

INFRARED SPECTROSCOPY

PURDUE UNIVERSITY INSTRUMENT VAN PROJECT

CLASSIFICATION OF ORGANIC COMPOUNDS

In this experiment we shall explore some of the methods employed in the classification of organic compounds. These will include tests for specific functional groups and the identification of functional groups from infrared spectra.

Functional Groups:

The emphasis in this experiment is on the methods of organic qualitative analysis. Nevertheless, a brief discussion of the properties and molecular structures of the substances to be tested should prove useful.

Organic compounds are often defined as those substances containing carbon; most contain hydrogen as well. Atoms and groups of atoms attached to the hydrocarbon chain are referred to as functional groups. One of the first steps in the characterization of an organic compound is the identification of its functional groups by specific chemical tests. A list of some of the most common functional groups together with the properties associated with them follows:

1. Hydroxyl (-OH) group. There are two broad classes:
 - a) Alcohols (R-OH), in which the hydroxyl group is attached to a chain of carbon atoms. Because of hydrogen bonding involving the -OH group, alcohols are higher boiling and more water soluble than hydrocarbons of similar molecular weight. Common alcohols are methyl alcohol (CH₃OH), sometimes referred to as wood alcohol; ethyl alcohol (CH₃CH₂OH), which is found in alcoholic beverages; and isopropyl alcohol (CH₃CH(OH)CH₃), which is rubbing alcohol.
 - b) Phenols (C₆H₅OH). When the hydroxyl group is attached directly to a benzene ring, the result is a phenol. Phenols are more acidic than alcohols, and the anions resulting from the loss of H⁺ form colored complexes with transition metal cations.
2. Carbonyl (R-C=O) group. These compounds are obtained from the mild oxidation of alcohols. They are intermediate between alcohols and hydrocarbons in boiling point and water solubility. Sugars contain both hydroxyl and carbonyl groups. There are two classes of carbonyls:
 - a) Aldehydes (R-C=O) have a hydrogen atom attached directly to the carbonyl carbon. Perhaps the most common aldehyde is formaldehyde (H₂C=O), the compound responsible for the characteristic odor of so many Biology labs. Aldehydes are the active ingredients in a number of perfumes and flavors, including vanilla. They are

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easily oxidized to carboxylic acids, a property which may be used to distinguish them from ketones.

- b) Ketones (R-C=O) In ketones there is no hydrogen attached to the carbonyl group. The most common ketone is acetone (CH₃)₂C=O.
3. Carboxylic Acids (R-C-OH) are characterized by the presence of the carboxylic group (-C-OH). Like alcohols, they have relatively high boiling points and a tendency toward water solubility. Like other acids, they have a sour taste and react with sodium bicarbonate solution to release carbon dioxide gas. The most common carboxylic acid is acetic acid (CH₃COOH), the active ingredient in vinegar. Aspirin is also a carboxylic acid.
4. Unsaturated hydrocarbons are hydrocarbons containing double and/or triple bonds between carbon atoms. Unlike saturated hydrocarbons (all single bonds) these substances react rapidly with halogens by addition across the double (or triple) bond.

PRECAUTIONS. Until you have identified your unknown you will not know to which hazard it belongs. Therefore, treat all unknowns as if they were corrosive, carcinogenic, and toxic until you prove otherwise.

PROCEDURE:

In your laboratory notebook, make a table listing the various functional groups. Space would be provided next to this list to record the observations for a positive test, the observations for a negative test, the observations for your unknown, and the conclusion as to whether the functional group was present or absent.

Part 1. Identification of the Unknown Functional Groups.

Obtain an unknown compound and record the number. It is possible that more than one functional group will be present in the unknown so all the tests should be done.

TESTS FOR FUNCTIONAL GROUPS:

HYDROXYL GROUP: Add 3 drops of ceric nitrate solution to three small test tubes or depressions in a spot plate. To the first test tube or well add 2 drops of the known alcohol.

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To the second add 2 drops of the saturated hydrocarbon (which will be negative test) and to the third add 2 drops of your unknown. Let them stand for 2 minutes. Note the colors and record your observations.

CARBONYLS: (Both aldehydes and ketones give positive results.) Add 10 drops of dinitrophenylhydrazine reagent (DNP) to four small test tubes or depressions in a spot plate. To the first test tube or well add 1 drop of the known ketone. To the second add one drop of the known aldehyde. To the third add one drop of the saturated hydrocarbon (which will be a negative test) and to the fourth add one drop of your unknown. Record your observations.

ALDEHYDES: To a clean test tube add 5 drops of 0.1M silver nitrate (AgNO_3) solution and 2 drops of 6 M ammonia. Add 2 or 3 drops of the known aldehyde and mix the contents thoroughly. Allow the test tube to stand in a hot water bath for a few minutes. A silver mirror should be deposited on the walls of the test tube if an aldehyde is present. If your unknown tested positive for a carbonyl with the DNP reagent, repeat the above test using your unknown in place of the aldehyde in order to establish whether or not it is an aldehyde or a ketone.

WASH THE TEST TUBE IMMEDIATELY. This reaction may produce silver fulminate, a powerful detonator when dry.

KETONES: If your test for the carbonyl group was positive, but the test for an aldehyde is negative, your unknown is a ketone.

