Experiment 10

Functional Group II: Reactions of Aldehydes, Ketones and Alcohols

Tests for Aldehydes, Ketones and Alcohols

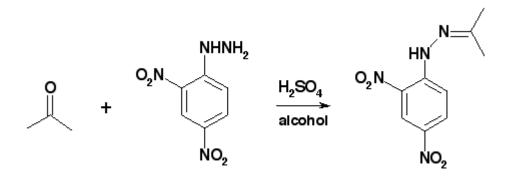
2,4-DNP Test for Aldehydes and Ketones

Tollen's Test for Aldehydes

Jones (Chromic Acid) Oxidation Test for Aldehydes

Iodoform Test for Methyl Ketones

1. 2,4-DNP Test for Aldehydes and Ketones



Standards

Cyclohexanone, Benzophenone, and Benzaldehyde

Procedure

Add a solution of 1 or 2 drops or 30 mg of unknown in 2 mL of 95% ethanol to 3 mL of 2,4-dinitrophenylhydrazine reagent. Shake vigorously, and, if no precipitate forms immediately, allow the solution to stand for 15 minutes. The 2,4-dinitrophenylhydrazine reagent will already be prepared for you.

Positive test

Formation of a precipitate is a positive test.

Complications

- •Some ketones give oils which will not solidify.
- •Some allylic alcohols are oxidized by the reagent to aldehydes and give a positive test.
- •Some alcohols, if not purified, may contain aldehyde or ketone impurities.

2. Tollen's Test for Aldehydes



$$\begin{array}{c} 0 \\ H \end{array} + 2 \operatorname{Ag(NH_3)_2OH} \longrightarrow \\ 2 \operatorname{Ag(S)} + 0 \\ H \end{array} + H_2O + 3 \operatorname{NH_3} \\ R 0 \\ R 0 \\ NH_4^+ \end{array}$$

Standards

Cyclohexanone and Benzaldehyde

Procedure

Add one drop or a few crystals of unknown to 1 mL of the freshly prepared Tollens reagent. Gentle heating can be employed if no reaction is immediately observed.

Tollens reagent: Into a test tube which has been cleaned with 3M sodium hydroxide, place 2 mL of 0.2 M silver nitrate solution, and add a drop of 3M sodium hydroxide. Add 2.8% ammonia solution, drop by drop, with constant shaking, u almost all of the precipitate of silver oxide dissolves. Don't use more than 3 mL of ammonia. Then dilute the entire solution to a final volume of 10 mL with water.

Positive Test

Formation of silver mirror or a black precipitate is a positive test.

Complications

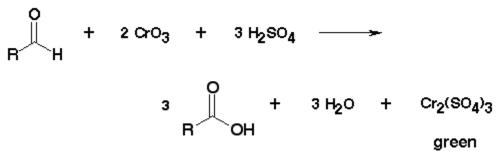
- •The test tube must be clean and oil-free if a silver mirror is to be observed.
- •Easily oxidized compounds give a positive test. For example: aromatic amine and some phenols.

Cleaning up

Place all solutions used in this experiment in an appropriate waste container.

3. Jones (Chromic Acid) Oxidation Test for Aldehydes

Aldehvdes



Standards

Cyclohexanone and Benzaldehyde

Procedure

Dissolve 10 mg or 2 drops of the unknown in 1 mL of pure acetone in a test tube and add to the solution 1 small drop o Jones reagent (chronic acid in sulfuric acid). A positive test is marked by the formation of a green color within 5 second upon addition of the orange-yellow reagent to a primary or secondary alcohol. Aldehydes also give a positive test, but tertiary alcohols do not.

The Jones reagent will already be prepared for you.

Positive Test

A positive test for aldehydes and primary or secondary alcohols consists in the production of an opaque suspension will green to blue color. Tertiary alcohols give no visible reaction within 2 seconds, the solution remaining orange in colo Disregard any changes after 15 seconds.

