***EXPERIMENT 4***

***IDENTIFICATION OF ALDEHYDES***

***AND KETONES***

Aldehydes are compounds of the general formula RCHO; ketones are compounds of the general formula RCOR'. The groups R and R' may be aliphatic or aromatic, and in one aldehyde, formaldehyde, R is a hydrogen atom.



Both contain the carbonyl group (C=O), which lends to their chief chemical and physical properties.

Examples of them include formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, salicylaldehyde, acetone, acetophenone, benzyl methyl ketone, and benzophenone.

**Chemical Reactions:**

1. **General test (2, 4-Dinitrophenylhydrazine).**

Both aldehydes and ketones give yellow or orange precipitate with 2,4-Dinitrophenylhydrazine reagent.



**Procedure:**

Add to 2 drops of the compound 3 drops of the reagent, a yellow or orange precipitate will be formed. If the compound is insoluble in water, dissolve it in 1 ml of methanol and then add the reagent

1. **Tests for differentiation between aldehydes and ketones.**

Differentiation between aldehydes and ketones is achieved by taking the advantage of the fact that aldehydes can easily oxidized while ketones cannot (they need stronger oxidizing agents).

Two reagents can be used for this purpose, Tollen's reagent or Fehling's reagent. Only aldehydes give positive results with these two reagents.

**A. Tollen's test (Reduction of ammonical silver nitrate).**

Tollen's reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. This reagent gives a silver mirror in the presence of aldehydes because the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid with an accompanying reduction of silver ion from this reagent to silver element in the form of a silver mirror.



The oxidation process needs alkaline medium; therefore sodium hydroxide solution is used, and in order to overcome the formation of the brown silver oxide precipitate (Ag2O), ammonium hydroxide is used to serve as a complexing agent for this precipitate making it a water soluble complex.

Note that since the medium is alkaline, salts of the produced carboxylic acid are formed rather than the acid itself.

**Procedure:**

* Tollen's reagent.

Add 2 – 3 drops of the compound to 2 – 3 ml of Tollen's reagent, a silver mirror will be formed. If no reaction occurs, warm the test tube in water bath for few minutes.

**B. Reduction of Fehling's reagent.**

This test, like Tollen's test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling's reagent (a deep blue solution) to give a red cuprous oxide precipitate (Cu2O).



**Procedure:**

* Add 5 drops of the compound to 1 ml of Fehling's solution, and then heat in water bath for 5 minutes (with shaking for water insoluble compounds).

Aldehydes change the color of Fehling's solution from blue to green, orange precipitate, and then red precipitate or copper mirror. Ketones don't change the color of this reagent. On the other hand, this test does not give sharp results with aromatic aldehydes.

1. **Special tests for aldehydes and ketones containing a terminal methyl group.**



These include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone.

**A. Iodoform (Haloform) test.**

For details about the procedure of this test see Iodoform test for alcohols that contain a terminal methyl group.

**B. Sodium nitroprusside test (Na2 [Fe (CN) 6 NO].2H2O)**.

To few drops of the compound add 1 ml of sodium nitroprusside solution and excess of 30% NaOH solution, a red color complex is a positive test.

1. **Polymerization reaction.**

To 0.5 ml of formaldehyde or salicylaldehyde add 0.2 gm of resorcinol and drop by drop concentrated sulfuric acid to get a red or reddish violet color, or a white ring that changes to a reddish violet ring.



1. **Cannizzaro reaction.**

Benzaldehyde, salicylaldehyde, and formaldehyde can undergo this reaction because they do not contain an alpha hydrogen atom.



In this type of reactions the aldehyde undergoes a self oxidation-reduction in the presence of a strong basic medium to yield a mixture of the corresponding alcohol and the salt of the corresponding carboxylic acid (or the acid itself). Therefore, one molecule of the aldehyde serves as the oxidizing agent while the other serves as the reducing agent.



**Procedure:**

To a few drops of benzaldehyde (or the other aldehydes) add 0.5 ml of 30% sodium hydroxide solution and heat slowly with shaking for five minutes. A precipitate of sodium benzoate is produced. Dissolve this precipitate by adding few drops of distilled water, and then add drops of concentrated hydrochloric acid to liberate benzoic acid as a white precipitate.

As mentioned earlier formaldehyde can undergo this reaction; however, this reaction can not be considered for testing formaldehyde since the acid produced formic acid, is liquid and can not be seen as compared to the solid benzoic acid resulted from benzaldehyde.