4. ALCOHOLS

Introduction

AIcohols are organic compounds that may be considered as derivatives of water in which one of the hydrogen atoms of water molecule (H-O-H) has been replaced by an alkyl or substituted alkyl group. Therefore, properties of alcohols may be related to properties of both water and hydrocarbons. The alkyl group could be primary, secondary, or tertiary, and may be open chain or cyclic. Accordingly, alcohols may be defined as organic compounds that contain hydroxyl groups attached to alkyl, substituted alkyl, or cyclic alkyl group.

PHYSICAL PROPERTIES

- ☒ Alcohols are colorless liquids with a special faint odor. Benzyl alcohol and cyclohexanol have characteristic odors.
- ☒ Aliphatic alcohols burn with blue flame (without smoke) while aromatic alcohols burn with yellow smoky flame.
- ☒ Boiling points of alcohols are considerably high (being associated liquids); they increase as the molecular weight (number of carbons) increases.
- ☒ Alcohols with number of carbon atoms up to **5** will be considered soluble in water; branched alcohols will be more soluble than straight chain alcohols with the same number of carbon atoms.

SOLUBILITY CLASSIFICATION

- Alcohols are polar compounds because of the presence of the hydroxyl group which is also responsible for their ability to form hydrogen bonding.
- The degree of the polarity depends on the size of the alkyl side chain; the polarity decreases as the size of the alkyl side chain increases, or in another word, as the

hydroxyl group/hydrocarbon ratio of alcohols increases, their water solubility increases and vice versa.

- Low molecular weight alcohols are soluble in water due to hydrogen bonding ability with water molecules. Therefore, alcohols that are soluble in water and ether are classified under class S_1, such as ethanol and methanol.
- Alcohols that are insoluble in water are related to class ***N***.

H.W// Which alcohol has solubility class S_2, what are the structural requirements present in this alcohol that made it under this solubility class?

CHEMICAL PROPERTIES

1) Alcohols are neutral compounds that don't change the colour of litmus paper.

2) All reactions of alcohols are related to its active hydroxyl group and are of two types:

a. ***Removal of the hydroxyl*** itself as in the reaction with hydrogen halides to form alkyl halides or in the dehydration reaction to form a double bond.

b. ***Removal of the proton*** only from the active hydroxyl as in the formation of esters or in the reaction with active metals such as sodium.

IDENTIFICATION OF ALCOHOLS

General test (Ceric ammonium nitrate reagent)

Ceric ammonium nitrate (yellow solution) is an oxidizing agent that reacts with alcohols to give a red complex and with phenols to give a brown to greenish brown precipitate

Each mole of the alcohol requires two moles of the reagent.

The red colored complex is an intermediate for the oxidation of alcohols by the Ce (IV) solution. This red colour disappears after a reasonable time due to completing the

oxidation of this intermediate and the reduction to the colorless Ce (III) solution producing the corresponding aldehyde or ketone.

Procedure

1. ***Water soluble (miscible) alcohols***

   mix two drops of the alcohol with one drop of ceric ammonium nitrate solution. A red complex indicates a positive test.

2. ***Water insoluble (immiscible) alcohols***

mix two drops of the alcohol with **0.5ml** dioxane, shake well, and add one drop of the reagent to get a positive red complex.

This test gives positive results with primary, secondary, and tertiary alcohols (up to 10 carbons), poly hydroxylated compounds such as carbohydrates, and hydroxylated carboxylic acids, aldehydes and ketones.

The overall sequence of reactions for a primary alcohol is as follows:

(a) $(NH_4)_2Ce(NO_3)_6 + RCH_2OH \longrightarrow (NH_4)_2Ce(NO_3)_5(OCH_2R) + HNO_3$

(yellow) (red)

(b) $(NH_4)_2Ce(NO_3)_5(OCH_2R) \longrightarrow RCH_2O\cdot + (NH_4)_2Ce(NO_3)_5 + HNO_3$

(red) (colorless)

(c) $RCH_2O\cdot + (NH_4)_2Ce(NO_3)_6 \longrightarrow R{-}C(=O){-}H + (NH_4)_2Ce(NO_3)_5 + HNO_3$

(yellow) (colorless)

The rates of the oxidation steps (b and c) depend upon the structure of the hydroxy compound.

IDENTIFICATION OF ALCOHOLS

Specific tests

1. Iodoform (Haloform) test

This test is specific for alcohols which have a free methyl group and a hydrogen attached to the carbon bearing the hydroxyl group such as ethanol and sec-butanol.

