

ORGANIC CHEMISTRY-I

UNIT 5 NOTES

CARBOXYLIC ACIDS

- ACIDITY OF CARBOXYLIC ACIDS
- INDUCTIVE EFFECTS
- QUALITATIVE TEST

ALIPHATIC AMINES

- BASICITY OF AMINES
- EFFECT OF SUBSTITUENTS
- QUALITATIVE TESTS



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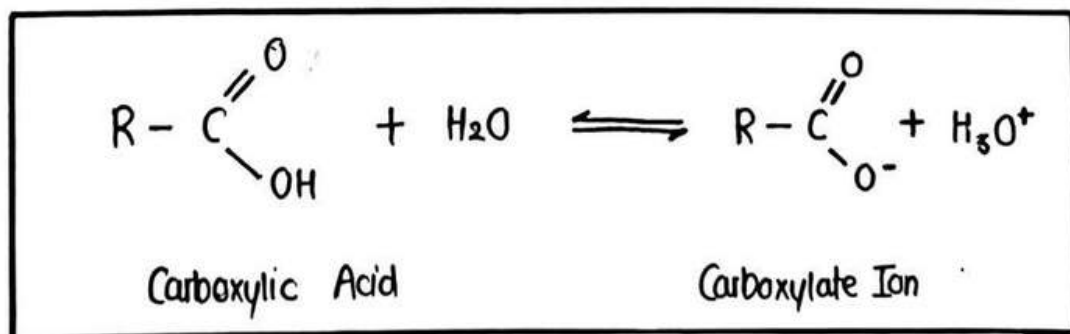
CARBOXYLIC ACIDS

- Carboxylic Acid is an organic compound that contains a carboxyl group ($-\text{COOH}$).
- This group consists of a carbonyl group ($\text{C}=\text{O}$) attached to hydroxyl group ($-\text{OH}$).
- They can be either aliphatic or aromatic.



ACIDITY OF CARBOXYLIC ACIDS

- Carboxylic acids are acidic in nature.
- The acidity of carboxylic acids refers to their ability to donate a proton (H^+) from the carboxyl group ($-\text{COOH}$) to form a carboxylate ion ($-\text{COO}^-$).
- When carboxylic acids dissociate in water, they form carboxylate ion & hydronium ion by donating H^+ to the water.

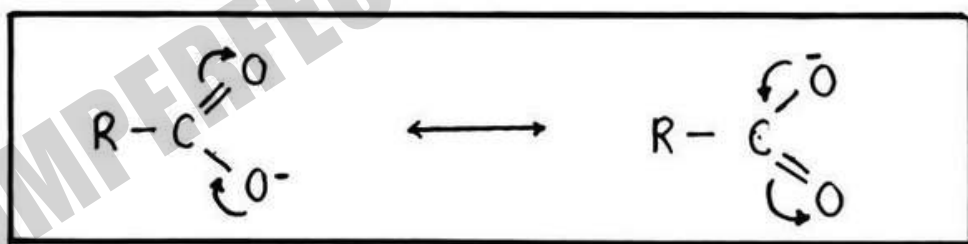


Now this carboxylate ion becomes very stable due to two major key factors :

- ① Resonance stabilization
- ② Electronegative Oxygen Atoms

① Resonance Stabilization

- When a carboxylic acid loses a proton (H^+), it forms a carboxylate ion ($R-COO^-$)
- This anion is stabilized by resonance, as negative charge can be delocalized between the two oxygen atoms.
- This delocalization lowers the energy of carboxylate ion making it more stable thus making loss of proton more favourable.



② Electronegative Oxygen Atoms

- The two oxygen atoms in carboxyl group are highly electronegative
- They pull electron density away from hydrogen in $-OH$ group making it easier for proton to leave & dissociate.
- Now these electronegative oxygen atoms stabilizes the negative charge on carboxylate ion.

- Also the pKa value of carboxylic acids are very less i.e., 4-5 indicating it as a strong acid compare to Alcohols & many other organic acids.

EFFECT OF SUBSTITUENTS ON ACIDITY OF CARBOXYLIC ACIDS

There are mainly two types of substituents that generally shows their effect on acidity of carboxylic acids:

- ① Electron Withdrawing Group
- ② Electron Releasing Group

Effect Of Electron Withdrawing Group

- Electron withdrawing groups increases the acidity of carboxylic acids because EWGs stabilizes the negative charge on the carboxylate ion through Inductive or resonance effect.
- In a carboxylic acid, the electron withdrawing groups pull electron density away from carboxyl group.
- This makes carboxylate ion more stable and thus making carboxylic acid more acidic

Effect Of Electron Releasing Group

- Electron Releasing Groups (ERGs) decreases the acidity of carboxylic acids
- This is because ERGs increases electron density to the carboxyl group, which destabilizes the carboxylate ion by reducing the ability of carboxylate ion to stabilize the -ve charge.

