8. ALDEHYDES, KETONES & CARBOXYLIC ACIDS

(R–CHO) R–(C=O)–R' (R–COOH)

STUDY NOTES

1. Aldehydes, Ketones & Carboxylic acids (Carbonyl group):

i) Common name : • Aldehydes, Ketones, Carboxylic acids

ii) IUPAC name : • Alkanols • Alkanones • Alkanoic acids

iii) General Formula : • **Aldehydes:** R-CHO (or) $C_nH_{2n}O$

• **Ketones:** R–(C=O)–R' $R-\overset{\overset{O}{\|}}{C}-R$

• **Carboxylic acids:** R–COOH (or) C_nH_{2n+1} –COOH

iv)Aldehydes Ex : HCHO (Formaldehyde / Methanal), CH_3CHO(Acetaldehyde / Ethanal)

v) Ketones Ex : • CH_3–(C=O)–CH_3 (Acetone/2- Propanone)

vi) Carboxylic acids Ex : HCOOH (Formic acid /Methanoic acid), CH_3COOH(Acetic acid / Ethanoic acid)

I) ALDEHYDES

2. Nature of Carbonyl Group (>C=O):

It consists of **carbon double bonded to oxygen.**

Carbon is **sp^2 hybridised.**

Structure is **trigonal planar.**

CO is highly **polar.**

3. Nomenclature:

(a) Common Names:

Aldehydes → derived from corresponding acids

Ex: HCHO → formaldehyde, CH_3CHO → acetaldehyde

Ketones → named as alkyl groups + ketone

Ex: CH_3COCH_3 → acetone

(b) IUPAC Names:

Aldehydes → suffix **–al**

Ketones → suffix **–one**

Numbering gives lowest position to carbonyl carbon

Ex: Methanal (HCHO), Ethanal(CH_3CHO), Propanal (CH_3CH_2CHO)

4. Preparation of Aldehydes and Ketones:

1) General Methods:

i) **Oxidation of alcohols:** Primary alcohol → aldehyde; Secondary alcohol → ketone

ii) **Dehydrogenation of alcohols:** Passing alcohol vapours over Cu catalyst

iii) **Ozonolysis of Alkenes.**

2) Preparation of Aldehydes:

i) **From acyl chlorides:** Rosenmund reduction

ii) **From nitriles and esters:** Controlled reduction

iii) **From hydrocarbons (Aromatic aldehydes):**

a) **Oxidation of methylbenzene:** Using chromyl chloride (Etard reaction)

b) **Side chain chlorination + hydrolysis**

c) **Gattermann–Koch reaction:** Benzene → benzaldehyde

II) KETONES

5. Preparation of Ketones:

i) **From acyl chlorides** ii) **From nitriles** iii) **From benzene:** Friedel–Crafts acylation

6. Physical Properties:

Boiling points higher than hydrocarbons (due to polarity)

Lower than alcohols (no H-bonding among themselves)

Lower members → soluble in water

7. Chemical Reactions

7.1. Nucleophilic Addition Reactions

i) **Mechanism:** Nucleophile attacks electrophilic carbon of C=O

ii) **Reactivity Order:** Aldehydes > Ketones(due to less steric hindrance and +I effect)

iii) **Important Reactions:**

a) **Addition of HCN:** Forms cyanohydrins

b) **Addition of $NaHSO_3$:** Forms bisulphite compound

c) **Addition of Grignard reagent:** Gives alcohols

d) **Addition of alcohols:** Forms hemiacetals and acetals

e) **Addition of ammonia derivatives:** Forms oximes, hydrazones

7.2. Reduction:

i) **To alcohols:** Aldehyde → primary alcohol; Ketone → secondary alcohol

ii) **To hydrocarbons:** Clemmensen reduction, Wolff–Kishner reduction

7.3. Oxidation:

i) **Tollens' Test:** Silver mirror formation (metallic Ag)

ii) **Fehling's Test:** Red precipitate (Cu_2O)

iii) **Haloform Reaction:** Methyl ketones→ CHX_3

7.4. Reactions due to α-Hydrogen:

Acidity of α- hydrogen: Due to resonance stabilization

i) **Aldol Condensation:** Formation of β-hydroxy aldehyde/ketone

ii) **Cross Aldol Condensation:** Between two different carbonyl compounds

7.5. Other Reactions:

i) **Cannizzaro Reaction:** Aldehydes without α-H undergo disproportionation

ii) **Electrophilic Substitution:** Occurs in aromatic aldehydes/ketones

III) CARBOXYLIC ACIDS

8. Nomenclature: Suffix **–oic acid Ex:** Ethanoic acid (CH_3COOH)

9. Structure of Carboxyl Group (–COOH)

Combination of **C=O and –OH.** Resonance stabilized

10. Preparation of Carboxylic acids:

i) From primary alcohols and aldehydes
ii) From alkylbenzenes
iii) From nitriles and amides
iv) From Grignard reagents
v) From acyl halides and anhydrides
vi) From esters

11. Physical Properties:

• High boiling points (due to **dimer formation**)
• Lower acids soluble in water

12. Chemical Reactions:

12.1 Cleavage of O–H Bond:

• Shows acidic nature
• Forms salts

12.2 Cleavage of C–OH Bond:

i) Formation of anhydride
ii) Esterification: Acid + alcohol → ester
iii) Reaction with PCl_5 / $SOCl_2$: Forms acid chlorides
iii) Reaction with ammonia: Forms amides

12.3 Reactions of –COOH Group:

i) Reduction: To primary alcohol
ii) Decarboxylation: Loss of CO_2.

12.4 Substitution in Hydrocarbon Part:

i) Halogenation: α-hydrogen substitution
ii)Ring substitution: In aromatic acids

13. Uses of Aldehydes and Ketones:

• Formaldehyde → preservative
• Acetone → solvent
• **Vanillin:** Artificial vanilla flavor
• Benzaldehyde → perfumes
• **Benzaldehyde:** Almond fragrance (perfumes & flavoring)

14. Uses of Carboxylic Acids:

• Formic acid → preservatives
• Acetic acid → vinegar
• Benzoic acid → food preservative

Quick Revision Points

- **Aldehyde→R–CHO**
- **Ketone→ R–CO–R**
- **Acid →R–COOH**
- C = O → Polar
- Reaction → Nucleophilic addition
- Reactivity → Aldehyde > Ketone
- Oxidation → Aldehyde→ Acid
- Acid → Strong, H-bonded
- Carbonyl carbon is **electrophilic**
- Aldehydes are **more reactive than ketones**
- α-hydrogen → responsible for **aldol reactions**
- Carboxylic acids are **most acidic** among these compounds
- **Tests:** Tollens→ silver mirror Fehling→ red ppt Haloform → yellow ppt