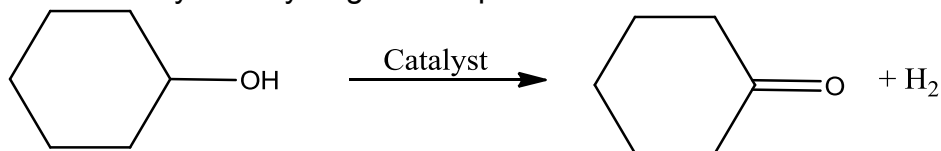


Reminder: These notes are meant to supplement, not replace, the laboratory manual.

Oxidation of Cyclohexanol to Cyclohexanone

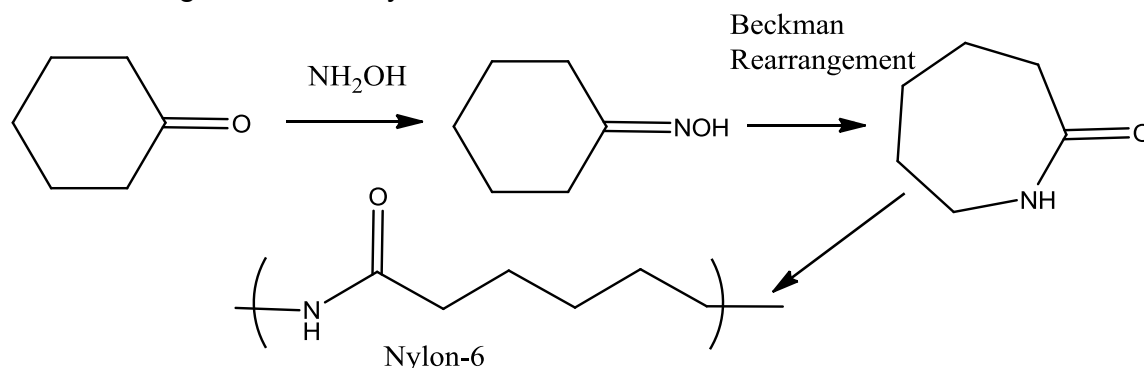
History and Application:

Oxidation reactions are incredibly important in the chemical and biochemical sciences. Re-dox reactions are critical in the NADH-NAD⁺ couple with ATP which provides energy to all cellsⁱ. The same reaction we are doing today, the transformation of cyclohexanol to cyclohexanone, is a commercially important process. In large chemical plants a catalytic dehydrogenation process is used instead of bleach.



This process was used to make 1.1 trillion pounds of cyclohexanone in the US in 1995.ⁱⁱ BASF is the largest North American manufacturer. They have a large plant just outside Houston in Freeport Texasⁱⁱⁱ.

Most of the commercial cyclohexanone goes on to make an oxime (similar to a later experiment in 2240), then it undergoes a rearrangement to form caprolactam which is the starting material of Nylon 6.



Nylon-6 is one of the most widely used nylons in the world. This polymer goes into such materials as nylon windbreakers, shoe strings, automobile components and automobile tire cord^{iv}.

Safety considerations for this experiment:

Cyclohexanol is an irritant. Avoid contact with skin, eyes, and clothing.

Glacial acetic acid is a dehydrating agent, an irritant, and causes burns. Handle it with care and dispense it in a fume hood and avoid contact with skin, eyes, and clothing.

Sodium hypochlorite solution emits chlorine gas, which is a respiratory and eye irritant. Handle it with care, and dispense it in a fume hood.

Keep the reaction in the hood until all of the excess oxidizing agent has been quenched with sodium thiosulfate.

1. Some terminology related to oxidation-reduction reactions:

Oxidation: In organic chemistry, increasing the oxygen content of an organic molecule or decreasing its hydrogen content. Also creating a C-Z bond, where Z is an element that is more electronegative than C such as N, Halogen, etc. More generally, the process of removing electrons from a substance.

