Functional Group Chemistry

Introduction

The chemistry of an organic molecule is primarily dictated by its functional groups. Some functional groups participate in acid-base chemistry: amines are weak bases while carboxylic acids and phenols are weak acids. Some functional groups participate in redox chemistry: aldehydes and some alcohols are readily oxidized while aldehydes and ketones are readily reduced. In substitution reactions, some functional groups act as nucleophiles (donating electrons) while others act as electrophiles (accepting electrons). Finally, multiple bonds, as in alkenes and alkynes, are required for addition reactions.

This predictable reactivity allows a chemist to attempt a variety of reactions on an organic compound and determine what functional group(s) are present. To use any reaction as a test for a functional group, it is necessary for the product mixture to appear significantly different from the reactants. This may be due to formation of a precipitate or coloured product, or it may be due to consumption of a solid or coloured reactant. It is also good practice to employ positive and negative controls to ensure that each test has been performed correctly. ***Before coming to lab, you must have looked up the structures of acetone, isopropanol, benzaldehyde, benzoic acid, 1-napthol, 4-nitroaniline and styrene so that you know whether they should give a positive or negative result for each test.***

Theory Behind Functional Group Tests

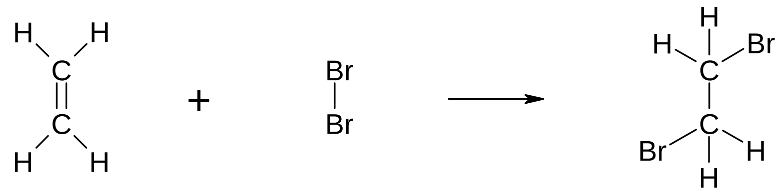
a. Solubility Tests for Carboxylic Acids, Phenols, Amines and Small Molecules

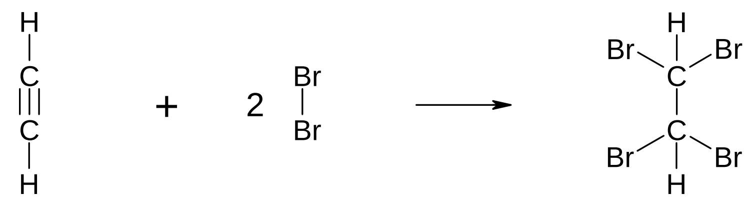
The solubility of an organic compound in water depends on both its size and polarity. Compounds with 4 carbons (or less) and at least one polar functional group tend to be water soluble. Larger compounds tend to be insoluble in water unless they have an ionized functional group or several polar functional groups.

Thus, an insoluble compound can be made water soluble if one of its functional groups can be ionized. For example, amines are weak bases. If an insoluble amine is reacted with strong acid, the amine will be protonated and become soluble in water. Similarly, carboxylic acids and phenols are weak acids. If an insoluble phenol is reacted with strong base, the phenol will be deprotonated and become soluble in water. Finally, phenols are much weaker acids than carboxylic acids. As such, there are some bases that are strong enough to deprotonate a carboxylic acid but not a phenol. One such base is $NaHCO_3$ (which will make a carboxylic acid soluble in water but not a phenol).

b. Bromine Test for Alkenes and Alkynes

Most halogens (chlorine, bromine and iodine) react readily with carbon-carbon multiple bonds that are not part of an aromatic ring:



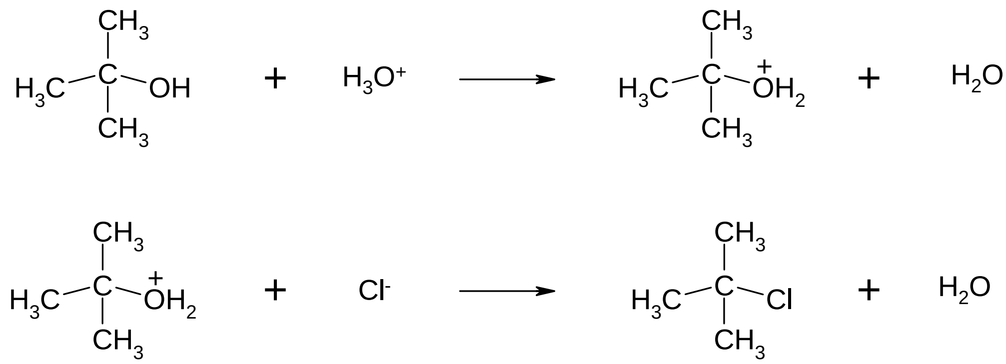


The products of these reactions are typically clear and colourless – just like the organic reactant. In order to determine whether or not the reaction has proceeded, it is therefore necessary to look at the halogen. Chlorine is a green gas, bromine a dark brown liquid and iodine a purple-black solid. Bromine is typically chosen as the test reagent for alkenes and alkynes because, if it reacts, its rich brown colour will disappear. If there the brown colour persists, it is because there are no alkenes or alkynes for the bromine to react with.