Complications

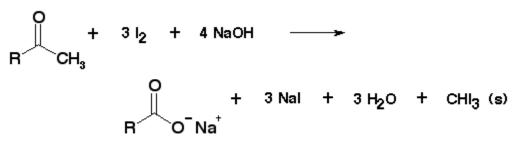
•Aldehydes are better characterized in other ways. The color usually develops in 5-15 seconds.

Cleaning up

Place the test solution in the appropriate waste container.

4. lodoform Test for Methyl Ketones

Ketone



Standard

Acetone

Procedure

If the substance to be tested is water soluble, dissolve 4 drops of a liquid or an estimated 50 mg of a solid in 2 mL of water in a large test tube. Add 2 mL of 3 M sodium hydroxide and then slowly add 3 mL of the iodine solution. Stopper the test tube and shake vigorously. A positive test will result in the brown color of the reagent disappearing and the yel iodoform solid precipitating out of solution. If the substance to be tested is insoluble in water, dissolve it in 2 mL of 1,2-dimethoxyethane, proceed as above, and at the end dilute with 10 mL of water.

Positive Test

Formation of solid iodoform (yellow) is a positive test. (lodoform can be recognized by its odor and yellow color and, m

Alcohols

Functional groups play a vital role in organic chemistry. The organic compound which has -OH functional group are called alcohols. Alcohols are compounds containing an -OH group bonded to a tetrahedral carbon atom. The general formula for alcohol is R-OH. Where R is an alkyl group

Aim:

To identify the presence of alcoholic functional group in a given organic compound.

Theory:

Any of the following test can be carried out to detect the alcoholic functional group.

Sodium metal test
Ester test
Ceric ammonium nitrate test
Acetyl chloride test
Iodoform test

1. Sodium Metal Test:

It is based on the appearance of *brisk effervescence* due to the liberation of hydrogen gas when alcohol reacts with active metals like sodium.

The chemical reaction is given below.

 $\mathbf{2R}\textbf{-}\mathbf{OH} + \mathbf{2Na} \rightarrow \mathbf{2R}\textbf{-}\mathbf{O}\textbf{-}\mathbf{Na} + \mathbf{H}_{2} \uparrow$

 $\mathbf{2CH_3}\text{-}\mathbf{OH} + \mathbf{2Na} \rightarrow \mathbf{2CH_3}\text{-}\mathbf{O}\text{-}\mathbf{Na} + \mathbf{H_2} \uparrow$

The alcohol to be tested should be dry because water also reacts with sodium. Sodium should be handled carefully, unreacted sodium should be destroyed by adding excess alcohol. This test is favourable if phenyl or <u>carboxyl groups</u> are absent.

Note: Evolution of hydrogen gas cause a brisk effervescence indicates an alcoholic group.

2. Ester Test:

Carboxylic acids reacts with alcohols forming a fruit smelling ester. The reaction between an alcohol and a carboxylic acid is called *esterification*. This reaction is a slow reaction catalysed by concentrated sulphuric acid.

The chemical reaction is given below.

$\textbf{R-OH} + \textbf{R-COOH} \rightarrow \textbf{R-COOR} + \textbf{H}_2\textbf{O}$

$\mathbf{CH_3OH} + \mathbf{CH_3}\text{-}\mathbf{COOH} \rightarrow \mathbf{CH_3}\text{-}\mathbf{COOCH_3} + \mathbf{H_2O}$

Note: A sweet smell indicates the presence of alcoholic group.

3. Ceric Ammonium Nitrate Test:

Alcohol or reaction with ceric ammonium nitrate forms a pink or red colour precipitate due to the formation of a complex compound and <u>ammonium nitrate</u>.

The chemical reaction is given below.

 $(NH_4)_2 \left[Ce(NO_3)_6\right] + 3ROH \rightarrow \left[Ce(NO_3)_4(ROH)_3\right] + 2NH_4NO_3(NH_4)_2 \left[Ce(NO_3)_6\right] + 3CH_3OH \rightarrow COORDER + 2NH_4NO_3(NH_4)_2 \left[Ce(NO_3)_6\right] + 3CH_4OH \rightarrow COORDER + 2NH_4NO_3(NH_4)_2 \left[Ce(NO_3)_6\right] + 3CH_4OH \rightarrow COORDER + 2NH_4NO_3(NH_4)_2 \left[Ce(NO_3)_6\right] + 3CH_4OH \rightarrow COORDER + 2NH_4OH \rightarrow CO$

 $[Ce(NO_3)_4(CH_3OH)_3] + 2NH_4NO_3$

Note: The appearance of wine red colour precipitate shows the presence of alcoholic group.

