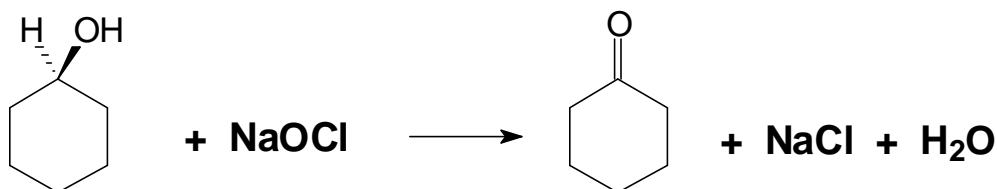


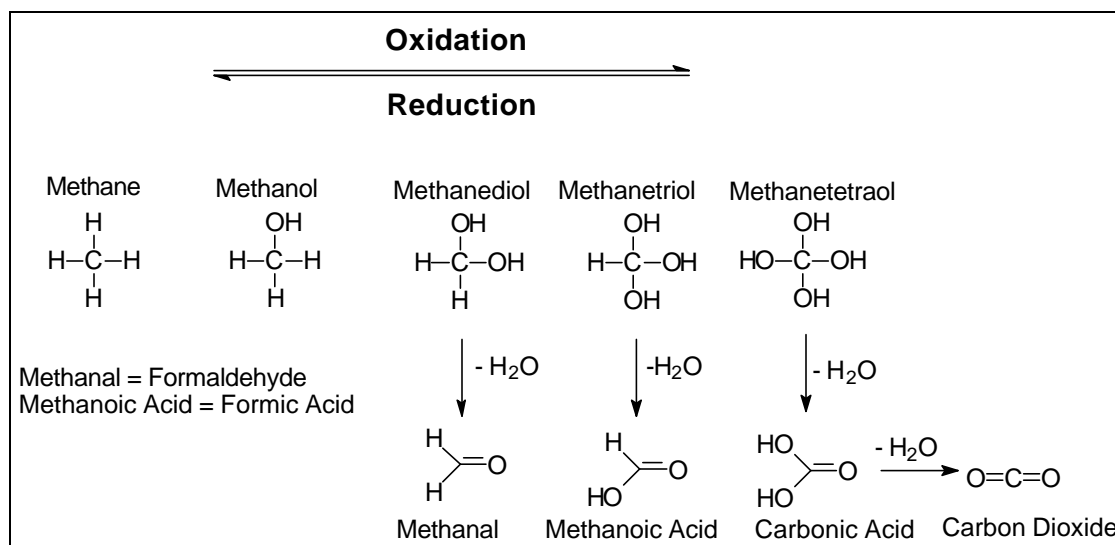
AN OXIDATION REACTION. CYCLOHEXANONE FROM CYCLOHEXANOL



THE PROBLEM TO BE INVESTIGATED: In this experiment cyclohexanone is synthesized by **oxidation** of cyclohexanol employing chlorine bleach as the **oxidizing agent**. Using **gas chromatography (GC)** and **infrared spectroscopy (IR)**, the **transformation** will be monitored for completeness of the reaction and a derivative of the product will be prepared and characterized.



BACKGROUND INFORMATION: **Oxidation-reduction** reactions are common; one cannot occur without the other. Simply put, an **oxidation** in organic chemistry is the gain of oxygen or the loss of hydrogens. Using methane as an example, the process is illustrated here.



Various **oxidizing agents** exist and are selective for specific transformations. With potassium permanganate as an example, "*mild*" conditions (neutral or basic pHs) will convert cyclohexanol to cyclohexanone, while under more "*drastic*" conditions (using acidic pH and higher temperatures), adipic acid (HO₂C-CH₂CH₂CH₂CH₂-CO₂H) or further oxidation products may result. Chromium and manganese oxidizing agents such as dichromate and permanganate ions have often been employed in the past, but are disfavored currently because of environmental and disposal problems. The following half reactions represent reductions of the oxidizing agents, Cr₂O₇²⁻ and MnO₄¹⁻, respectively:



THE NATURE OF THIS INVESTIGATION: We will control our oxidation of cyclohexanol by using hypochlorite (OCl⁻) in bleach. Generally, laundry bleach is an approximately 4% solution of NaOCl in water, and in commercial bleach used for swimming pools, the concentration is approximately 10%. The resultant ketone will be further characterized by using the 2,4-DNP (2,4-dinitrophenylhydrazine) test reagent. This test is **positive** for aldehydes and ketones, and generally **negative** for amides and esters. The reagent is often used in the preparation of derivatives. As in the case of acetanilide, this reaction is important because a **solid derivative** is often used in characterization of unknown substances.

