Al-Mustaqbal University

College of Science

Qualitative Analytical Chemistry

First Year Students / 1st Lecture

Qualitative Functional Group Analysis

2025-2026

By

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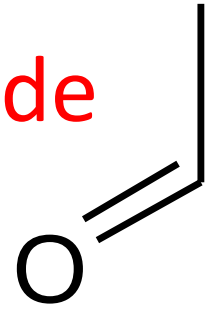
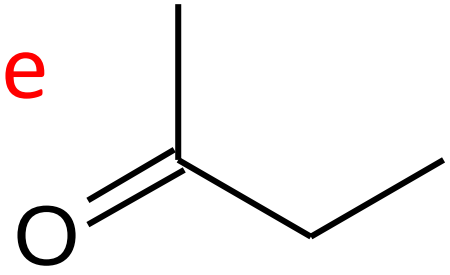
Functional group class

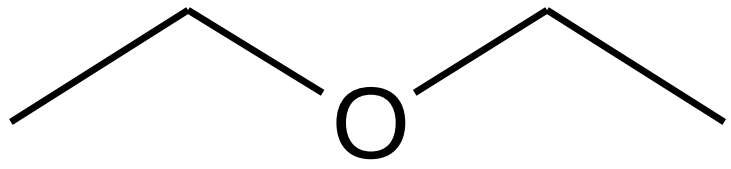
aldehyde



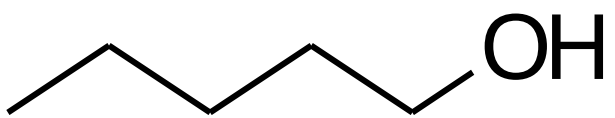
ketone



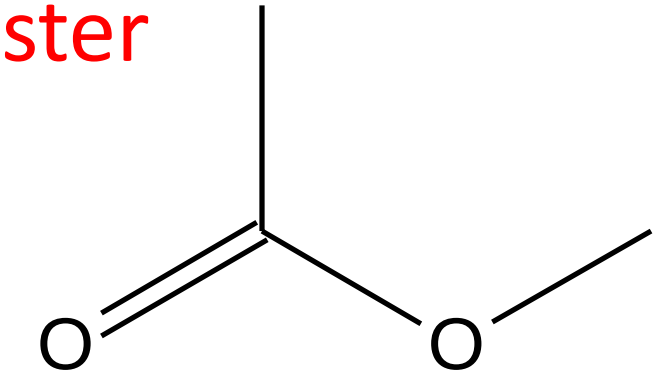
ether



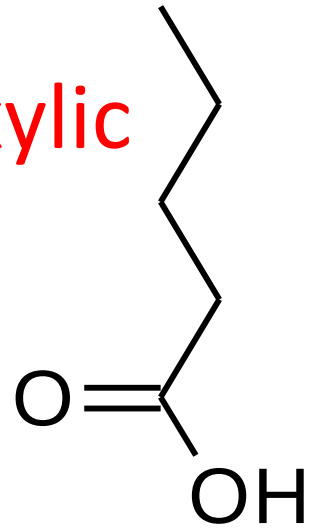
alcohol



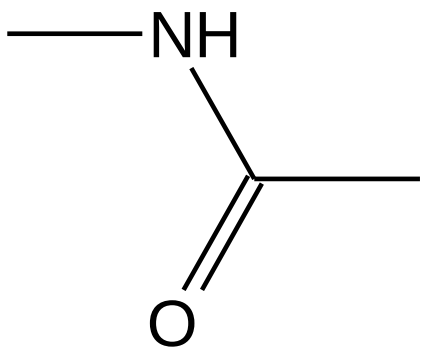
ester



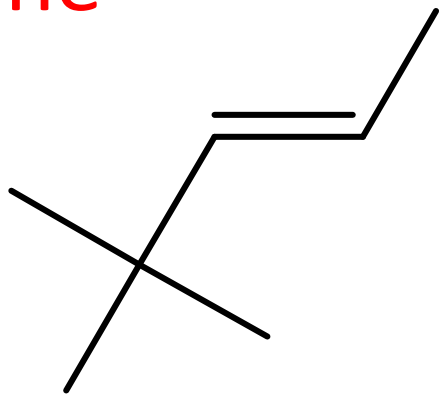
carboxylic acid



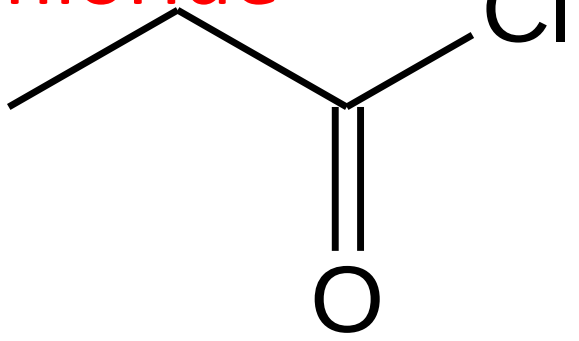
amide



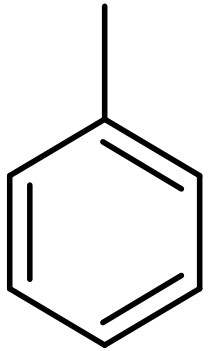
alkene



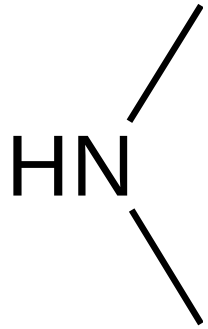
Acid (acyl) chloride



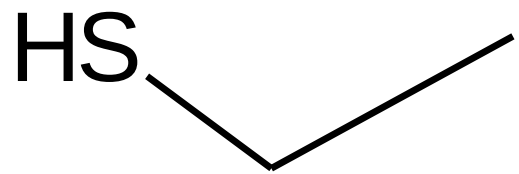
Aromatic=arene



amine



thiol



Name that condensed form

RCOOR’

ester

ROR’

ether

RCOR’

ketone

RCOCl

Acyl chloride

RCHO

aldehyde

RCOOH

carboxylic acid

Do it backwards condensed → name

$RCONH_2$

amide

RR'C=CRR'

alkene

RCl

Alkyl halide

ROH

alcohol

RSR'

sulfide

RNH_2

Primary amine

Tests for Functional Groups

I. Tests for Unsaturation

Theory