CARBOXYLIC ACIDS: Place a few drops of the known carboxylic acid in a small test tube or the well of a spot plate. In a second test tube or well place a few drops of the saturated hydrocarbon (which will give a negative test.) In a third test tube or well place a few drops of your unknown. To each test tube or well add a few drops of 10% sodium bicarbonate solution. Record your results.

UNSATURATED HYDROCARBONS: Place a few drops of the known unsaturated hydrocarbon in a small test tube or the well of a spot plate. In a second test tube or well place a few drops of the saturated hydrocarbon (which will give a negative test.) In a third test tube or well place a few drops of your unknown. To each test tube or well add one drop of Br_2/TTE solution. Record your observations.

ALTERNATIVE TEST FOR UNSATURATED HYDROCARBONS: Place a few drops of the known unsaturated hydrocarbon in a small test tube or the well of a spot plate.

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In a second test tube or well place a few drops of the saturated hydrocarbon (which will give a negative test.) In a third test tube or well place a few drops of your unknown. To each test tube or well add one drop of ethyl alcohol and one drop of 2% potassium permanganate (KMnO_4). Record your observations.

SATURATED HYDROCARBON: If all the above tests are negative, your unknown is a saturated hydrocarbon.

CONCLUSION: On the basis of the above experimental information, what functional groups seem to be present in your unknown?

INFRARED SPECTRUM:

Obtain an infrared spectrum of your unknown. Follow the instructions which come with the instrument.

On your copy of the infrared spectrum, mark the regions of ALL the functional groups listed on the table of CHARACTERISTIC INFRARED ABSORPTION BANDS. It is just as important to note that a particular functional group is not present as it is to note that one is present.

On the basis of your infrared spectrum, what functional groups are present in your unknown?

If your experimental results and your spectral results do not agree, redo them to see if an error has been made.

Identify the functional groups present in the unknown.

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CHARACTERISTIC INFRARED ABSORPTION BANDS

GROUP	WAVENUMBER (cm ⁻¹)
-OH (hydrogen bonded alcohol)	3200-3400
H C=C (aromatic or olefinic C-H)	3010-3040
-C-H (saturated C-H)	2840-2980
O -C-OH (carboxylic acid)	1700-1725
O -C-H (aldehyde)	1720-1740
O -C- (ketone)	1705-1725
C=C (simple olefin)	1620-1680
aromatic ring	1450-1600 (several bands)
-C-H (saturated C-H, bending mode)	1350-1475
-C-O- (ethers, alcohols, esters)	1060-1410

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TEACHERS GUIDE

This is a basic straightforward experiment which could be done at any level, even Physical Science.

CURRICULUM INTEGRATION

During an Organic Chemistry Unit

STUDENT TIME

The tests for functional groups will take about 30 minutes. The infrared spectrums will take longer. Allow 2 class periods.

MATERIALS

Reagents should be in dropper bottles. Organic liquids are both volatile and smelly. Furthermore they will react with plastic.

The following amounts would be made for 4 classes of 20 students.

100 mL ceric ammonium nitrate solution

Dissolve 20 g of ceric ammonium nitrate in 100 mL of 2M HNO₃.

100 mL dinitrophenylhydrazine reagent (DNP)

Dissolve 3.0 g of 2,4-dinitrophenylhydrazine in 15 mL of 18 M H₂SO₄. This solution is added slowly, with constant stirring, to a solution of 20 mL water and 70 mL 95% ethanol.* The solution is mixed thoroughly and filtered.

* The 95% ethanol must be specially denatured with isopropyl alcohol. Plain denatured alcohol will contain methyl ethyl ketone which will precipitate with the 2,4-dinitrophenylhydrazine.

100 mL of 0.1 M Silver Nitrate

Dissolve 1.7 g of AgNO₃ in 100 mL of solution

100 mL of 6M NH₃

100 mL of 10% Sodium Bicarbonate Solution

100 mL of Br₂ in TTE

or 100 mL of 2% KMnO₄ and 100 mL of ethyl alcohol

KNOWN SOLUTIONS

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These are just examples. Any compound will do.

alcohol isopropyl alcohol
aldehyde formaldehyde
ketone acetone
carboxylic acid acetic acid (vinegar)*
unsaturated hydrocarbon . . . cyclohexene
saturated hydrocarbon . . . cyclohexane

*Vinegar is an aqueous solution of acetic acid. It works well as a known solution for the chemical tests but it cannot be given as an unknown because the water will ruin the salt plates when the IR is taken.

It is not always possible to distinguish between aldehydes and ketones. If the aldehyde is not very soluble in water the silver mirror does not always form.

If the Infrared Spectrophotometer is working properly, the students should be able to take the spectrum of their unknown. If, however, the need should arise, infrared spectra are given for the following compounds.

Alcohols:

110 isobutanol
120 ethylene glycol
140 isoamyl alcohol
150 cyclohexanol

Ketones:

210 cyclohexanone
220 2-butanone
230 acetophenone
240 cyclopentanone

Aldehydes:

330 benzaldehyde
340 cinnamaldehyde

Acids:

430 oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
440 lactic acid $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$

Hydrocarbons:

520 cyclohexene
530 cyclohexane

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540 toluene
550 o-xylene

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