PRELAB PREPARATION: If you have not previously done so in your laboratory reports, tabulate your starting materials and products citing the MW, moles, boiling points, *etc.*

PROCEDURE

Caution. Bleach is an oxidant and caustic. Observe caution in handling chemicals.

Preparation of cyclohexanone: Put 10.0 g of **cyclohexanol**, 15 mL **glacial acetic acid** and a stirring bar into a **250 mL Erlenmeyer flask**. Secure the flask over a stirrer and position a **thermometer** so that the stirring bar moves freely. Set up an **addition funnel** to add 75 mL of **bleach** (pool bleach) to the flask. Keep a water bath ready in case it is needed to lower the temperature. Start the stirrer and add the bleach at a rate that maintains the temperature between 40 and 50° C. (Use your ice-water bath if necessary.)

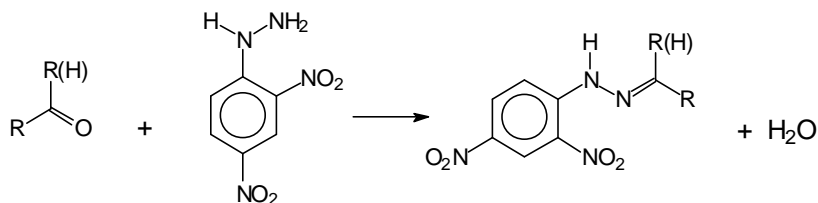
After all the bleach has been added, test the solution with potassium iodide starch test paper. A blue/black color indicates an excess of bleach. If a blue color is not obtained, add an additional 2 mL of bleach and stir for another 15 minutes. Add a saturated **solution of sodium bisulfite** (a few drops) until the solution tests negative for bleach; *i.e.*, iodide-starch paper no longer turns blue.

Transfer the reaction mixture to a **separatory funnel**. Rinse the reaction flask with 30 mL of t-butyl methyl ether and add the ether to the separatory funnel. Shake and separate the layers (**CAUTION** - pressure!!). Wash the ether layer twice with 10 mL portions of 10% NaOH to remove the acetic acid. Test the second wash with pH paper to be certain it is basic. Then, wash the ether layer with 10 mL of water. Pour the ether layer into a dry Erlenmeyer flask and dry the ether by adding **anhydrous magnesium sulfate**. Stopper the flask, and allow it to stand for a few minutes. It should be clear, although it may have a little color to it. Set up a distilling apparatus using oven-dried glassware. Then gravity-filter into a dry 50 mL distilling flask, add a boiling chip and distill the product. When the temperature reaches ~140° C, begin collecting the distillate in a dry tared screw-top vial. Collection should be discontinued if the boiling point goes beyond ~157° C. Be sure to record the full boiling point range. This is your product. Pour the ether into the waste bottle provided in the hood.

Calculate the theoretical and percentage yields for the synthesis. Retain the product for GC and IR analyses.

Taking into consideration the IR and GC data, what can you conclude about the effectiveness of the oxidation reaction? In your interpretation and discussion section, note and comment on the significant changes in the infrared spectrum. Use the IR spectrum of cyclohexanol (posted) for comparison. The relevant absorption bands should be cited and referenced. Also, what information can be gleaned from the eluting peak(s) when your product was analyzed by GC? If you have more than one peak in the gas chromatogram, how would you determine the identity of the compound(s) responsible for the peak(s)? Comment on the purity of your product based on your **GC** and **IR** data.

Test for and Derivative of a ketone: The 2,4-DNP reagent will be used to test for and prepare a derivative from your product. The following is a general procedure:



The compounds to be tested are: (1) acetanilide, (2) methyl benzoate, and (3) your sample of cyclohexanone.