Organic compounds containing $>C=C<$ and / or $-C\equiv C-$ bonds are called unsaturated compounds. These compounds undergo addition reaction with bromine water or the solution of bromine in carbon tetrachloride, chloroform or glacial acetic acid. Addition of bromine to an alkene results in the formation of vicinal dibromide. The reddish orange colour of the solution of bromine in carbon tetrachloride disappears on reaction with an alkene. The reaction is as follows :

$$H_2C=CH_2 + Br_2 \rightarrow \underset{\text{(colourless)}}{H-\overset{Br}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-H}$$

Alkenes decolourise the neutral/alkaline $KMnO_4$ solution and vicinal glycols are formed (**Bayer's test**). Reaction takes place as follows :

$$\underset{\text{(purple)}}{3CH_2=CH_2 + 4H_2O + 2MnO_4^-} \rightarrow 3\underset{OH}{\overset{OH}{\overset{|}{CH_2}-\overset{|}{CH_2}}} + 2OH^- + 2MnO_2$$

Both the above reactions are used as tests for unsaturation.

https://www.youtube.com/watch?v=mxvB1xLmPI4

II. Test for Alcoholic (R–OH) Group

Theory

Alcoholic compounds on reaction with ceric ammonium nitrate give a red colouration due to the formation of a complex.

$$(NH_4)_2[Ce(NO_3)_6] + 3ROH \longrightarrow [Ce(NO_3)_4(ROH)_3] + 2NH_4NO_3$$

Ceric ammonium nitrate — Red complex

Distinction between primary, secondary and tertiary alcohols can be done on the basis of iodoform test and Lucas test.