4. Acetyl Chloride Test:

Alcohol reacts with acetyl chloride results in the formation of ester and hydrogen chloride. The resulting hydrogen chloride on contact with ammonium hydroxide forms a white fumes of ammonium chloride and water.

The chemical equation is given below.

$\textbf{R-OH} + \textbf{CH}_3 \textbf{-} \textbf{CO-Cl} \rightarrow \textbf{CH}_3 \textbf{-} \textbf{COOR} + \textbf{HCl} \textbf{HCl} + \textbf{NH}_4\textbf{OH} \rightarrow \textbf{NH}_4\textbf{Cl} + \textbf{H}_2\textbf{O}$

Note: The formation of white fumes indicates the presence of alcohol.

5. Iodoform test:

This test is given by secondary alcohols, ketones and acetaldehyde. First the compound is heated with sodium hydroxide solution and iodine. A formation of yellow precipitate of iodoform shows the presence of alcohol.

The chemical reactions are given below.

 $CH_3\text{-}CH(OH)\text{-}CH_3 + I_2 + 2NaOH \rightarrow CH_3\text{-}CO\text{-}CH_3 + 2NaI + 2H_2O$

 $CH_3\text{-}CO\text{-}CH_3 + 3I_2 + 4NaOH \rightarrow CHI_3(Iodoform) + CH_3COONa + 3NaI + 3H_2OONa + 3H$

Note: The formation of yellow precipitate shows the presence of alcohol, acetaldehyde or methyl ketones.

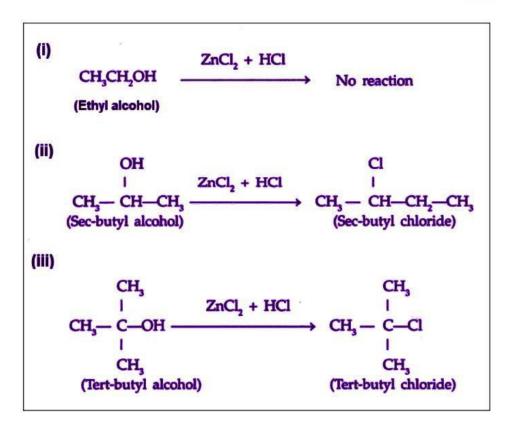
* Distinction Between Primary, Secondary and Tertiary Alcohols: Lucas

Test:

The mixture of <u>zinc chloride</u> and concentrated hydrochloric acid is called Lucas reagent. It reacts with primary, secondary and tertiary alcohols at different rates. This reagent forms a cloudiness on reacting with alcohols. Tertiary alcohols reacts immediately and give cloudiness, secondary alcohols reacts slowly and gives cloudiness after 5 to 10 minutes and there is no reaction with primary alcohols.

The chemical reactions are given below.





Note:

Cloudiness appears immediately \rightarrow Tertiary alcohols Cloudiness appears within five to ten minutes \rightarrow Secondary alcohols Cloudiness appears only on heating \rightarrow Primary alcohols

Materials Required:

Sodium metal
Acetic acid
Ceric ammonium nitrate
Acetyl chloride
Ammonium hydroxide
Iodine
Sodium hydroxide
Calcium sulfate
Lucas reagent (zinc chloride and Con.HCl)
Test tubes

11. Test tube holder

12. Filler

Apparatus Setup:

Lucas test





Cloudiness appears only on heating or clear solution -> Primary alcohols

Cloudiness appears within five to ten minutes -> Secondary alcohols



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Cloudiness appears immediately -> Tertiary alcohols

Procedure:

Preparation of Reagents:

1.Ceric Ammonium Nitrate: Take 20gm of orange crystals of ceric ammonium nitrate in 200ml of warm dilute nitric acid.