If too much bromine is added to a solution, a false negative result may be generated as all of the alkene/alkyne is consumed before the bromine.

c. Lucas Test for Alcohols (2˚ and 3˚)

Alcohols are very weak bases (comparable to water) which react slightly with strong acids. The product of such a reaction is an electrophile with a very good leaving group. In the presence of a good nucleophile, a substitution reaction results. This is the basis of the Lucas test.



Tertiary alcohols (in which three carbon atoms are attached to same carbon as the –OH group) react very quickly in the Lucas test, producing alkyl halides that are insoluble in the aqueous Lucas reagent. Secondary alcohols (in which two carbon atoms are attached to same carbon as the –OH group) react more slowly while most primary alcohols (only one carbon atom is attached to the same carbon as the –OH group) do not react at all.

Because a positive test is indicated by formation of a product that is insoluble in water, the Lucas test is only useful for compounds that are water soluble.

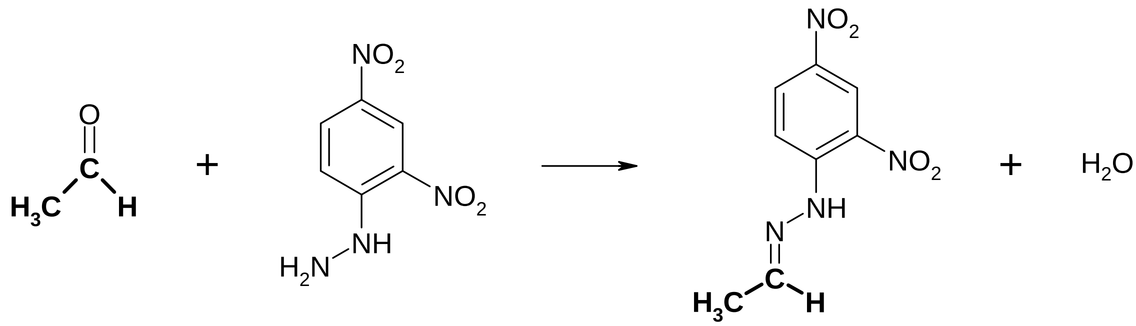
d. Jones Oxidation Test for Alcohols (1˚ and 2˚) and Aldehydes

Primary and secondary alcohols are readily oxidized to aldehydes and ketones respectively. Aldehydes, in turn, can be oxidized to carboxylic acids.

The products of these reactions are typically similar in appearance to the organic reactants. In order to determine whether or not an oxidation has taken place, we must therefore use an oxidizing agent that changes appearance in the reaction. In a Jones oxidation, orange-brown chromic acid (H_2CrO_4) is reduced to green Cr^{3+} salts as it oxidizes an alcohol or aldehyde.

e. 2,4-Dinitrophenylhydrazone (2,4-DNP) Test for Ketones and Aldehydes

Aldehydes and ketones are excellent electrophiles; 2,4-DNP is an excellent nucleophile. As such, aldehydes and ketones react readily with 2,4-DNP:



The products of these reactions are typically brightly coloured (red, orange or yellow) and insoluble in ethanol. They can be isolated by filtration and characterized to help determine the identity of the aldehyde or ketone. For the purposes of this experiment, recognizing that a product has formed is sufficient.

f. Schiff's Test for Aldehydes

As noted on the previous page, aldehydes can be oxidized to carboxylic acids. Schiff's reagent is a selective oxidizing agent that will oxidize aldehydes but not alcohols. It contains an oxidized form of the bright pink dye, fuschin. When the Schiff's reagent reacts with an aldehyde, the dye is reduced back to its pink form and the solution turns pink.

General Procedures for Functional Group Tests

a. Solubility Tests for Carboxylic Acids, Phenols, Amines and Small Molecules

- Perform the solubility tests below on benzoic acid, 1-napthol, 4-nitroaniline, acetone and your unknown.
- Add ~20 mg of compound to be tested to a clean dry test tube (2 drops of liquid or a spatula tip of solid) to a clean dry test tube. Add 0.5 mL of water to the test tube and swirl to mix.
- <u>If the compound dissolves in water</u> (even partially), this indicates that the unknown is a small polar molecule (typically containing less than 5 carbon atoms). Use universal indicator paper to estimate the pH of the solution. If the paper turns red, indicating a pH of 2-3, the compound is a carboxylic acid. If the paper turns blue, indicating a pH of 10-11, the compound is an amine. If the paper remains yellow, indicating a pH of 6-8, the compound may be an alcohol, ketone, aldehyde, ester or other small polar molecule.
- <u>If the compound does not dissolve at all in water</u>, repeat the test using 10% HCl instead of water. If the compound is significantly more soluble in acid than in water, it is an amine.