BASICITY OF ALIPHATIC AMINES

- Aliphatic amines are organic compounds that contain an amino group ($-NH_2$) attached to an aliphatic carbon chain.
- It can also be defined as aliphatic derivatives of Ammonia (NH_3) in which 1 or more hydrogen atom of ammonia is replaced by alkyl groups.



Classification of Aliphatic Amines

- Aliphatic Amines are classified as Primary, Secondary or Tertiary depending upon whether 1, 2 or all 3 atoms of hydrogen have been replaced by Alkyl Groups
- ① Primary Aliphatic Amines (NH_2CH_3)
 - ② Secondary Aliphatic Amines ($NH(CH_3)_2$)
 - ③ Tertiary Aliphatic Amines ($N(CH_3)_3$)

Basicity Of Aliphatic Amines

- Aliphatic amines are basic in nature.
- The basicity of aliphatic amines refers to their ability to accept protons (H^+ ions) from acids, which is a measure of their strength as bases.
- Also they have the ability to donate their lone pair of electrons present on nitrogen atom



Factors Influencing basicity of Aliphatic Amines

Several factors influence basicity of aliphatic amines :

① Alkyl Groups

Alkyl Groups attached to the nitrogen atom increase its electron density, enhancing its ability to donate lone pair of electrons & thus increasing basicity.

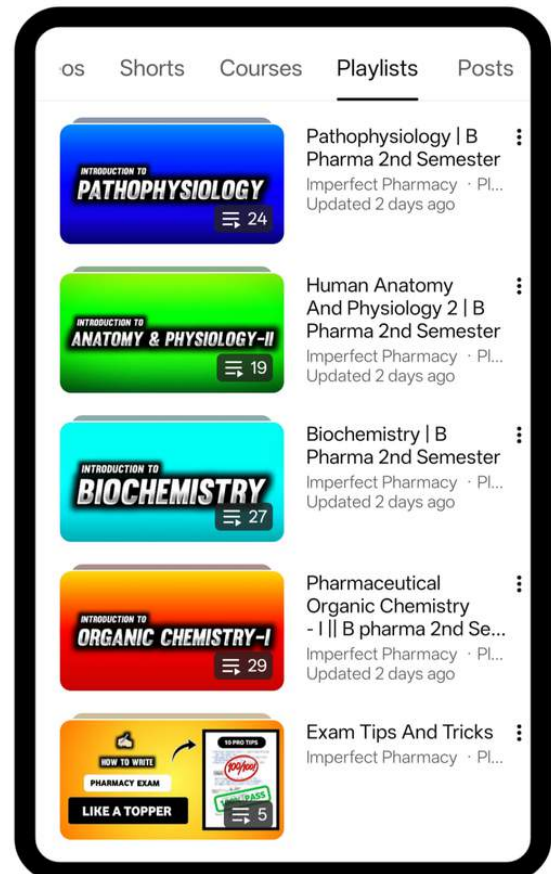
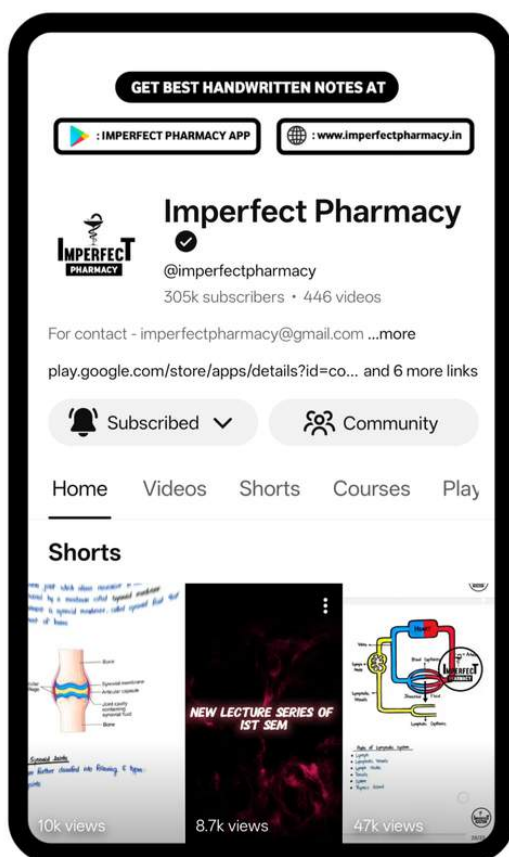
② Steric Effects

In tertiary amines, steric hindrance can reduce the availability of lone pair, potentially decreasing its ability compared to primary & secondary amines.

