

Oxidation of Cyclododecanol & Introduction to Infrared Spectroscopy

Part A, p. 543: Oxidation of cyclododecanol with bleach. (4th ed. p.531)

Part B, p. 237-260: FT-IR spectrum of starting material & product.

(5th ed. p. 233-256) *First formal report.*

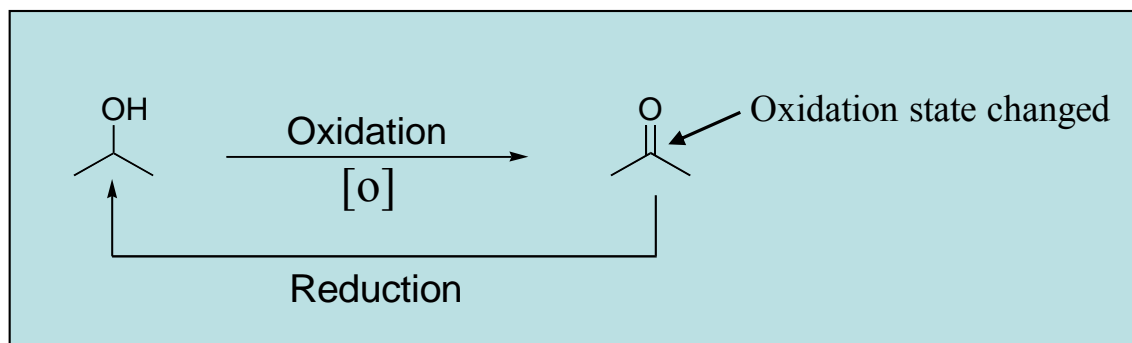
Important Concepts

- Oxidation/Reduction
- Oxidizing agents (bleach)
 - Reaction Mechanisms
 - % Yield Calculations
- Infrared Spectroscopy: functional group identification
 - Starch-Iodide test

Oxidation & Reduction

Oxidation: The net *loss* of electrons or addition of oxygen to a molecule. Usually there is an *increase* in the oxidation state of the molecule.

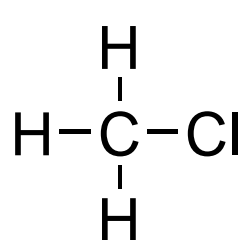
Reduction: The net *gain* of electrons or addition of hydrogen to a molecule. Usually there is a *decrease* in the oxidation state of the molecule.



Calculating the Oxidation State of Carbon

- a) +1 for each bond to a hydrogen atom or atom that is less electronegative than carbon.
 - b) -1 for each bond to an atom that is more electronegative than carbon. (e.g. O, N, S, halogen)
 - c) +0 for each bond to another carbon atom.
-

$$\sum (\text{sum}) + \text{Oxidation State (OS)} = \text{charge on the atom}$$




methylchloride

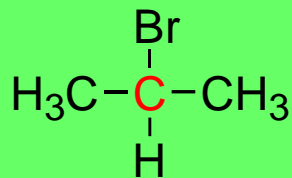
$$\text{H: } 3(+1) = +3$$

$$\text{Cl: } 1(-1) = -1$$

$$\text{C: } 0(0) = 0$$

$$\begin{array}{c} \hline +2 + \text{OS} = 0 \\ \text{so OS} = -2 \end{array}$$


Calculating the Oxidation State - cont.



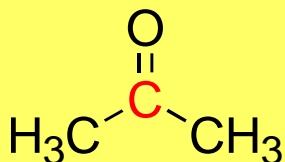
2-bromopropane

$$\text{H: } 1(+1) = +1$$

$$\text{Br: } 1(-1) = -1$$

$$\text{C: } 2(0) = 0$$

$$\begin{array}{r} 0 \\ \hline 0 + \text{OS} = 0 \end{array} \quad \text{so} \quad \text{OS} = 0$$



acetone

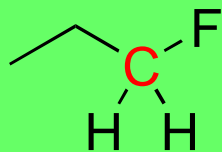
$$\text{H: } 0(+1) = 0$$

$$\text{O: } 2(-1) = -2$$

$$\text{C: } 2(0) = 0$$

$$\begin{array}{r} -2 \\ \hline -2 + \text{OS} = 0 \end{array} \quad \text{so} \quad \text{OS} = +2$$

Calculating the Oxidation State - cont.



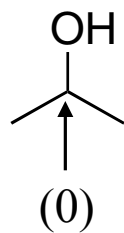
1-fluoropropane

$$\text{H: } 2(+1) = +2$$

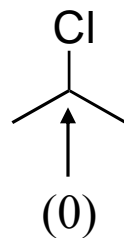
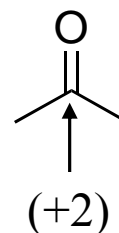
$$\text{F: } 1(-1) = -1$$

$$\text{C: } 1(0) = 0$$

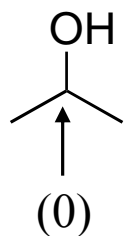
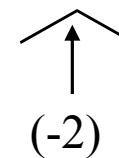
$$\underline{+1} + \text{OS} = 0 \quad \text{so} \quad \text{OS} = -1$$