2.Lucas Reagent: Take 135gm of anhydrous zinc chloride and dissolved in 100ml of concentrated hydrochloric acid.

3.Iodine Solution: Dissolve 5gm of potassium iodide in 40ml of water. To that solution add 1gm of solid iodine and dissolve it completely.

1. Sodium Metal Test:

- 1. Take the organic compound to be tested in a dry test tube.
- 2. Add 1gm of anhydrous calcium sulfate and shake well to remove excess water.
- 3. Decant the solution to another clean test tube.
- 4. Add a small piece of sodium metal.
- 5. If brisk effervescence appears due to the evolution of hydrogen gas indicate the presence of alcoholic group.

2. Ester Test:

- 1. Take 1ml of the organic liquid to be tested in a clean dry test tube.
- 2. Add 1ml of glacial acetic acid and 2-3 drops of conc. sulfuric acid.
- 3. Heat the mixture in a water bath for 10 minutes.
- 4. The hot mixture is poured into a beaker containing cold water.

- 5. Smell the water in the beaker.
- 6. A fruity smell confirms the presence of alcoholic group.

3. Ceric Ammonium Nitrate Test:

- 1. Take 1ml of given compound in a dry test tube.
- 2. Add a few drops of ceric ammonium nitrate reagent and shake the solution well.
- 3. Observe the solution.
- 4. If red precipitate appears then the presence of alcoholic group is conformed.

4. Acetyl Chloride Test:

- 1. Take 2ml of given organic compound in a clean test tube
- 2. Add 1gm of anhydrous calcium sulfate and shake well.
- 3. Filter the solution. To the filtrate add 3 to 4 drops of acetyl chloride and shake well.
- 4. Take a glass rod dipped in ammonium hydroxide solution.
- 5. Bring the glass rod near the mouth of the test tube.
- 6. If white fumes occurs then the presence of alcoholic group is conformed.

5. Iodoform Test:

- 1. Take 1ml of given organic compound in a clean dry test tube.
- 2. Add 1ml of 1% iodine solution to it.
- 3. Add dilute sodium hydroxide solution drop wise until the brown colour of iodine is discharged.
- 4. Heat the mixture gently in water bath.
- 5. The formation of yellow precipitate indicates the presence of either ethanol or acetaldehyde or methyl ketone.

Observations:

Sodium Metal Test	Brisk effervescence indicates an alcoholic group
Ester Test	Sweet smell indicates the presence of alcoholic group
Ceric Ammonium Nitrate Test	Appearance of wine red colour precipitate shows the presence of alcoholic group
Acetyl Chloride Test	Formation of white fumes indicates the presence of alcohol
lodoform Test	Formation of yellow precipitate shows the presence of alcohol

Results and Discussions:

The given organic compound is ____. (primary alcohol, secondary alcohol or tertiary alcohol)

Precautions:

1.Sodium metal should be handled carefully, Since it reacts with water violently. 2.Iodine should not be inhaled as it can cause irritation to nose.

Keep visiting BYJU'S to learn more about class 12 CBSE chemistry practicals.

Frequently Asked Questions

What is Lucas reagent?

The mixture of anhydrous zinc chloride in 100ml of concentrated hydrochloric acid is called Lucas reagent.

What is the use of Lucas reagent?

Lucas ' reagent is a concentrated hydrochloric acid solution of anhydrous zinc chloride. Used to classify low molecular weight alcohols. The reaction is a substitution reaction where a hydroxyl group is replaced by the chloride.

Name any four functional groups.

Some functional groups are,

- •Hydroxyl group (-OH)
- ●Amino group (-NH₃)
- Acid group (-COOH)
- •Aldehyde group (-CHO)

Why the given alcohol is dried completely before carrying out sodium metal test?

Alcohol is dried completely before carrying out sodium metal test because sodium itself reacts with water vigorously.

Which is more acidic and alcohol or phenol?

Alcohols are less acidic than phenols because the removal of H ion from alcohol is very difficult. Phenol can easily lose ion because the formed phenoxide ion is somewhat stabilized by resonance.