Ethanol and secondary alcohols which contain CH_3—CH(OH)R group (iodoform reaction) give positive iodoform test. To carry out reaction, potassium iodide and sodium hypochlorite solution are added to the compound in the presence of sodium hydroxide solution. Probably sodium hypochlorite first oxidses potassium iodide into potassium hypoiodite, which oxidises CH_3—CH(OH)R group to CH_3COR group and then iodinates it in the alkaline medium of the reaction mixture by replacing the α-hydrogen attached to the carbon atom adjacent to carbonyl group by iodine. Iodoform is formed after cleavage of C—C bond.

$$CH_3CH_2OH \xrightarrow[\text{hypoiodite}]{\text{Potassium}} CH_3CHO \xrightarrow[\text{hypoiodite}]{\text{Potassium}} CI_3CHO \xrightarrow{NaOH} CHI_3 + HCOONa$$

Lucas Test

Lucas reagent contains zinc chloride and concentrated hydrochloric acid. This reagent reacts with primary, secondary and tertiary alcohols at different rates. Tertiary alcohols react almost instantaneously, secondary alcohols react in about 1-5 minutes and primary alcohols react very slowly. The reaction may take 10 minutes to several days.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} \text{No reaction/Slow reaction}$$

$$R_2CHOH + HCl \xrightarrow{ZnCl_2} R_2CHCl + H_2O$$

$$R_3COH + HCl \xrightarrow{ZnCl_2} R_3CCl + H_2O$$

Alcohols are soluble in Lucas reagent but the formed alkyl halides are not soluble. Therefore, formation of two layers in the reaction medium indicate the occurrence of the reaction.

Primary alcohols – Layers do not separate

Secondary alcohols – Layers separate within 1-5 minutes

Tertiary alcohols – Layers separate immediately

https://www.youtube.com/watch?v=ZuAKxcxdDF8

https://www.youtube.com/watch?v=HSGlfbV7W84&t=140s

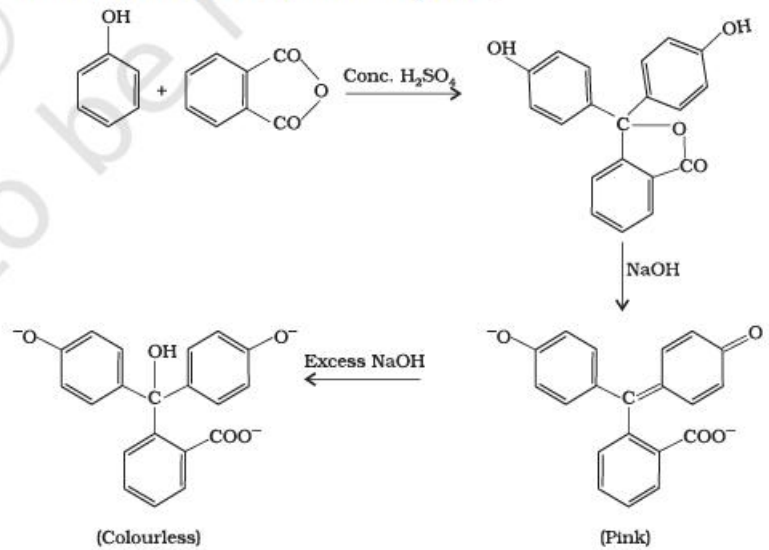
III. Phenolic (Ar-OH) Group

Theory

The –OH group attached directly to the ring carbon of an aromatic ring is called phenolic –OH group. Phenols are weakly acidic, therefore they are soluble in NaOH solution but at the same time they are not sufficiently acidic to be soluble is sodium hydrogencarbonate solution. Phenols give coloured complex with neutral ferric chloride solution. For example, phenol gives a complex of violet colour as follows :