In a large test tube, place 3 mL of the prepared 2,4-DNP reagent (2,4-dinitrophenylhydrazine, H_2SO_4 and ethanol) and add 3-5 drops of the sample liquid. [If a sample is a solid (as in case of acetanilide), it should be dissolved in a minimal amount of ethanol (heating may be required) and the solution added to the test reagent.] A **positive test** is a yellow, orange or red precipitate.

Helpful Hints - CYCLOHEXANONE

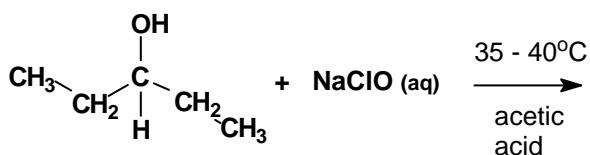
- * Anhydrous magnesium sulfate is a better (faster, but more expensive) drying agent than anhydrous sodium sulfate.
- * Check and record the pH of the bleach solution. Consider why glacial acetic acid rather than water is used as the solvent.
- * Acetone should not be used in cleaning and drying your test tubes for the 2,4-DNP tests unless the test tube is dried thoroughly. "False positives" may result from residual acetone.

REFERENCE

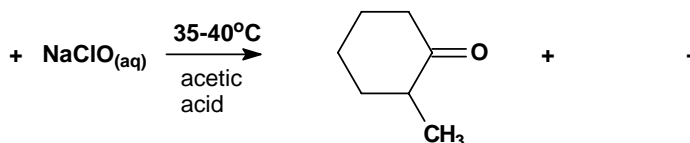
Mohrig, J.R., *et al.*, *J. Chem. Ed.*, 1985, 62, 519-521.

SYNTHESIS OF CYCLOHEXANONE - HOMEWORK PROBLEMS

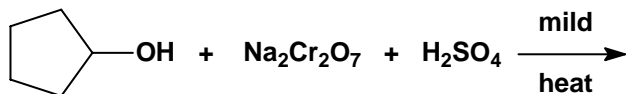
1. Complete and Balance the following equation.



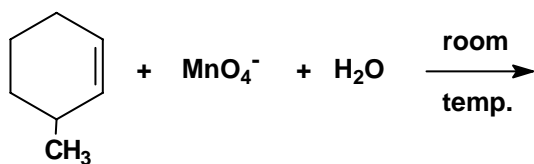
2. Complete and Balance the following equation.



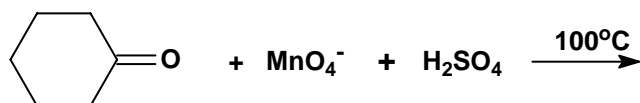
3. Complete the following equation showing products, but not necessary to balance.



4. Complete the following equation showing organic and inorganic products; need not be balanced.



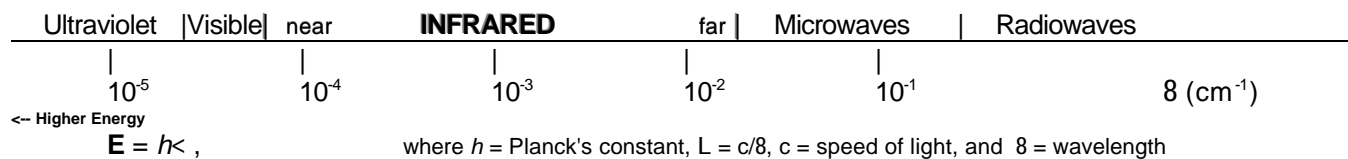
5. Complete the following equations showing products, but not necessary to balance



INSTRUMENTAL METHODS IN ORGANIC CHEMISTRY.

INFRARED SPECTROPHOTOMETRY

BACKGROUND INFORMATION: In organic chemistry regions of the electromagnetic spectrum are used to study the structure of molecules: **radio frequencies** in Nuclear Magnetic Resonance (NMR) and **infrared** in InfraRed (IR) spectroscopy. In earlier experiments, we have measured a portion of the **electronic** spectrum-- in particular, the visible region. Now, we will be introduced to the **infrared** portion of the spectral region where the **rocking, bending, and stretching** modes of bonded atoms will be used to identify functional groups by correlating the absorptions with published data.