- If the compound does not dissolve at all in either water or 5% HCl, repeat the test using 5% $NaHCO_3$. If the compound is significantly more soluble in weak base than in water, it is a carboxylic acid.
- If the compound does not dissolve at all in either water, 5% HCl or 5% $NaHCO_3$, repeat the test using 5% NaOH. If the compound is significantly more soluble in strong base than in weak base, it is a phenol.

b. Bromine Test for Alkenes and Alkynes

*****Bromine is corrosive. Wear gloves and handle with care.*****

- Perform the bromine test on isopropanol, styrene and your unknown.
- In a clean dry test tube, dissolve ~20 mg of compound in 0.5 mL of dichloromethane (CH_2Cl_2). Add one drop of 2% Br_2 solution (in CH_2Cl_2) and mix. If the brown colour of the bromine disappears, the compound contains at least one alkene or alkyne.

c. Lucas Test for Alcohols (2˚ and 3˚)

*****Lucas Reagent contains concentrated hydrochloric acid. Wear gloves and handle with care.*****

- Perform the Lucas test on acetone, isopropanol and your unknown (if soluble in water).
- In a clean dry test tube, combine ~100 mg (5 drops if liquid; weigh if solid) of compound and 1 mL of Lucas reagent ($ZnCl_2$ in HCl). Stopper the test tube and shake vigorously. If either an emulsion or a second layer forms, the compound contains an alcohol. A positive test may take up to 10 minutes to develop.
- *Not all alcohols react with Lucas reagent! A negative test result does not indicate absence of an alcohol.*

d. Jones Oxidation Test for Alcohols (1˚ and 2˚) and Aldehydes

*****Jones Reagent contains Cr(VI) which is carcinogenic. Wear gloves and handle with care.*****

- Perform the Jones test on acetone, isopropanol, benzaldehyde and your unknown.
- In a clean dry test tube, dissolve ~20 mg of compound in 1 mL of acetone. Add one drop of Jones reagent (chromic acid in sulfuric acid) and mix. If a green precipitate appears, the

compound contains an oxidizable functional group such as a 1° alcohol, 2° alcohol or aldehyde.

- *Not all alcohols react with Jones reagent! A negative test result does* <u>*not*</u> *indicate absence of an alcohol.*

e. 2,4-Dinitrophenylhydrazone (2,4-DNP) Test for Ketones and Aldehydes

- Perform the 2,4-DNP test on acetone, isopropanol, benzaldehyde and your unknown.
- In a clean dry test tube, dissolve ~100 mg (or ~0.1 mL) of compound in 0.5 mL of ethanol. Add 1 mL of the 2,4-DNP reagent and mix. If a bright yellow, orange or red precipitate forms, the compound contains an aldehyde or ketone.

f. Schiff's Test for Aldehydes

- Perform the Schiff's test on acetone, isopropanol, benzaldehyde and your unknown.
- To a clean dry test tube, add 1 mL of Schiff's reagent. Then, add 3 drops of compound, mix and let sit for 10 minutes. If a distinct pink colour appears, the compound contains an aldehyde.
- *Some ketones will give a very pale pink colour in a Schiff's test. Performing a positive control (i.e. testing a known aldehyde) ensures that we do not confuse this with the strong pink produced by an aldehyde.*

Report

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Pre-Lab Questions

The standards used in this experiment are acetone, isopropanol, benzaldehyde, benzoic acid, 1-napthol, 4-nitroaniline and styrene.

1. Draw the structure of each of the standards.
2. Identify the reactive functional group in each of the standards.
3. Which of the standards will give a positive reaction in the bromine test?
4. Which of the standards will give a positive reaction in the Lucas test?
5. Which of the standards will give a positive reaction in the Jones test?
6. Which of the standards will give a positive reaction in the 2,4-DNP test?
7. Which of the standards will give a positive reaction in the Schiff test?
8. What is the molecular formula for bromine, and what does bromine look like?
9. Is the bromine test an example of an addition, substitution or redox reaction?
10. Is the Lucas test an example of an addition, substitution or redox reaction?
11. Is the Jones test an example of an addition, substitution or redox reaction?
12. Why is an amine soluble in acid? Show the relevant reaction.
13. Why is a carboxylic acid soluble in base? Show the relevant reaction.