$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{[Fe(C_6H_5O)_6]^{3-}} + 3HCl + 3H^+$$

Resorcinol, *o*–, *m*– and *p*–cresol give violet or blue colouration, catechol gives green colour which rapidly darkens. 1 and 2–Naphthol do not give characteristics colours. Phenols condense with phthalic anhydride in the presence of concentrated H_2SO_4, Phenol condeses to give phenolphthalein which gives a dark pink colour with NaOH solution. This is called phthalein dye test.



https://www.youtube.com/watch?v=HSGlfbV7W84

IV. Aldehydic and Ketonic Groups (–CHO and $-\overset{\overset{O}{\|}}{C}-$)

Theory

Both aldehydes and ketones contain carbonyl group (>C = O) and are commonly known as carbonyl compounds. Identification of aldehydes and ketones is done by two important reactions of carbonyl group i.e.

(i) addition reaction on double bond of >C = O group and

(ii) oxidation of carbonyl group.

Addition reactions of derivatives of ammonia are important from the point of view of identification of carbonyl compounds. Addition is generally followed by elimination resulting in the formation of unsaturated compound.

$$>C=O + RNH_2 \longrightarrow \overset{OH}{\underset{NHR}{C}} \xrightarrow{-H_2O} >C=NR$$

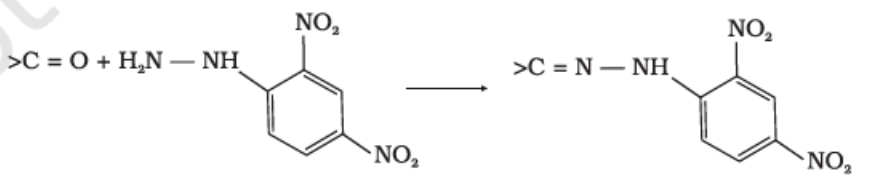
(R = alkyl, aryl or C_6H_5NH etc.)

These reactions are catalysed by an acid or a base and do not occur under strongly acidic or basic conditions. Each reaction requires an optimum pH for its occurrence. Therefore, maintenance of pH is very important while carrying out these reactions.

As far as oxidation is concerned, aldehydes are easily oxidised to carboxylic acids while ketones require relatively stronger oxidising agents. Distinction can be made between these two types of carbonyl compounds on the basis of difference in their reactivity.

Following tests are performed for the identification of aldehydic and ketonic groups:

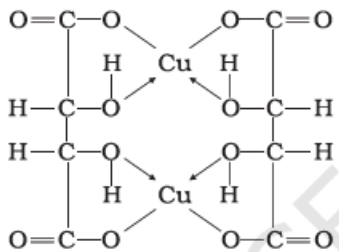
(i) On reaction with 2,4-dinitrophenylhydrazine (2,4-DNP), they form the respective 2,4–dinitrophenyl hydrazones.



2, 4-Dinitrophenylhydrazine

2, 4 – Dinitrophenyl hydrazone of carbonyl compound

These two carbonyl compounds (aldehydes and ketones) are distinguished on the basis of tests using mild oxidising reagents, like Tollen's reagent and Fehling's reagent or Benedict's reagent. Tollen's reagent is an alkaline solution of silver cation complexed with ammonia, and Fehling's and Benedict's reagents are alkaline solutions containing cupric ions complexed with tartarate and citrate ions respectively. Fehling's reagent is freshly prepared by mixing equal amounts of Fehling's solution A and Fehling's solution B. Fehlings reagent deteriorates on keeping while Fehling's solutions A and B are quite stable. Fehling's solution A is an aqueous copper sulphate solution while Fehling's solution B is an alkaline solution of sodium potassium tartarate (Rochelle's salt). The reagent contains Cu^{2+} ion complexed with tartarate ions. The structure of the complex is given below :



Copper tartarate complex

Benedict modified the original Fehling's test by using a single solution which is more convenient for the test. Benedict's solution is more stable than Fehling's reagent and can be stored for a long time. It is an alkaline solution containing a mixture of copper sulphate and sodium citrate ($2Na_3C_6H_5O_7.11H_2O$).

Complex formation decreases the cupric ion concentration below that necessary for precipitation of cupric hydroxide. These two reagents oxidize aldehydes while ketones remain unaffected. The chemistry of these tests is as follows:

$$RCHO + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow 2Ag + 3NH_3 + H_2O + RCOONH_4$$

From Tollen's reagent

$$RCHO + 2Cu^{2+}\text{(complexed)} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Fehling's solution

However, aromatic aldehydes do not give positive Fehling's test. In Benedict test also, Cu^{2+} ions are reduced to Cu^+ ions in the same manner as in the case of Fehling's reagent.

Aldehydes also give pink colour with Schiff's reagent (the reagent is prepared by decolourising aqueous solution of *p*-rosaniline hydrochloride dye by adding sodium sulphite or by passing SO_2 gas). Ketones do not respond to this test.

https://www.youtube.com/watch?v=pehXI484Cwc

https://www.youtube.com/watch?v=E2xNpSj_A4U

V. Carboxyl Group (—COOH)

Theory

Organic compounds containing carboxyl functional groups are called carboxylic acids.

The term carboxyl, derives its name from the combination of words carbonyl and hydroxyl because carboxylic functional group contains both of these groups ($-\overset{\overset{O}{\|}}{C}-OH$). These acids turn blue litmus red and react with sodium hydrogencarbonate solution to produce effervescence due to the formation of carbon dioxide. This is a test that distinguishes carboxylic acids from phenols.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$

These react with alcohols in the acidic medium to produce esters.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xrightarrow[\Delta]{\text{Conc.}H_2SO_4} \underset{\text{Ester}}{RCOOR'} + H_2O$$

VI. Amino Group (—NH_2)

Theory

Organic compounds containing amino group are basic in nature. Thus they easily react with acids to form salts, which are soluble in water.

Both, aliphatic and aromatic amines are classified into three classes namely– primary(–NH_2), secondary(-NH-) and tertiary (-N<), depending upon the number of hydrogen atoms attached to the nitrogen atom. Primary amine has two hydrogen atoms, secondary has one while tertiary amine has no hydrogen atom attached to nitrogen.

(i) Carbylamine test

Aliphatic as well as aromatic primary amines give carbylamine test in which an amine is heated with chloroform.

$$R\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

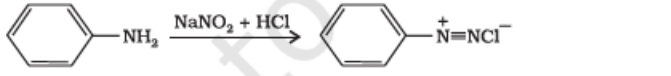
(R=alkyl or aryl group) (Carbylamine)

Caution!

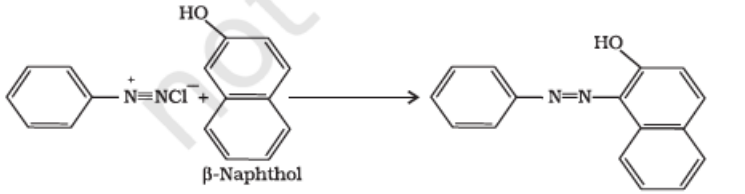
Carbylamine so formed is highly toxic and should be destroyed immediately after the test. For this cool the test tube and add carefully an excess of conc. HCl.

(ii) Azo dye test

Aromatic primary amines can be confirmed by azo dye test. Primary amine e.g. aniline reacts with nitrous acid generated in situ by the reaction of sodium nitrite with HCl at 0–5°C to produce diazonium salt. This couples with β-naphthol to give a scarlet red dye, which is sparingly soluble in water.



Benzene diazonium chloride



β-Naphthol

β-Naphthol azo–dye
(Scarlet red)

https://www.youtube.com/watch?v=XopvgYTP_AI