Electronic Supplementary Information (ESI)

Effect of copper salts on hydrothermal oxidative decarboxylation: A study of phenylacetic acid

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I. EXPERIMENTAL SECTION

Materials

Benzyl alcohol (99%), benzoic acid (99%), benzaldehyde (>99%), phenylacetic acid (99%), p-tolylacetic acid (99%), and p-fluorophenylacetic acid (98%) were obtained from Sigma Aldrich and used as received. Copper (II) salts including copper chloride (99%), copper acetate (98%), copper sulfate (98%), and copper trifluoromethanesulfonate (98%) were purchased from Sigma Aldrich, whereas copper nitrate (>99%) was purchased from Fisher Chemicals. Magnesium nitrate (>99%), zinc nitrate (98%), and nickel (II) nitrate (>99%) were all obtained from Sigma Aldrich. Dichloromethane (99.9%) was obtained from VWR and n-dodecane (99%) was purchased from Sigma Aldrich. Deionized water was obtained from a Barnstead Nanopure system with a resistivity of 18.2 MΩ·cm. Fused silica glass tubes were obtained from GM Associates, Inc. and rinsed with dichloromethane before use.

Methods

Hydrothermal experiments were performed in fused silica glass tubes (2 mm inner diameter and 6 mm outer diameter) using a previously developed method. In short, 0.03 mmol of phenylacetic acid was weighed and carefully transferred into the tube through a Pasteur pipette. A 0.3 mL aliquot of metal salts solution (0.2 molal in degassed and deionized water) was subsequently added using a gas-tight micro-syringe, to reach a molar ratio of 1:2 between phenylacetic acid and the divalent metal ions. In sodium salts experiments, the anions concentrations were kept the same as those in copper salts experiments, with a molar ratio of 1:4 between phenylacetic acid and the sodium ions, except for sodium sulfate (1:2). The headspace air in silica tubes was evacuated through three pump-freeze-thaw cycles and the tubes were sealed with an oxyhydrogen flame under vacuum. The sealed tubes were then heated in a gas
chromatography (GC) oven at 200 ºC for up to 6 hours. The pressure inside the tube was calculated
to be ca. 15 bar (P_{sat} at 200 ºC) based on thermodynamics calculations using SUPCRT92.\textsuperscript{2}

The hydrothermal experiments were quenched by submerging the silica tubes in a cold
water bath and the cooling process took less than one minute. The tubes were cut open and the
products were quickly transferred into a 3.0 mL dichloromethane solution with \textit{n}-dodecane as the
GC internal standard. Reaction products were analyzed using an Agilent 7820 GC equipped with
an autosampler (Agilent 7650) and a flame-ionization detector, and the product identification was
verified by a GC-MS (Agilent 7890A/5975C). Product concentrations were quantified by GC
calibration curves that were generated with standard solutions. The GC oven was programmed to
start at 50 ºC (hold 8 min), ramp at 10 ºC min\textsuperscript{-1} to 220 ºC (hold 10 min), and ramp at 20 ºC min\textsuperscript{-1}
to 300 ºC (hold 5 min). The injector temperature was set at 300 ºC.

The absorbance of dissolved copper (II) in solution before and after the hydrothermal
reaction was measured using a UV-Vis spectrometer (Agilent). To minimize oxidation of copper
(I) to copper (II) by air, the aqueous samples after the hydrothermal process were quickly extracted
with 3.0 mL DI water, filtered through a 0.45 µm-membrane filter, and transferred to a cuvette
before the spectroscopy analysis in a wavelength range of 500 to 900 nm. The absorbance of
copper (II) was measured at 799 nm, and the copper (II) concentration was determined based on a
calibration curve built with copper (II) standards. Concentration of copper (I) was not quantified
because of the low solubility of the copper (I) salts, and insoluble solids were observed after the
reaction, which are consistent with formation of copper (I) products.