Reduction: In organic chemistry, increasing the hydrogen content of an organic molecule or decreasing its oxygen content. Also removing C-Z bonds. More generally, the process of adding electrons to a substance.

Oxidizing agent: A substance that causes an oxidation by accepting one or more electrons from a substrate. The oxidizing agent is reduced in the reaction.

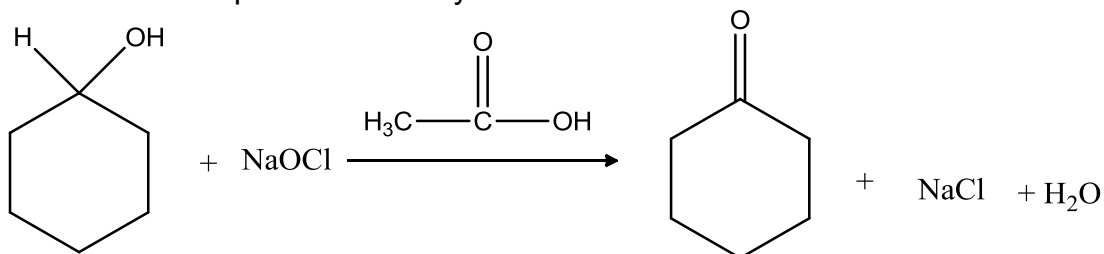
Reducing agent: A substance that causes a reduction by donating one or more electrons to a substrate. The reducing agent is oxidized in the reaction.

Exothermic reaction: A reaction in which energy is released from the system as the reaction proceeds ($-\Delta H$). Typically the reaction container heats up as the reaction proceeds.

Endothermic reaction: A reaction in which energy is absorbed into the system as the reaction proceeds ($+\Delta H$). Typically the reaction container cools as the reaction proceeds.

Solubility: The amount of one material that will dissolve in a liquid. Typically solubility is discussed as grams of solute per 100 grams of solvent. Something is soluble when 3 or more grams of it will dissolve in 100 g of a solvent. Insoluble is defined as less than 0.001g of material will dissolve in 100 g of solvent. Slightly and sparingly soluble are in between these levels.

2. The balanced equation for the cyclohexanol oxidation with NaOCl is:



3. Reagents used in this experiment are:

Sodium hypochlorite: NaClO, Bleach solution. This is the oxidizing agent.

Acetic Acid, CH₃CO₂H. This further activates the sodium hypochlorite and forms hypochlorous acid.

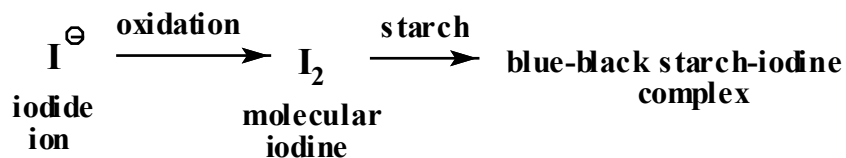
Sodium thiosulfate: Na₂S₂O₃, is a reducing agent that reacts with and quenches any remaining oxidizing agent.

Sodium Sulfate: Na₂SO₄, a drying agent. This removes the residual water from the organic product.

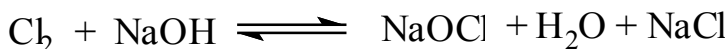
Sodium bicarbonate or Sodium hydrogen carbonate: NaHCO₃. This is baking soda. This is a weak base which neutralizes any remaining acetic acid.

Sodium Chloride, NaCl, table salt. This reduces the solubility of the organic product in the aqueous phase thus increasing the amount of product isolated.

