

## Selective Oxidation of Benzyl Alcohol to Benzaldehyde

Adapted from literature by Ketí Assor, Irvin Levy, Erin Thames and Rowan Walker

### Background

Traditionally oxidation of alcohols to aldehydes requires the use of hazardous, heavy-metal reagents, such as pyridinium chlorochromate (PCC). In fact, PCC has been widely considered an appropriate agent for the oxidation, appearing in many undergraduate textbooks as the only viable method to produce aldehydes from alcohols. Both PCC and the usual solvent for its reaction, dichloromethane, are hazardous, cancer suspect agents. In this particular reaction, an environmentally safer oxidizing agent is formed from sodium molybdate to make an efficient catalyst that is activated by aqueous hydrogen peroxide. In addition, hydrogen peroxide serves not only as an activating agent, but also as the solvent for this transformation.

### Purpose

This experiment provides an excellent example of selective oxidation. In addition it demonstrates the synthesis and use of a catalyst in reaction. Other green lessons include replacement of a hazardous reactant with a safer alternative, the elimination of hazardous solvents, and reduction of waste.

### Procedure

#### Preparation of tetra(benzyltriethylammonium) octamolybdate catalyst

*Scheme 1:*



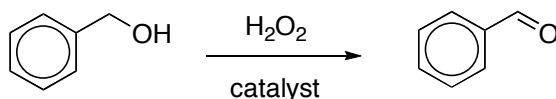
*Method:*

To prepare the catalyst, sodium molybdate dihydrate (0.30 g; 1.2 mmol), and 4 M HCl (0.5 mL; 2.0 mmol) were added to a vial. About 1 mL of water was added to complete dissolution. Into a second vial benzyl tri-ethyl ammonium chloride (BTEAC) (0.525 g; 2.30 mmol) and *ca.* 3 mL water were stirred until dissolved. The BTEAC solution was heated at 70 °C with stirring. To the stirred solution was added the molybdate solution dropwise. After addition was complete, the solution was stirred for an additional five minutes, then removed from heat and vacuum filtered.

The solid was washed with *ca.* 5 mL while on the filter. The catalyst produced could be used wet or saved for later use.

## Preparation of Benzaldehyde

*Scheme II:*



*Method:*

For preparation of benzaldehyde, benzyl alcohol (5 mL; 50 mmol) was added to a 50 mL round bottom flask containing dry catalyst (0.25 g; 0.2 mol%). Next, 15wt% hydrogen peroxide (12 mL; 60 mmol) was added to the flask. The mixture was then refluxed for one hour then cooled to near room temperature. The product was isolated by simple distillation yielding benzaldehyde and water in the distillate. Water was removed with a pipet and the product was dried over sodium sulfate, weighed and IR spectrum was recorded.

### Prelab

1. In this oxidation reaction, hydrogen peroxide is reduced to water. What is the balanced reaction for the oxidation step?
2. How many millimoles of hydrogen peroxide are in a 15wt% solution of peroxide? Recall that wt% means mass of solute per mass of solution. To answer this you will need the density of the solution, estimating that a 15wt% solution has density is 1.05 g/mL.
3. Look up information, hazards, and safety on all materials used in this procedure. Since you will not find the safety information for 15wt% peroxide, look up 30% and 3%.
4. What makes the benzaldehyde oxidation reaction *selective*?
5. What is the atom economy of each reaction scheme?
6. What is the approximate e-factor of each part of this synthesis?
7. What one change could you make to significantly improve the greenness of this method?

### References

- 1 Guo, Ming-Lin; Li, Hui-Zhen Li. Selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide over tetraalkylpyridinium octamolybdate catalysts. *Green Chem.* **2007**, 9, 421-423.
- 2 ACS. Selection from "Introduction to green chemistry". **2002**. Web access: [http://domin.dom.edu/faculty/jbfriesen/chem254lab/atom\\_economy.pdf](http://domin.dom.edu/faculty/jbfriesen/chem254lab/atom_economy.pdf)
- 3 Anastas, Paul T.; Warner, John C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
- 4 Levy, Irvin J. The goal is zero; E-factor as a green chemistry metric. Web access: <http://www.cs.gordon.edu/~ijl/visualizingWaste/>