Energy requirements for excitation of electrons depend upon the functional group; *i.e.*, for pi electrons, the $\pi \rightarrow \pi^*$ transition involves **higher energy** in the ultraviolet region vs. the rocking, bending, and stretching (rotational and translational) motions in the infrared region. In contrast, **lower energy** is utilized in the IR region where the absorption peaks are more numerous and detailed (complex). Given the approximate ranges, students may calculate the energies. Consult your text. For the region of interest, **Fig. 1** is presented in units commonly expressed in wavelength (λ) or wave number (cm^{-1}).

SPECTRAL REGION	SPECTRAL RANGE	ABSORPTION BANDS
Electronic	200 - 800 nm	Broad
INFRARED	4000 - 600 cm^{-1}	sharp, specific, detailed

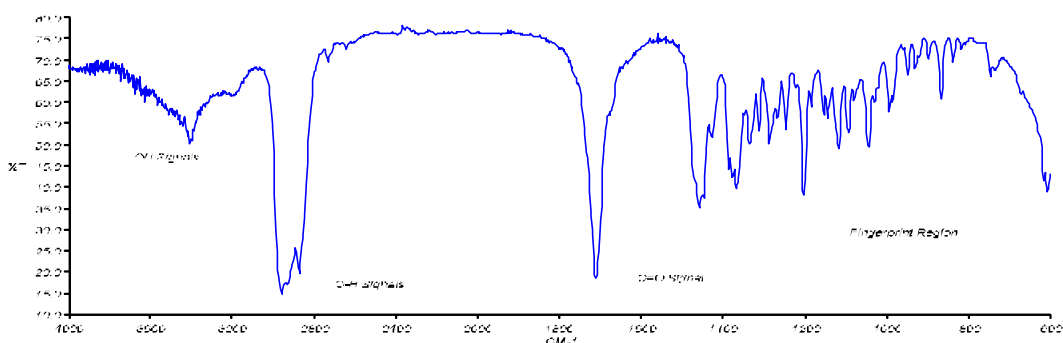


Figure 2. Absorptions to the left of the 3000 cm^{-1} "marker" suggest **-OH** and/or **-NH(R)** functional groups. The absence of a 1700 cm^{-1} absorption eliminates possibilities of a carboxylic acid (or ketone, aldehyde, ester). The third region ("fingerprint") is complex. Accordingly, the IR spectrum suggests an alcohol or an amine (possibly aromatic).

3000 cm^{-1}	C-H stretch
1700 cm^{-1}	C=O stretch indicative of: aldehydes, ketones, acids, esters, etc.
"left" of 3000 cm^{-1}	-O-H & -N-H indicative of: alcohols, amines, carboxylic acids (? ,check for carbonyl)

PROCEDURE - Preparation of Sample for Infrared Analysis

Samples for analysis may be (1) neat, *i.e.*, no solvent if a liquid, (2) dispersed in a nujol (high MW hydrocarbon) matrix, (3) dispersed in a KBr matrix, or (4) dissolved in an organic solvent. In our laboratories, methods 1 - 3 are used extensively. Procedures 1 and 2 require two polished NaCl plates and the sample is placed between these. In methods 2, the liquid or solid sample is blended (mortar and pestle) into the nujol, whereas in 3 the solid KBr is the medium. In the latter method, the powdered mixture is rendered "transparent" under pressure and the disk is subjected to infrared radiation.

For liquid samples, we shall use method 1. Be sure that the NaCl plates are clean before and after analysis by wiping the plates onto several Kimwipes[®] (saturated with ca. 0.5 mL of acetone solvent).

Students will generally use the Mattson FTIR infrared spectrophotometer. Although the instruments are relatively easy to operate, consult your instructor or teaching assistant before you run you sample. Before exiting the Spectroscopy Laboratory, the NaCl plates and general work area must be cleaned, and the instrument log book signed and dated.