Potassium iodide-starch test paper: indicates the presence of oxidizing agents by the formation of a colored I₂-starch complex, as shown here:



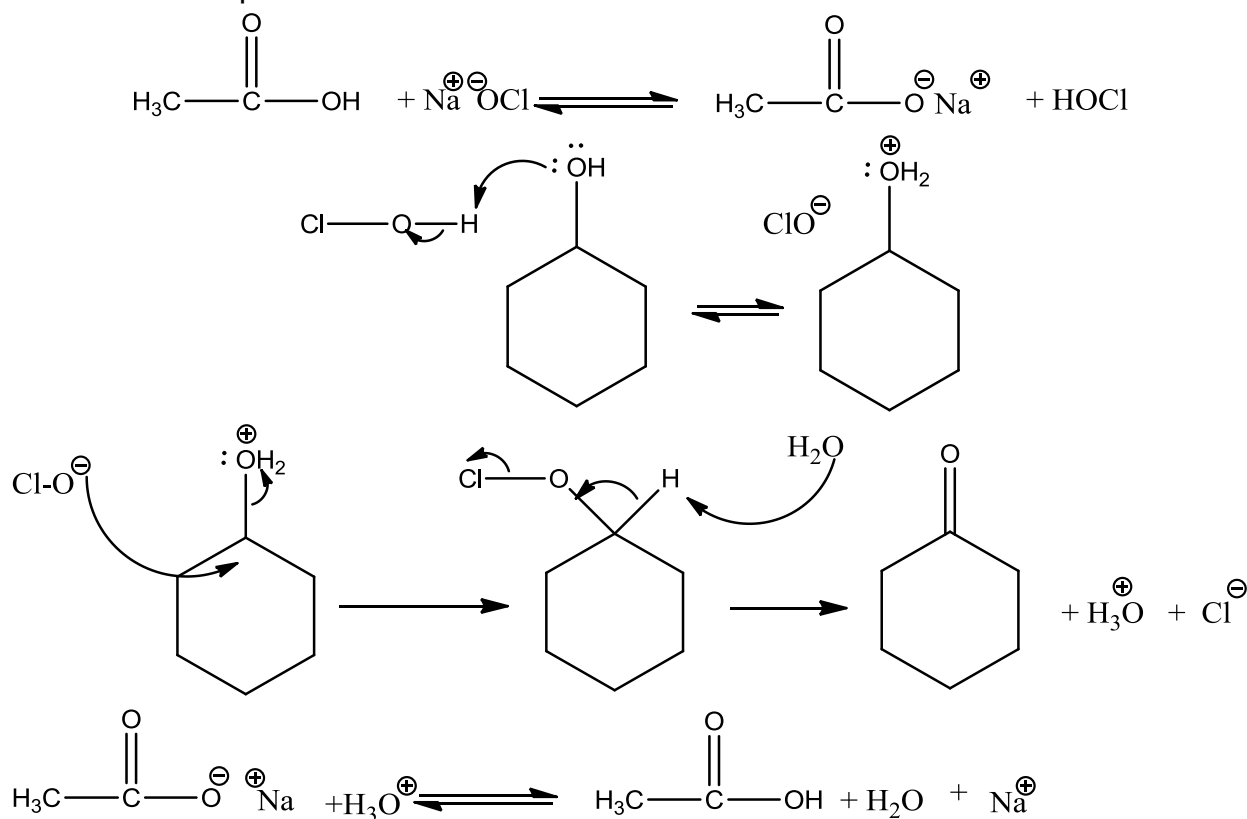
4. Ordinary household bleach is the source of the oxidizing agent, NaOCl. Most bleaches are prepared by the addition of chlorine gas to aqueous sodium hydroxide, as shown here:



Bleach is an approximately 0.74 M solution of Sodium hypochlorite in water.

5. The acetic acid is a catalyst which transforms the sodium hypochlorite into hypochlorous acid, which is believed to be the active oxidizing agent. The acetic acid is regenerated in this cycle. It does not react in a stoichiometric manner with the reagents. Notice that oxidation state of chlorine in HOCl is +1, and the deficiency of electrons in the valence shell of Cl⁺ makes it more reactive than chloride ion.