Raman measurements were collected through the wall of sealed silica tubes using a Horiba
Xplora Plus Raman microscope, similar to a previous approach.\textsuperscript{3} In a typical measurement, the
laser was first focused on the top of the silica tube above a region containing fluid. The stage was
then raised 1500 µm to bring the focus of the laser ~500 µm within the tube. All Raman spectra were acquired using a 473 nm laser with perpendicular polarization through a 50x long-working distance objective (0.50 NA) with ~25 mW power at the sample surface, a 100 µm confocal pinhole, a 100 µm monochromator slit, a 1200 groove mm\(^{-1}\) dispersive grating, 60 s acquisition time, and 3 co-averaged scans. Each Raman spectrum was subjected to a 10th-order polynomial smoothing algorithm following collection. Displayed spectra have had the water signal from a CuCl\(_2\) solution subtracted following smoothing. The phonon band at 520.7 cm\(^{-1}\) from crystalline silicon was used to calibrate all Raman spectra.
II. FIGURES AND TABLES

Figure S1. Absorbance of copper (II) in standard solutions with a concentration ranging from 0.002, 0.005, 0.01 to 0.05 molal.
Figure S2. Calibration curve built with copper (II) absorbance versus copper (II) concentrations. The absorbance of copper (II) was measured at the wavelength of 799 nm.

\[y = 6.6074x + 0.0052\]

\[R^2 = 0.99996\]
Figure S3. Absorbance of copper (II) in solutions before (green curve) and after the hydrothermal experiments of PAA with copper chloride (blue curve), copper sulfate (orange curve), and copper nitrate (red curve) at 200 °C and 15 bar after 2 hours. The starting concentrations of PAA and copper (II) were 0.1 and 0.2 molal, respectively. The samples were diluted 10 times before the UV-Vis analysis to ensure the absorbance values were not higher than 1.
**Table S1.** Major products concentration and reaction conversion of PAA with 2 and 4 equivalent of copper (II) salts in H$_2$O at 200 ºC and 15 bar after 2 hours. The starting concentration of PAA was 0.1 molal. The initial concentrations of 2 and 4 equivalent of copper (II) were 0.2 and 0.4 molal, respectively.

<table>
<thead>
<tr>
<th>Copper (II) salts</th>
<th>Copper (II)/PAA ratio</th>
<th>PAA decomposition (%)</th>
<th>Benzaldehyde (mmolal)</th>
<th>Benzoic acid (mmolal)</th>
<th>Remaining Cu$^{2+}$ (molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA CuCl$_2$</td>
<td>2</td>
<td>42.2</td>
<td>30.4</td>
<td>10.7</td>
<td>0.02</td>
</tr>
<tr>
<td>PAA CuCl$_2$</td>
<td>4</td>
<td>68.9</td>
<td>61.8</td>
<td>7.1</td>
<td>-</td>
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<tr>
<td>PAA CuSO$_4$</td>
<td>2</td>
<td>34.1</td>
<td>12.0</td>
<td>20.8</td>
<td>0.02</td>
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<tr>
<td>PAA CuSO$_4$</td>
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<td>44.7</td>
<td>25.7</td>
<td>18.9</td>
<td>-</td>
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<tr>
<td>PAA Cu(OAc)$_2$</td>
<td>2</td>
<td>39.4</td>
<td>24.7</td>
<td>14.7</td>
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<td>PAA Cu(NO$_3$)$_2$</td>
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<td>66.6</td>
<td>49.2</td>
<td>17.4</td>
<td>-</td>
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<td>PAA Cu(NO$_3$)$_2$</td>
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<td>8.7</td>
<td>62.6</td>
<td>0.01</td>
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<tr>
<td>PAA Cu(OTf)$_2$</td>
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<td>14.6</td>
<td>4.6</td>
<td>9.1</td>
<td>-</td>
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<tr>
<td>PAA Cu(OTf)$_2$  + NaNO$_3$</td>
<td>2</td>
<td>53.7</td>
<td>10.9</td>
<td>42.8</td>
<td>-</td>
</tr>
</tbody>
</table>
References:

