

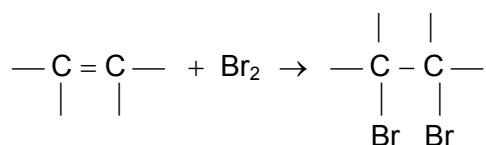
LABORATORY 5

DETECTION OF FUNCTIONAL GROUPS IN ORGANIC COMPOUNDS

I. Characteristic reactions differentiating saturated aliphatic hydrocarbons from unsaturated aliphatic hydrocarbons

1. The test of bromine addition.

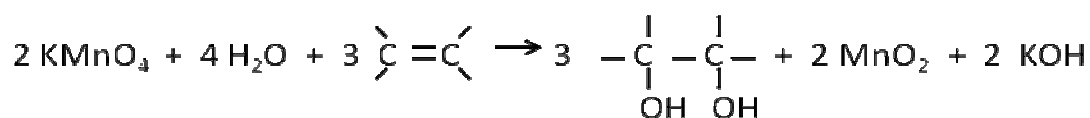
Unsaturated hydrocarbons and other compounds with unsaturated bonds decolorize bromine solution in consequence of addition reaction.



Procedure: Add dropwise 1 % acetic acid solution of bromine to about 0.5 ml of sample dissolved in acetic acid or other organic solvent. Mix carefully the contents of the test tube. The pink color of bromine quickly disappears to the moment, when total multiple bonds are saturated.

2. The test with potassium permanganate by Lehman.

The solution of KMnO_4 submits decolorization in the presence of compounds with unsaturated bonds. This is the consequence of manganese reduction from +7 to +2. During reaction, the solution becomes alkaline (KOH is formed) and the brown precipitate of manganese dioxide can appear in the reaction mixture.



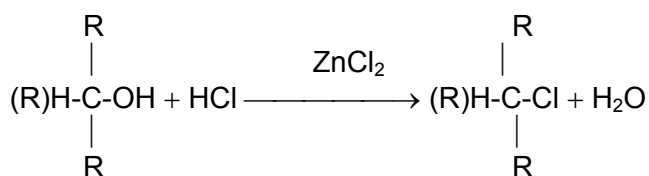
Procedure: Add dropwise 0.1 % acetone solution of KMnO_4 to about 1 ml of examined sample. Mix the solution carefully after addition of each drop and wait for disappearance of KMnO_4 pink color. The quantity of decolorized solution and the speed of its decolorizing depend on the amount of multiple bonds in the molecule of examined compound.

II. Characteristic reactions of alcohols

1. The Lucas test (1 test per group).

Primary, secondary and tertiary alcohols react in different way with Lucas' reagent (the solution of anhydrous zinc chloride in concentrated hydrochloric acid). Primary alcohols, containing less than six carbon atoms, do not react with the reagent, and give clear, slightly dark solution. With secondary alcohols, turbidity of the solution

appears, forming two phase solution after 1-1.5 hours. In the presence of tertiary alcohols, the solution turbidity and solution separation for two phases form very quickly. Tertiary alcohols react with concentrated HCl even in the absence of $ZnCl_2$.



Procedure: Add 5 ml of Lucas' reagent to three dry test tubes with ground-in stoppers, containing respectively primary, secondary and tertiary alcohols (0.5 ml). Mix the content for a while, put them away to the laboratory rack, and check the time difference, necessary in each case for turbidity and two phase solution formation.

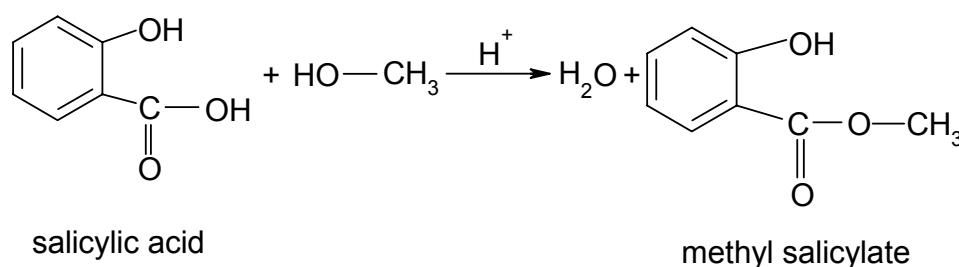
2. The test with mercury sulfate (HgSO_4) for tertiary alcohols by Deniges.

Only tertiary alcohols submit to this reaction. After dehydration, they form unsaturated hydrocarbons. In these conditions, secondary alcohols form only turbid solution and primary ones only opalescence, because of very low speed of alkenes formation.

Procedure: Add 1-2 drops of tertiary alcohol solution to about 1 ml of Deniges reagent (the solution of mercury sulfate in diluted sulfuric acid). Heat the sample in the boiling water bath until a yellow sediment appears.

3. The esterification test – detection of methanol.

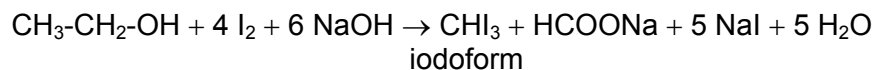
Salicylic acid methyl ester (methyl salicylate) is formed by heating of methyl alcohol with salicylic acid in the presence of concentrated sulfuric acid, acting both as a catalyst and a water bonding agent.



Procedure: Add a pinch of salicylic acid and about 1 ml of concentrated H_2SO_4 to 1 ml of methanol. After mixing, heat the sample in the boiling water bath. After a few minutes, specific resinous aroma of methyl salicylate will appear.

4. The iodoformic test by Lieben – detection of ethanol.

Among primary alcohols, only ethanol undergoes iodination reaction. This is the summarized notation of the reaction:



Procedure: To 0.5 ml of ethanol solution add about 1 ml of iodine in potassium iodide solution (Lugol's solution). Then add dropwise (2-4 drops) of 5 % NaOH water solution, till yellow color of iodine will disappear. After mixing and heating the tube content to 60° C, specific aroma and yellow crystals of iodoform will appear.

5. Reaction of phenol with ferric chloride

Ferric chloride reacts with the hydroxyl groups of phenols and phenol derivatives and forms stable-colored complexes: violet, violet-bluish, blue, green and red. This reaction depends on the structure and presence of complex-created groups (aldehyde, ketone, carboxylic, hydroxyl, or sulfonic) located in the orto-position of phenols. Phenols without complex-created groups in the orto-position react with FeCl₃ only in water, forming unstable complex color compounds.

Procedure: Add 1 drop of 2% FeCl₃ solution to 1% phenol water solution (3 ml). A violet color of this mixture will form. The color disappears after addition of some drops of 1 M sulfuric acid.

III. Characteristic reactions of aldehydes and ketones

1. Schiff's reagent test – detection of aldehydes

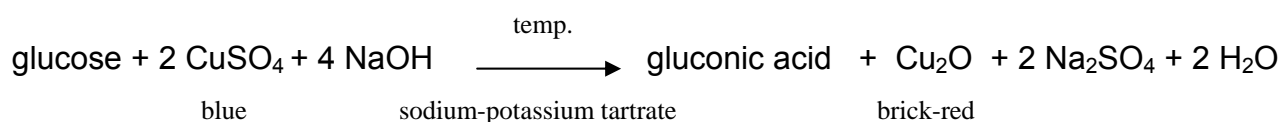
Procedure: To 2 ml of formic aldehyde solution add a few drops of Schiff's reagent (basic fuchsin in sodium meta-bisulfite solution) and mix. After a few minutes, a purple (amaranth) color will appear.

2. Reduction tests of aldehydes

These tests reveal reducing properties of aldehydes and carbohydrates. They are based on the reduction of heavy metal ions and simultaneous oxidation of carbonyl group of aldehydes or monosaccharides to carboxyl group.

a. Fehling's test

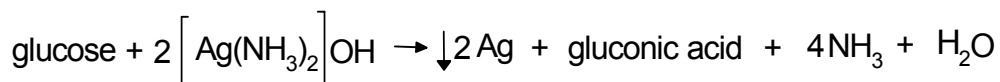
The Fehling reagent is composed of two separate solutions: Fehling I is solution of CuSO₄ in diluted H₂SO₄, and Fehling II is sodium potassium tartrate in diluted NaOH. In an alkaline milieu, the insoluble blue sediment Cu(OH)₂ is released, however, in the presence of tartrate it remains in solution in a form of tartrate complex compound:



Procedure: In a test tube, mix 1 ml of Fehling I reagent and 1 ml of Fehling II. Heat until boiling and then add a few drops of formic solution. Mix well and prolong the heating in water bath. Observe the precipitation of the orange-red colored sediment of cuprous oxide Cu_2O .

b. Tollens' test (1 test per group)

In this test, silver ions are reduced to metallic silver, producing a silver mirror on a test tube walls.



Procedure: To carefully cleaned test tube add 1 ml of 0.1 M AgNO_3 solution and then start adding dropwise 2 M water ammonia solution (ammonium base NH_4OH). After mixing, initial AgOH precipitate will solubilise, forming $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ complex compound. Add to the tube 5 drops of glucose solution, mix, and heat tube in a boiling water bath. Watch the appearance of a silver mirror on the tube walls.

3. Legal's test for methylketones

The most known methylketone is acetone (propanone, dimethylketone), however in acetone homologous series, a single methyl group can be replaced with longer hydrocarbon chains.

Procedure: Dissolve a single crystal of sodium nitroprusside in a test tube containing 2 ml of acetone water solution. Add two drops of 2 M NaOH solution. The solution will become a brownish-red and the colour slowly disappears. The brownish red colour can be restored on addition of a few drops of acetic acid.

IV. Characteristic reactions of carboxylic acids

Carboxylic acids are weaker comparing to mineral acids, but stronger than carbonic acid. Specific reactions of carboxylic acids depend on organic part that is connected to carboxylic group or the presence of additional functional group.

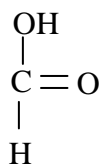
1. Reaction of carboxylic acids with sodium bicarbonate NaHCO_3 .

