Short Notes for CUET UG Chemistry

Unit VIII: Aldehydes, Ketones and Carboxylic Acids

1. Introduction to Carbonyl Compounds

In organic chemistry, compounds containing a carbon-oxygen double bond ($> C = O$) are called carbonyl compounds. They are widely distributed in nature and are crucial in biological processes and industrial applications.

- **Aldehydes:** The carbonyl group is bonded to at least one hydrogen atom ($-CHO$).
- **Ketones:** The carbonyl group is bonded to two carbon atoms ($> C = O$).
- **Carboxylic Acids:** The carbonyl group is bonded to a hydroxyl group ($-COOH$).
- **Derivatives:** Acid chlorides ($-COCl$), Amides ($-CONH_2$), Esters ($-COOR$), and Anhydrides ($-CO - O - CO-$).

2. Nomenclature

- **Aldehydes:** The IUPAC name is derived by replacing the terminal 'e' of the corresponding alkane with **-al** (e.g., CH_3CHO is Ethanal). The aldehyde carbon is always numbered as carbon-1.
- **Ketones:** The IUPAC name is derived by replacing the terminal 'e' of the alkane with **-one** (e.g., CH_3COCH_3 is Propanone). Numbering begins from the end nearer to the carbonyl group.
- **Carboxylic Acids:** The IUPAC name is derived by replacing the terminal 'e' of the alkane with **-oic acid** (e.g., CH_3COOH is Ethanoic acid). The carboxyl carbon is always numbered as carbon-1.

3. Structure of the Carbonyl Group

The carbonyl carbon atom is sp^2 **hybridized** and forms three sigma (σ) bonds.

- The fourth valence electron of carbon remains in an unhybridized p-orbital, which overlaps sideways with a p-orbital of oxygen to form a pi (π) bond.
- The geometry around the carbonyl carbon is **trigonal planar** with bond angles of approximately 120°.
- **Polarity:** Oxygen is more electronegative than carbon, making the carbon-oxygen double bond highly polarized. The carbon acts as an electrophile (Lewis acid), and the oxygen acts as a nucleophile (Lewis base).

4. Preparation of Aldehydes & Ketones

A. Common Methods (For both Aldehydes and Ketones)

1. **Oxidation of Alcohols:** 1° alcohols yield aldehydes (using PCC); 2° alcohols yield ketones (using CrO_3).
2. **Dehydrogenation of Alcohols:** Vapors of 1° or 2° alcohols passed over heavy metal catalysts (Cu or Ag) at 573 K.
3. **Ozonolysis of Alkenes:** Alkenes react with ozone followed by cleavage with zinc dust and water.
4. **Hydration of Alkynes:** Addition of water to ethyne in the presence of H_2SO_4 and $HgSO_4$ gives ethanal. Other alkynes give ketones.

B. Specific Methods for Aldehydes

1. **Rosenmund Reduction:** Hydrogenation of acyl chlorides over a catalyst like palladium on barium sulfate ($Pd/BaSO_4$), poisoned with sulfur or quinoline.
   $$R - COCl + H_2 \xrightarrow{Pd/BaSO_4} R - CHO + HCl$$
2. **Stephen Reaction:** Nitriles are reduced to corresponding imines with stannous chloride ($SnCl_2$) and HCl, which on hydrolysis give aldehydes.
   $$R - CN + SnCl_2 + HCl \rightarrow R - CH = NH$$
3. **Etard Reaction:** Chromyl chloride (CrO_2Cl_2) oxidizes the methyl group of

toluene to a chromium complex, which on hydrolysis yields benzaldehyde.

4. **Gatterman-Koch Reaction:** Benzene reacts with carbon monoxide and hydrogen chloride in the presence of anhydrous $AlCl_3$ or $CuCl$ to yield benzaldehyde.

C. Specific Methods for Ketones

1. **From Acyl Chlorides:** Treatment of acyl chlorides with dialkylcadmium (prepared from Grignard reagents).
   $$2R - Mg - X + CdCl_2 \rightarrow R_2Cd + 2Mg(X)$$
   $$2R' - COCl + R_2Cd \rightarrow 2R' - CO - R + C$$
2. **From Nitriles:** Treatment of a nitrile with a Grignard reagent followed by hydrolysis.
3. **Friedel-Crafts Acylation:** Benzene reacts with an acid chloride in the presence of anhydrous $AlCl_3$ to form a ketone.

5. Physical Properties of Aldehydes & Ketones

- **Boiling Points:** Higher than hydrocarbons and ethers of comparable molecular mass due to weak molecular association arising from dipole-dipole interactions. However, they are **lower than alcohols** of similar mass because they lack intermolecular hydrogen bonding.
- **Solubility:** Lower members (methanal, ethanal, propanone) are miscible with water in all proportions because they can form hydrogen bonds with water molecules. Solubility decreases rapidly as the alkyl chain length increases.

