Efficient, Metal-Free Production of Succinic Acid by Oxidation of Biomass-Derived Levulinic Acid With Hydrogen Peroxide

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Materials
All materials were used as received. Levulinic acid (98%) and sulfuric acid (98%) were purchased from Sigma-Aldrich. 3M sulfuric acid was prepared by dilution of concentrated sulfuric acid (98%). Trifluoroacetic acid (99%), diethyl ether, and dichloromethane were purchased from Fischer Scientific. Hydrogen peroxide (30% aq) was purchased from Macron Chemicals.

Experimental Procedures

Oxidation of levulinic acid to succinic acid with hydrogen peroxide in 3M sulfuric acid

\[
\text{O} - \text{C} - \text{OH} \quad \xrightarrow{\text{H}_2\text{O}_2 / \text{H}_2\text{SO}_4} \quad \text{HO} - \text{C} - \text{OH}
\]

Levulinic acid (2.00 g, 17.2 mmol) was dissolved in 3M H$_2$SO$_4$ (20 mL) and 30% aq H$_2$O$_2$ (8 mL) was carefully added. The colorless solution was placed in an oil bath at 90 °C and stirred for 3.5 h. Additional 30% aq H$_2$O$_2$ (2.0 mL) was added, followed 20 min later by another aliquot of 30% aq H$_2$O$_2$ (2.0 mL). After 20 min the mixture was cooled to RT and a measured quantity of 1,4-dioxane was added as an internal standard. The $^1$H NMR spectrum was measured and the yields were estimated as follows: succinic acid (48%), acetic acid (50%), formic acid (24%) and methanol (17%).

Oxidation of LA by hydrogen peroxide in TFA

\[
\text{O} - \text{C} - \text{OH} \quad \xrightarrow{\text{H}_2\text{O}_2 / \text{TFA}} \quad \text{HO} - \text{C} - \text{OH}
\]
Levulinic acid (2.00 g, 17.2 mmol) was dissolved in TFA (40 mL) and 30% aq H$_2$O$_2$ (2.0 mL) was carefully added. The flask was mounted with a water-cooled condenser and -78 °C volatiles trap, and the colorless mixture was placed in an oil bath at 90 °C and stirred for 20 min. Additional 30% aq H$_2$O$_2$ (8.0 mL) was added portionwise at a rate of 2 mL every 20 min. The reaction was allowed to stir a further 20 min after the final addition, at which point the LA had been completely consumed as indicated by $^1$H NMR analysis. The mixture was cooled to room temperature and a measured amount of 1,4-dioxane was added as an internal standard. The $^1$H NMR spectrum was measured and the yields were estimated as follows: succinic acid (62%), acetic acid (43%), 3-hydroxypropanoic acid (9%), and formic acid (45%). Methyl trifluoroacetate (45%) was obtained in the cold trap. The volatiles were evaporated to give a white solid (1.70 g) which was triturated with Et$_2$O (2 × 2 mL) to give succinic acid (1.22 g, 60%).

**Scale-up of the oxidation of LA by hydrogen peroxide in TFA**

Levulinic acid (10.00 g, 86.12 mmol) was dissolved in TFA (200 mL) and 30% aq H$_2$O$_2$ (10 mL) was carefully added. The flask was mounted with a water-cooled condenser and -78 °C volatiles trap, and the colorless mixture was placed in an oil bath at 90 °C and stirred for 20 min. Additional 30% aq H$_2$O$_2$ (40 mL) was added portionwise at a rate of 10 mL every 20 min. The reaction was allowed to stir a further 30 min after the final addition, at which point the LA had been completely consumed as indicated by $^1$H NMR analysis. The volatiles were evaporated under reduced pressure to give a white solid. The crude product was triturated with 1:1 Et$_2$O/DCM (3 × 6 mL) to give succinic acid (6.00 g, 59%). In the cold trap, methyl trifluoroacetate was isolated as a colorless liquid (4.40 g, 40%).
**Figure S1.** $^1$H NMR spectrum of succinic acid in D$_2$O.
Figure S2. $^{13}$C NMR spectrum of succinic acid in D$_2$O.