Procedure: Add about 1 ml of 5% NaHCO_3 solution to 1 ml of short-chain carboxylic acid solution (formic acid - HCOOH). After shaking, observe the release of CO_2 gas bubbles, gathering on the tube walls.

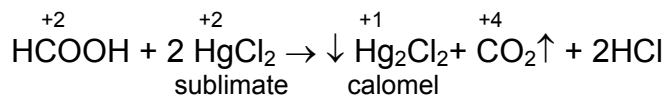


2. Formic acid (methanoic acid) detection

Formic acid is the only one, which possesses both carboxyl and aldehyde groups activities:



The reducing property of formic acid can not be demonstrated using a typical reducing test (in alkaline medium), because of its strong acidic dissociation in water solution. However, Its reducing property can be demonstrated in the following reaction:



Procedure: Add a few drops of 5% mercuric chloride HgCl_2 (a corrosive sublimate) to 1 ml of formic acid solution. Heat in a water bath to obtain the white precipitate of mercurous chloride (calomel).

3. Lactic acid (α -hydroxypropionic acid) detection

Organic acids with α -hydroxyl group change the color of Uffelmann's reagent to yellow-greenish.

Procedure: Prepare Uffelmann's reagent in test tube by adding 1-3 drops of FeCl_3 solution to 2 ml 1% solution of phenol (**one reagent for all the students**). Mix, and add a few drops of the reagent to 1 ml of lactic acid solution. Lactic acid solution changes the violet color of the reagent to light yellow-greenish.

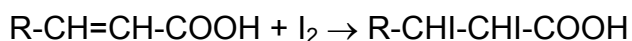
4. Salicylic acid detection

Procedure: Add to test tube 1 ml of water, a few crystals of salicylic acid and 1 drop of FeCl_3 solution. Observe the violet color, similar to previously performed FeCl_3 reaction with phenol solution.

5. Detection of unsaturated fatty acids

a. addition reaction with iodine solution

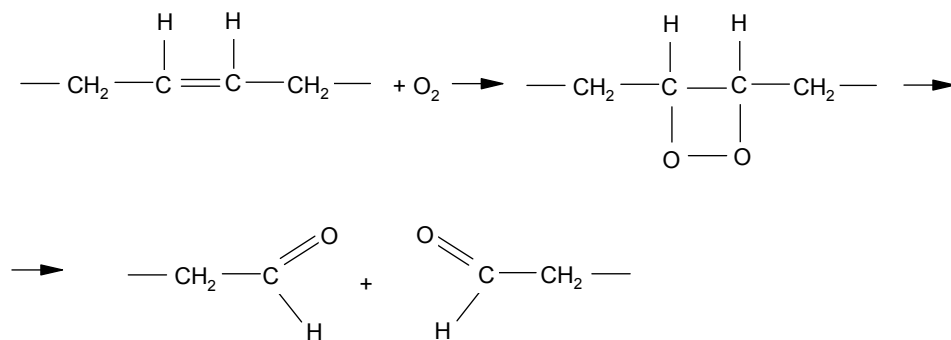
Unsaturated fatty acids react with iodine (and other halogens) discoloring the iodine solution and yielding iodine addition products.



Procedure: Add a few drops of Hübl's reagent (iodine in alcoholic solution of HgCl_2) to 1 ml of olive oil (oleic acid), and shake. After a few minutes the solution becomes colorless.

b. oxidation reaction

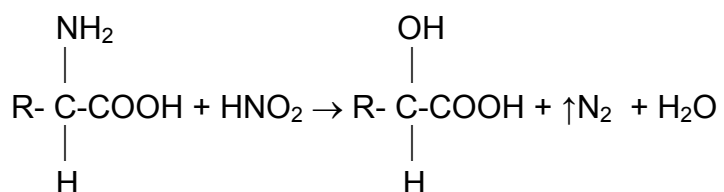
Double bonding in unsaturated fatty acids is sensitive to oxidation. In the presence of oxidizing reagents (also oxygen and its free radicals) the molecule of unsaturated fatty acid, in the place where double bonding exists, is broken into two molecules of aldehyde. This process can be observed after a few days exposition of fat to open air and sunlight (rancid process).



Procedure: Add 3 drops of olive oil to 1 ml of sodium carbonate (Na₂CO₃) solution and then a few drops of potassium permanganate solution (KMnO₄), and mix. After a few minutes, the permanganate solution becomes colorless.

V. Characteristic reaction of aliphatic amines

The primary (1°) amino group, present on alpha carbon atom of each amino acid, reacts with nitrous acid producing alpha-hydroxy acid, nitrogen gas and water.



Procedure: Dissolve a small amount of sodium nitrite salt (NaNO₂) in 1 ml of 2 M sulfuric acid solution. Observe slow bubbling of released nitric oxide gas. Then, **in a hood compartment**, add to the tube a few drops of amino acid (glycine) solution. Observe a massive bubbling of nitrogen gas, forming gas bubbles settled on the tube walls.