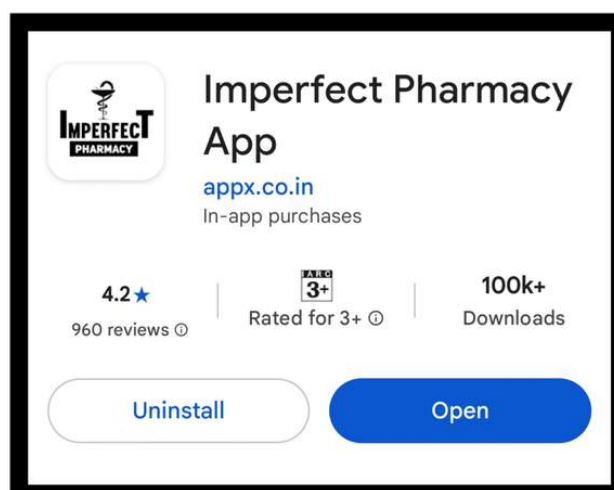
③ Hybridization

In aliphatic amines, there is sp^3 hybridization compared to aromatic amines (sp^2) making stronger base than other amines.

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Order of basicity of Aliphatic Amines

$2^\circ \text{ Amines} > 3^\circ \text{ Amines} > 1^\circ \text{ Amines} > \text{Ammonia}$

- 2° Amines have greater basicity compared to 3° Amines because of steric hindrance effect.

EFFECT OF SUBSTITUENTS ON BASICITY OF ALIPHATIC AMINES

① Effect of Electron Releasing Groups

- Electron Releasing Groups increases the electron density on ~~Aromatic Amines~~ Aliphatic Amines, hence they tends to increases the basicity of aliphatic amines.
- Example : $-\text{CH}_3$, $-\text{OH}$ etc.

② Effect of Electron Withdrawing Groups

- Electron Withdrawing Groups due to their high electronegativity decreases electron density on nitrogen atom, reducing its ability to accept protons & thus decreases basicity.
- Example : $-\text{CH}_3$, $-\text{OH}$ etc.

INDUCTIVE EFFECT

- The partial shift / displacement of electrons from a less electronegative atom towards a more electronegative atom is known as Inductive effect.
- Now this inductive effect is of two types :
 - ① Positive Inductive Effect (+I)
 - ② Negative Inductive Effect (-I)

① +I Effect

- This effect occurs when a substituent or group in a molecule increases electron density to the rest of the molecule.
- Basically this effect is shown by Electron Releasing Groups
- example : Alkyl Groups (Methyl, Ethyl).

② -I Effect

- This effect occurs when a substituents or group in a molecule decreases electron density to the rest of the molecule.
- Basically, this effect is shown by Electron Withdrawing Groups
- example : Halogens (Cl, Br).

QUALITATIVE TEST FOR CARBOXYLIC ACIDS

① Litmus Test

Place a drop of solution of carboxylic acid sample on a blue litmus paper.

If blue litmus turns red, it indicates the presence of acid.

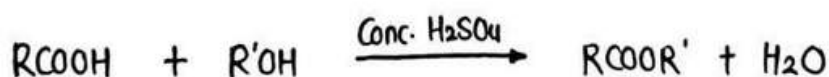
② Sodium Bicarbonate Test

Carboxylic acids react with sodium bicarbonate to produce salt of carboxylic acid along with effervescence of CO_2 .



③ Ester Formation Test

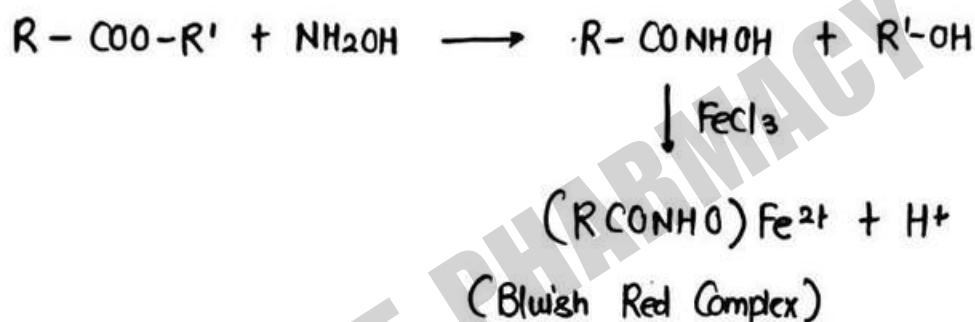
On heating carboxylic acids with an alcohol in presence of small amount of sulphuric acid, a fruity smell of ester is obtained.



QUALITATIVE TEST FOR ESTERS

① Hydroxamic Acid Test

Esters upon reaction with hydroxylamine yields hydroxamic acid, which upon treatment with ferric chloride forms ferric hydroxamate complex with Bluish red/ violet colour.



