2$ atmosphere for 24 h. Afterwards, Pd/C was removed by centrifugation and filtration over a 0.4 µm PTFE filter. Pd/C was again extracted with 50 mL of methanol, centrifuged and filtered, after which the combined methanol solutions were concentrated in vacuo. The resulting oil was dissolved in 100 mL diethyl ether, which was subsequently washed with 100 mL 1M HCl, 100 mL saturated aqueous NaHCO$_3$, 100 mL 0.1 M NaOH solution and brine. The ethereal
layer was dried (MgSO₄), filtered and concentrated in vacuo to obtain dimethyl adipate (0.77 g, 4.42 mmol, 48%) as very pale yellow oil. Analysis was identical to the experiment described above.

S2 Additional Catalysis Data

Table S1 Results of the catalytic dioxygenation of catechol, using an in-situ prepared catalyst with varying amounts of piperidine and catalyst.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Base</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>MB (%)</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(ClO₄)₃</td>
<td></td>
<td></td>
<td>3a 3b 4a 4b 5c 5b 5c 3d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>5%</td>
<td>2 eq</td>
<td>92 5 48 2 13 - -</td>
<td>88 16</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>1%</td>
<td>2 eq</td>
<td>18 2 12 - 3 -</td>
<td>103 25</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>2%</td>
<td>2 eq</td>
<td>50 3 27 - 7 -</td>
<td>93 21</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>10%</td>
<td>2 eq</td>
<td>100 3 44 8 16 - -</td>
<td>87 8</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>5%</td>
<td>1 eq</td>
<td>76 4 42 1 8 - -</td>
<td>88 13</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>10%</td>
<td>4 eq</td>
<td>83 5 35 2 8 - 6</td>
<td>81 14</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Fe(ClO₄)₃</td>
<td>5%</td>
<td>8 eq</td>
<td>78 4 15 3 4 11</td>
<td>63 9</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

*a Amount of piperidine, in equivalents relative to iron precursor ¹ Conversion of catechol ² Mole balance as moles of C₆ units found divided by starting amount of catechol ³ Turnover number ⁴ Turnover frequency

S3 UV-Vis-NIR Traces of Diluted Reaction Mixtures

Figure S1 UV-Vis-NIR spectra of the diluted (20x) catalytic dioxygenation reaction mixture in time, using 5 mol% Fe(ClO₄)₃, 5 mol% tpa and 10 mol% piperidine.
**Figure S2** UV-Vis-NIR spectra of the diluted (20x) catalytic dioxygenation reaction mixture in time, using 5 mol% Fe(ClO$_4$)$_3$, 5 mol% tpa and 20 mol% piperidine.
Figure S3 UV-Vis-NIR spectra of the diluted (20x) catalytic dioxygenation reaction mixture in time, using 5 mol% FeCl$_3$, 5 mol% tpa and 10 mol % piperidine. The absorption bands at 518 and 812 nm indicate [Fe(tpa)(catecholato)]$^+$ forms initially, but disappears with the formation of a new complex which absorbs at 420 nm, with a concomitant decrease in catalytic activity. Thus, while the active catecholato complex can apparently be formed from [Fe(tpa)Cl$_2$]$^+$, it appears that during the reaction another chloride-containing complex is formed, to which catechol can no longer coordinate. Based on the UV-Vis-NIR spectrum, several possibilities for the identity of this complex can be excluded, including [Fe(tpa)Cl$_2$]$^+$, [Fe$_2$(tpa)$_2$(µ-O)Cl$_2$]$^{2+}$ and catecholato complexes. However, we were unable to isolate this iron complex from the reaction mixture in order to determine its identity.
S4 Spectral Data of μ-oxo,μ-carboxylato Dibridged Species

Figure S4 UV-Vis-NIR spectrum of the complex isolated from a stoichiometric reaction (acetone, 289 μg/mL). The maxima at 693 nm, 490 nm and 457 nm are in good agreement with those previously reported for μ-oxo, μ-carboxylato dibridged species with the tris(2-pyridyl)amine ligand.2,9
Figure S5 $^1$H NMR spectrum of the complex isolated from a stoichiometric reaction (acetone-d6). The relatively narrow spectral width of the observed peaks is indicative of strongly anti-ferromagnetically coupled iron centres, while the positions of the tris(2-pyridylmethyl)amine protons are similar to those previously reported for 12.²
Figure S6 ATR-IR spectrum of the complex isolated from a stoichiometric reaction (solid state). The energy difference of 170 cm\(^{-1}\) between the C=O asymmetric stretch (1608 cm\(^{-1}\)) and C=O symmetric stretch (1438 cm\(^{-1}\)) vibration modes is indicative of a bridging binding mode.\(^{11}\)
Figure S7 zTOCSY $^1$H NMR spectrum of the products of the dioxygenation reaction under standard conditions; depicted is the region where unsaturated compounds are expected. Colour-coded boxes indicate cross-peaks for the muconate hydrogens of minor products 3c and 4a-c. The catecholato hydrogens of the catechol-esters appear between 6.75 - 7.10 ppm, but couple extremely weakly to the muconate hydrogens.
S6 Analytical Data for Dimethyl Adipate

**Figure S8** $^1$H NMR spectrum (CDCl$_3$) of isolated dimethyl adipate.

**Figure S9** $^{13}$C NMR (CDCl$_3$) spectrum of isolated dimethyl adipate.
**Figure S10** Chromatogram of isolated dimethyl adipate and corresponding mass spectrum at the peak maximum.
References