Conversion of Saccharides into Formic Acid using Hydrogen Peroxide and a Recyclable Palladium(II) Catalyst in Aqueous Alkaline Media at Ambient Temperatures

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The calibration curve of a DMSO standard was taken with known amounts of formic acid. The $^1$H NMR of 20, 40, 80, and 120 μmol of formic acid was taken in 0.75 mL of D$_2$O with a sealed capillary DMSO standard.

The equation of the line is:

\[ y = 10.315x \]

\[ R^2 = 0.99372 \]
The calibration curve of a DMSO standard was taken with known amounts of glycolic acid. The \(^1\)H NMR of 1, 5, 10, and 20 µmol of glycolic acid was taken in 0.75 mL of D\(_2\)O with a sealed capillary DMSO standard.

\[ y = 3.4771x \]
\[ R^2 = 0.99756 \]
### Lewis Acid Additive Results

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$</td>
<td>34.6</td>
</tr>
<tr>
<td>CrCl$_3$</td>
<td>79.9</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>64.9</td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Reaction conditions: 100 μmol of substrate, 5 μmol of Lewis acid, and 600 μmol NaOH were dissolved in 0.44 mL H$_2$O. 60 μL 30% H$_2$O$_2$ was added and the mixture stirred at 25 °C for 16 hours. 0.25 mL of D$_2$O was then added to the reaction mixture with a sealed capillary DMSO standard. The solution was then analyzed using wet1D NMR.
(53.185 \times 10.315) = 109.7 \text{ TON}

Formic Acid

DMSO Standard

100 \mu\text{mol} \text{ D-Glucose (0.2 M aqueous solution) } \xrightarrow{600 \mu\text{mol} 30\% \text{ H}_2\text{O}_2, 600 \mu\text{mol} \text{ NaOH}} 5 \text{ mol} \% \text{ Pd(II) catalyst, 16 hrs., 25 \degree C} \xrightarrow{109.7 \text{ TON}}
Formic Acid

Carbonyl Carbon

100 μmol D-Glucose
600 μmol 30% H₂O₂
600 μmol NaOH
5 μmol Fe₃⁺/Pd(II) catalyst, 16 hrs., 25 °C

108.7 TON
$$\frac{(53.899 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 111.2 \text{ TON}$$

From Acid

DMSO Standard
Formic Acid

\[
\frac{(58.032 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 119.7 \text{ TON}
\]
Formic Acid

\[
\frac{(56.670 \times 10.315)}{5 \text{ mol} \% \text{ catalyst}} = 116.9 \text{ TON}
\]

100 μmol D-Xylose (0.2 M aqueous solution) 600 μmol 30% H₂O₂, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C

116.9 TON
100 µmol D-Fructose (0.2 M aqueous solution)  
600 µmol 30% H₂O₂, 600 µmol NaOH  
5 mol % Pd(II) catalyst, 16 hrs., 25 °C

\[
\begin{align*}
\text{Formic Acid: } & \quad \frac{(40.266 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 83.1 \text{ TON} \\
\text{Glycolic Acid: } & \quad \frac{(20.851 \times 3.4771)}{5 \text{ mol } \% \text{ catalyst}} = 14.5 \text{ TON}
\end{align*}
\]
100 μmol D-Tagatose (0.2 M aqueous solution) 600 μmol 30% H₂O₂, 600 μmol NaOH
5 mol % Pd(II) catalyst, 16 hrs., 25 °C

Formic Acid

\[
\frac{(43.307 \times 10.315)}{5 \text{ mol % catalyst}} = 89.3 \text{ TON}
\]

Glycolic Acid

\[
\frac{(23.440 \times 3.4771)}{5 \text{ mol % catalyst}} = 16.3 \text{ TON}
\]

DMSO Standard
Formic Acid

\[
\frac{(41.667 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 86.0 \text{ TON}
\]
100 µmol D-Lactose (0.2 M aqueous solution) → 600 µmol 30% H₂O₂, 600 µmol NaOH, 5 mol % Pd(II) catalyst, 16 hrs., 60 °C → 98.7 TON

\[
\frac{(47.823 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 98.7 \text{ TON}
\]
\[
\frac{(47.228 \times 10^{3.15})}{5 \text{ mol } \% \text{ catalyst}} = 97.4 \text{ TON}
\]
Formic Acid

\[
\frac{(13.246 \times 10.315)}{5 \text{ mol} \% \text{ catalyst}} = 27.3 \text{ TON}
\]
Formic Acid

\[
\frac{(7.710 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 15.9 \text{ TON}
\]

DMSO Standard

100 \, \mu\text{mol D-Melezitose (0.2 M aqueous solution)} \quad 600 \, \mu\text{mol 30\% H}_2\text{O}_2, 600 \, \mu\text{mol NaOH} \\
5 \, \text{mol} \% \text{ Pd(II) catalyst, 16 hrs., 60 }^\circ\text{C}

15.9 \text{ TON}
Formic Acid

\[
\frac{(13.807 \times 10.315)}{5 \text{ mol} \% \text{ catalyst}} = 28.5 \text{ TON}
\]
Formic Acid

\[
\frac{(18.935 \times 10.315)}{5 \text{ mol } \% \text{ catalyst}} = 39.1 \text{ TON}
\]