② Hydrolysis Test

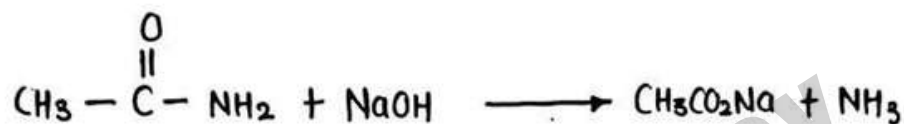
Alkaline hydrolysis of esters converts esters into acid salt and alcohol.



QUALITATIVE TEST FOR AMIDE

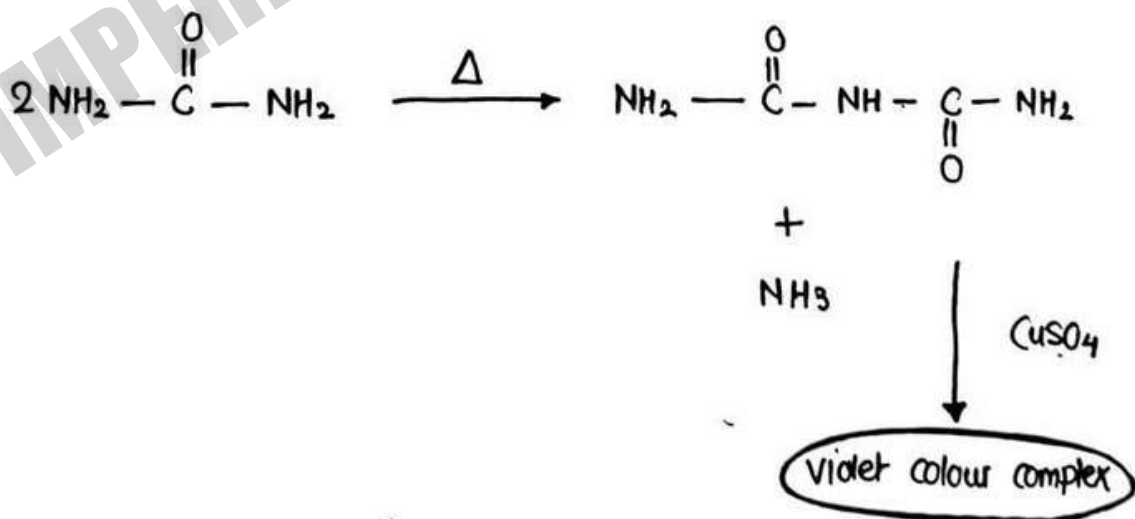
① Alkali Test

Simple primary amide can be decomposed by boiling with Alkali and thereby evolving ammonia

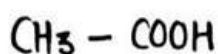


② Biuret Test

When aliphatic diamide is heated at temperature above its melting point, ammonia is evolved, this biuret in alkali medium gives violet colour with a drop of copper sulphate solution



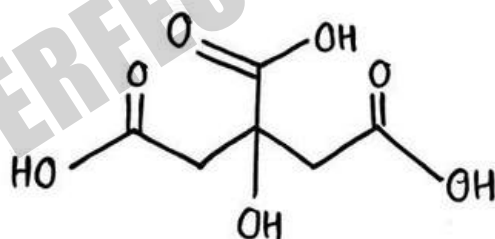
① Acetic Acid



Uses

- It is widely used in food industry
- It serves as precursor for synthesis of various chemicals.
- It is also used as cleansing agent.
- It is used as preservatives.

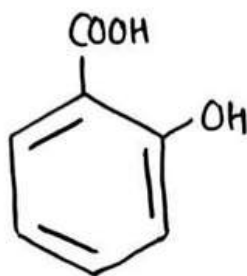
② Citric Acid



Uses

- It is used as flavour enhancer
- It is used as cleansing agent
- It is used in cosmetic industry
- Also used in various medications

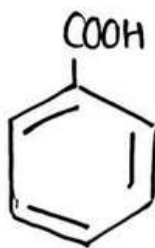
③ Salicylic Acid



Uses

- Precursor of aspirin
- in various cosmetic products
- As plant hormone
- For acne treatment

④ Benzoic Acid



Uses

- As preservatives
- In cosmetics
- As antiseptics

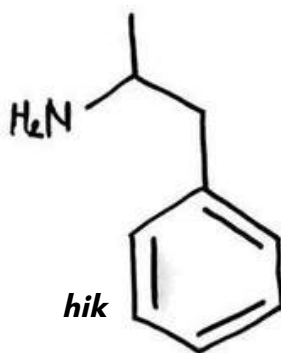
⑤ Ethylene Diamene



Uses

- Formulation of fertilizers
- Used in various pharmaceuticals.
- synthesis of various chemicals.

⑥ Amphetamine



Uses

- Appetite suppressant
- performance enhancer

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