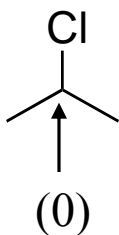
Oxidation



Reduction

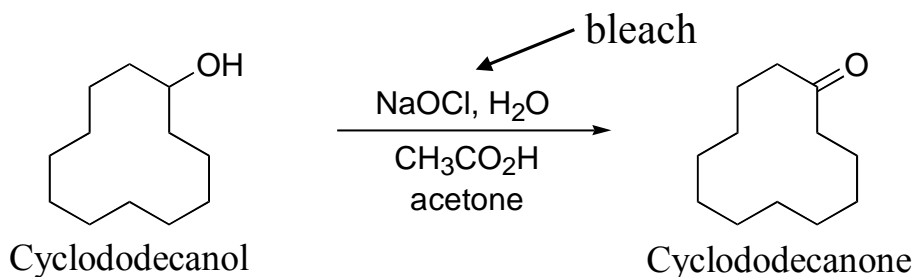


Neither

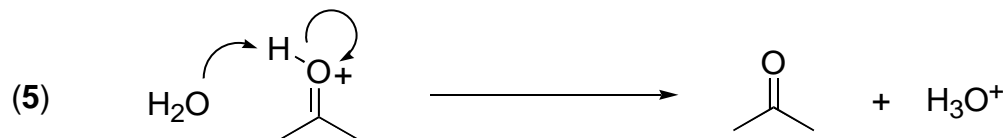
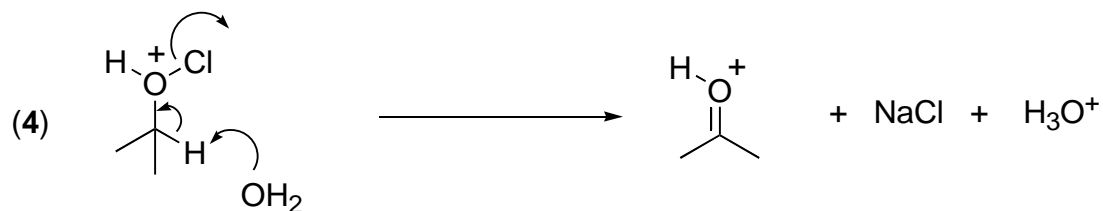
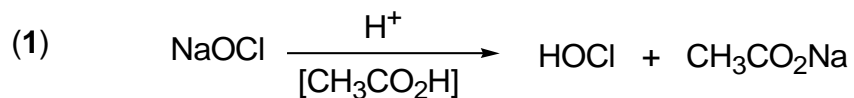


Our Reaction

Reaction Scheme



Mechanism



Procedural Details

- use 8 ml bleach initially.
- heat to gentle reflux rather than monitoring temperature. No need for thermometer. (b.p. acetone ~ 56 °C)
- after 30 minutes of gentle reflux, allow solution to cool.
- use long Pasteur pipette to remove a few drops of the aqueous layer. You may need to remove the condenser to do this.
- place a drop of the aqueous layer onto the starch/iodide paper. You should be able to test several spots on one piece of paper.
- if paper turns black, then the reaction is complete and you can proceed to workup. If not, add ~ 1 ml bleach and continue heating for an additional 20 minutes and then proceed to the workup procedure.

Procedural Details - cont.

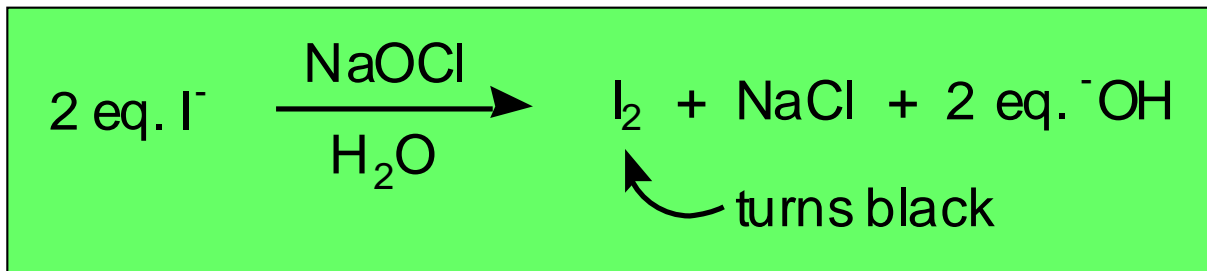
Workup - Week 1

- use disposable Pasteur pipette instead of filter-tip pipette.
- wash organic layer three times:
 - a) NaHCO_3 \longrightarrow neutralizes excess acid (acetic acid)
 - b) NaHSO_3 \longrightarrow reduces excess bleach
 - c) NaCl \longrightarrow removes excess water from organic phase
- dry organic layer over anhydrous Na_2SO_4 .
- use the rotovap to remove the organic solvent.
- stop here during week 1.

Week 2

- recrystallize from methanol/water.
- acquire IR spectrum of your purified product.
- no oxime or semicarbazone derivatives.

Starch Iodide Test



% Yield Calculation

Method A

$$\frac{\text{moles product}}{\text{moles limiting reagent}} \times 100 = \% \text{ yield}$$

bleach is 5.25% NaOCl in water,
density ~1 g/ml

Method B

$$\frac{\text{mass of product (g)}}{\text{Theoretical yield (g)}} \times 100 = \% \text{ yield}$$

Theoretical yield (g) = [moles of limiting reagent] • [molecular mass product]

Limiting Reagent = least # moles for a stoichiometric reagent

Required Data

- Yield, % yield
- m.p.
- Results of Starch/I₂ test
- IR of product, we will supply IR of starting material

Safety Issues

- bleach is a strong oxidizing agent, avoid contact with skin.