The alcohol is oxidized to the corresponding aldehyde or ketone by the action of the produced oxidizing agent ***sodium hypoiodite***, which also causes the aldehyde or ketone to be tri-iodinated on the terminal methyl group; the tri-iodinated methyl group will then leave by the action of excess sodium hydroxide as a yellow precipitate, iodoform.

a. Dissolve the compound (**2-3 drops or 100mg**) in water (**2-3ml**) in a test tube and add **1ml of 10% sodium hydroxide**.

b. To this add a saturated solution of iodine-potassium iodide in water with stirring until the dark colour of iodine persists.

c. Heat the solution in a **boiling water bath** for **1-2 minutes** or **hot water bath for 5 minutes**; shaking the test tube occasionally. It is likely that some or all of the dark color of the iodine reagent will be discharged.

d. If the dark color of the iodine reagent is still apparent following heating, add **dropwise 10% sodium hydroxide** solution until the dark color of the iodine reagent has been discharged. Shake the mixture in the test tube (corked) during the addition of sodium hydroxide. Care need not be taken to avoid adding excess sodium hydroxide.

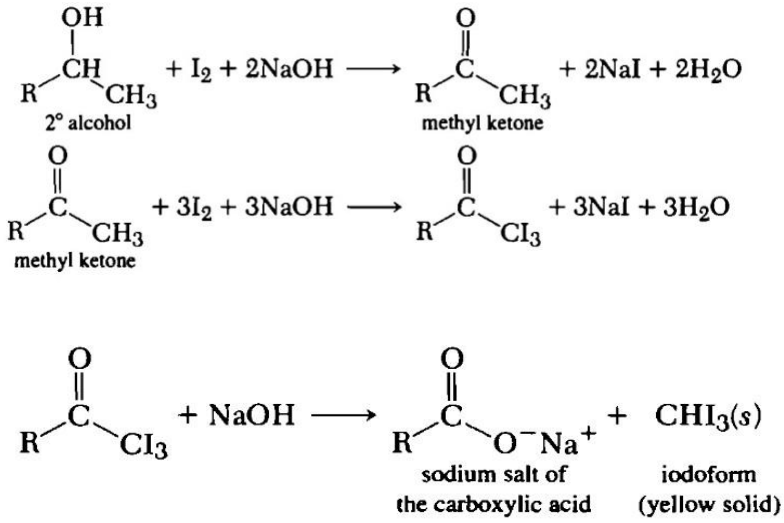
e. After the dark iodine color of the solution has been discharged, fill the test tube with water to within **2cm** of the top. Cork the test tube and shake it vigorously.

Allow the tube to stand for at least **15minutes** at room temperature. The appearance of a pale yellow precipitate of iodoform constitutes a positive test.

f. The yellow precipitate usually settles out slowly onto the bottom of the test tube. Sometimes, the yellow color of iodoform is masked by a dark substance.

It is important to proceed through all these steps so that only at the final step you can say that the test is negative.

Both ethanol and sec-butanol give positive iodoform test and they can be differentiated only by testing their solubility in water; sec-butanol is less soluble in water than ethanol.

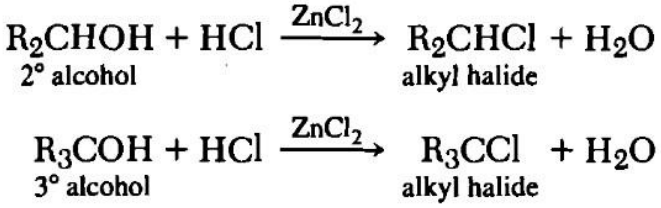


2. Lucas Test

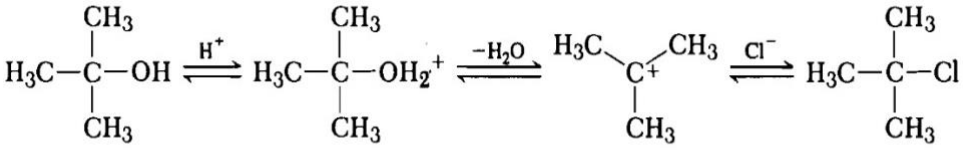
This test often provides classification information on alcohols and is used to distinguish between the different types of alcohols (primary, secondary, or tertiary). It depends on the formation of alkyl chloride as a second liquid phase.

Lucas reagent is prepared from anhydrous zine chloride and concentrated hydrochloric acid. Zinc chloride is added to increase the ionization of hydrochloric acid.

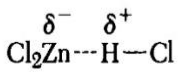
Benzyl alcohol shows the fastest positive result. Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols. Primary alcohols and methanol don't react and don't form two layers.



The mechanism of the Lucas test is an S_N1-type process as follows:



The role of the $ZnCl_2$ is to enhance the reactivity of the HCl by polar coordination:



Procedure

Mix **2-4** drops of the alcohol with ***few*** drops of Lucas reagent and observe the results:

- **i.** Benzyl alcohol gives immediate result as shown by the appearance of two phases.
- **ii.** Tertiary alcohols give two phases that separate within **2-3** minutes.
- **iii.** Secondary alcohols give two phases that separate after **15-20** minutes (giving a cloudy solution).
- **iv.** In primary alcohols one layer appears.