- 6.. One accepted mechanism^{vi} for this oxidation is:

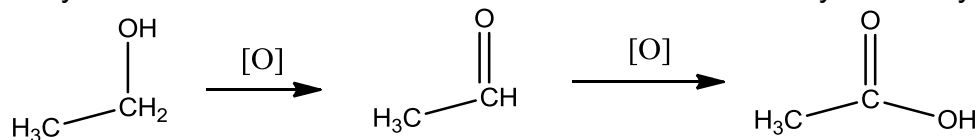


Notice that the chlorine atom that is transferred to the substrate as part of hypochlorite ion is in the +1 oxidation state. This same chlorine leaves as Cl^{-1} . The chlorine has undergone a reduction (from Cl^{+1} to Cl^{-1}) by accepting two electrons from cyclohexanol. The cyclohexanol is thereby oxidized to cyclohexanone.

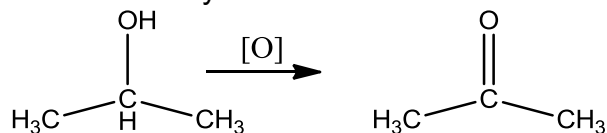
- You are required to calculate a theoretical and a percent yield for this experiment. For instructions and examples on how to do this, see the examples in the Percent Yield Instruction sheet. Note that one of the starting materials was added as a neat liquid, the other material was added as an aqueous solution.
- Cyclohexanol and cyclohexanone have different solubilities in water. This allows the product to be isolated without distillation. The roughly 2 mL of cyclohexanol is soluble in the 30 mL of bleach and acetic acid. When they are mixed, one layer results. Cyclohexanone has a lower solubility in water than cyclohexanol. The cyclohexanone which forms is not very soluble in the water, so it separates and forms a new layer. Cyclohexanol is a hydrogen bond donor and a hydrogen bond acceptor. Cyclohexanone is very polar but is not a hydrogen bond donor. Cyclohexanone has a density of $0.9478 \text{ g/mL}^{\text{vii}}$ which is lower than the density of water. This causes the new layer to float on the surface of the water. If cyclohexanone had a density greater than water this new layer would be on the bottom of the flask.
- Alcohols can form a variety of oxidation products depending up on their structure. Some alcohols cannot be oxidized.

Primary alcohols are easily oxidized to carboxylic acids.

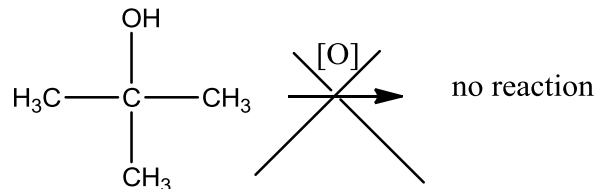
Primary alcohol can under certain conditions be oxidized only to aldehydes.



Secondary alcohols are readily oxidized to ketones.



Tertiary alcohols are impervious to oxidation.



ⁱ Lehninger, *Principles of Biochemistry*, Worth, New York, 1982, p 472-475

ⁱⁱ Weissrnel, K, Arpe, H.-J., *Industrial Organic Chemistry, 3rd Completely Revised Edition*, VCH, New York, 1997

ⁱⁱⁱ BASF Optimizes Plant Performance, <http://www.chemicalprocessing.com/articles/2003/299.html> (September 27, 2011)

^{iv} Raghavendra R. Hegde, Atul Dahiya, M. G. Kamath, Nylon Fibers, <http://www.engr.utk.edu/mse/Textiles/Nylon%20fibers.htm> (September 27, 2011)

^v Formulation in Pharmacy Practice. Appendix B <http://www.pharminfotech.co.nz/manual/Formulation/mixtures/pages/solubilities.html> (September 27, 2011)

^{vi} Mohrig, J.R, Nienhuis, D.M, Linck, C.F., Van Zoeren, C. Fox, B. G, Mahaffy, P.G., *Journal of Chemical Education*, **1985**, 62, 519-521

^{vii} *CRC Handbook of Chemistry and Physics*, 65th, CRC Press, 1984, ppC-251