Green Chemistry:
An Environmentally Benign Synthesis of Adipic Acid

Adapted by R. Minard and B. Barracough (Penn State Univ.) from a micrscale procedure used by the University of Oregon, Eugene. This procedure is based on an experiment by Scott M. Reed and James E. Hutchison. *J. Chem. Educ.* 2000, 77, 1627-1629.

**Introduction:**

Adipic acid, which is used to make nylon 6,6\(^1\), is traditionally synthesized using either phenone or phenol and nitric acid. This reaction uses organic solvents and causes a by-product of nitrous oxide (a toxic gas), so a more environmentally cautious synthesis was recently devised\(^2\).

This experiment is an oxidation of cyclohexene by hydrogen peroxide in water, using sodium tungstate as a catalyst. Stark’s catalyst can be used as the phase transfer catalyst, as long as potassium hydrogen sulfate is used also to provide the hydrogen sulfate counter ion\(^1\).

\[
\text{Na}_2\text{WO}_4 + \text{H}_2\text{O}_2 + \text{KHSO}_4 \rightarrow \text{C}_6\text{H}_{12}\text{O}_4 + \text{H}_2\text{O} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}
\]

**Cautions:**

Gloves and goggles must be worn when handling 30% hydrogen peroxide, as it is known to cause severe burns on the skin and in the eyes. Stark’s catalyst is toxic, and gloves should be worn when handling this product also.

**Synthesis:**

Place a stir bar, 0.25 g sodium tungstate dihydrate, 0.25 g Stark’s catalyst, 6.0 g hydrogen peroxide (30%), and 0.185 g KHSO\(_4\) into a 50-mL round bottom flask that is fitted with a condenser. Add 1.0 g cyclohexene to the stirred mixture. While stirring, heat the mixture to a reflux on a heating mantle (no sand) until the reaction no longer separates into two separate layers (about 2 h).

**Isolation and Purification:**

Remove the round-bottom flask from the sand bath and transfer the aqueous layer to a clean beaker while it is still hot. Crude adipic acid will precipitate upon cooling. Using a Hirsch funnel, separate the acid from the liquid. Recrystallize the crude sample from a minimal amount of hot water to yield the purified product.

**Cleaning Up:**

After the reaction, Stark’s catalyst will be left in the bottom of your round-bottom flask. This can be washed down the drain with some acetone. The filtrate should be allowed to evaporate to dryness in a beaker in your locker and the tungstate catalyst recycled. If it is not recycled, the sodium tungstate can be placed in the heavy metals container.

**Analysis:**

Analyze final product using \(^1\)H NMR and IR analyses.

**Final Report:**

Why must the aqueous layer be transferred to a flask while it is still hot?

**References**

Results

Yield needs to be improved over what is below. Read the literature!

The product, adipic acid, was prepared by an oxidation of cyclohexene with 30% hydrogen peroxide. Sodium tungstate was used as a catalyst, and Stark’s catalyst paired with KHSO₄ served as a phase transfer catalyst. This reaction produced a 20% yield of crude adipic acid, mp 144-148 °C. Recrystallization from hot water yielded 8% of the purified product, mp 146-148 °C (lit³ mp: 148-150 °C).

Analysis by ¹H NMR showed peaks at 2.38 ppm and 1.62 ppm. The peak at 1.62 ppm indicated secondary hydrogens, and the peak at 2.38 ppm also indicated secondary hydrogens. These were shifted slightly, however, due to the carboxylic acid functional group that they are closer to. There should have been a peak at about 13 ppm for the hydrogen on the carboxylic acid, however, this did not appear. The reason for this is that the acidic hydrogen interchanged with the deuterium on the solvent (D₂O).

Analysis by IR showed two regions of interest: a wide peak from about at 2400-3300 cm⁻¹ and peaks in the fingerprint region around 1700 cm⁻¹. The wide peak at the 2400-3300 cm⁻¹ range was an indication of the carboxylic acid functional group. The other area indicated the straight carbon chain part of the molecule.

This experiment fulfilled its purpose of utilizing “greener” chemical concepts. The phase transfer catalyst and the sodium tungstated were both able to be recycled, which cut down on waste. Also, this experiment was different than the old synthesis in that it eliminated organic solvents, and it eliminated the use of nitric acid which caused a toxic side product (nitrous oxide).