6. Chemical Properties of Aldehydes & Ketones

Aldehydes are generally **more reactive** than ketones towards nucleophilic addition due to less steric hindrance and less +I effect from alkyl groups.

1. **Nucleophilic Addition Reactions:**
   - **Addition of HCN:** Yields cyanohydrins.
   - **Addition of $NaHSO_3$:** Yields bisulfite addition compounds (useful for purification/separation).
   - **Addition of Grignard Reagents:** Yields alcohols.
   - **Addition of Alcohols:** Aldehydes yield hemiacetals and acetals; ketones yield ketals (using ethylene glycol).
   - **Addition of Ammonia Derivatives:** React with $NH_2 - Z$ to form $> C = N - Z$ derivatives (e.g., oximes, hydrazones, 2,4-DNP derivatives).
2. **Reduction:**
   - **To Alcohols:** Using $LiAlH_4$, $NaBH_4$, or catalytic hydrogenation.
   - **To Hydrocarbons (Clemmensen Reduction):** Using zinc amalgam ($Zn - Hg$) and concentrated HCl.
   - **To Hydrocarbons (Wolff-Kishner Reduction):** Using hydrazine (NH_2NH_2) followed by heating with KOH/ethylene glycol.
3. **Oxidation:**

  - Aldehydes are easily oxidized to carboxylic acids using mild agents.
  - **Tollens' Test:** Aldehydes reduce Tollens' reagent (ammoniacal silver nitrate) to a "silver mirror" (Ag). Ketones do not respond.
  - **Fehling's Test:** Aldehydes reduce Fehling's solution to a red precipitate of Cu_2O. Ketones do not respond.
  - **Haloform Reaction:** Methyl ketones (CH_3-CO-R) react with sodium hypohalite ($NaOX$) to yield a haloform (CHX_3) and a carboxylic acid salt. (Iodoform test gives a yellow precipitate of CHI_3).

4. **Reactions due to α-Hydrogen:** (Carbonyl compounds with at least one α-hydrogen are acidic).
   - **Aldol Condensation:** Two molecules of an aldehyde or ketone with α-hydrogen react in the presence of dilute alkali to form β-hydroxy aldehydes (aldols) or β-hydroxy ketones (ketols), which upon heating lose water to form α,β-unsaturated carbonyls.
   - **Cross-Aldol Condensation:** Carried out between two different aldehydes/ketones.
5. **Cannizzaro Reaction:** Aldehydes **lacking** an α-hydrogen (e.g., $HCHO$, C_6H_5CHO) undergo self-oxidation and reduction (disproportionation) upon heating with concentrated alkali, yielding an alcohol and a carboxylic acid salt.

7. Structure & Preparation of Carboxylic Acids

Structure of Carboxyl Group

The carboxyl carbon is sp^2 hybridized. The carboxyl group is stabilized by resonance, and the bonds are planar. The carbonyl oxygen has a partial negative charge, while the hydroxyl oxygen shares its lone pair with the carbonyl carbon.

Preparation of Carboxylic Acids

1. **From 1° Alcohols & Aldehydes:** Oxidation with alkaline $KMnO_4$ or acidified $K_2Cr_2O_7$.
2. **From Alkylbenzenes:** Vigorous oxidation of alkylbenzenes with chromic acid or alkaline $KMnO_4$ yields benzoic acid (regardless of the alkyl chain length).
3. **From Nitriles and Amides:** Hydrolysis catalyzed by H^+ or OH^-.
4. **From Grignard Reagents:** Reaction with solid carbon dioxide (dry ice) followed by acid hydrolysis.

$$R-MgX+CO_2 \rightarrow R-COOMgX \xrightarrow{H_3O^+} R$$

5. **From Acyl Halides and Anhydrides:** Hydrolysis with water.
6. **From Esters:** Acidic or basic hydrolysis (saponification).

8. Physical Properties of Carboxylic Acids

- **Boiling Points:** Higher than aldehydes, ketones, and even alcohols of comparable molecular masses. This is due to more extensive intermolecular hydrogen bonding. Most carboxylic acids exist as **dimers** in the vapor phase or in aprotic solvents.

- **Solubility:** Simple aliphatic carboxylic acids (up to 4 carbon atoms) are miscible in water due to hydrogen bonding. Solubility decreases with increasing alkyl chain length.

9. Chemical Properties of Carboxylic Acids

1. **Reactions Involving Cleavage of O-H Bond (Acidity):**
    - Turn blue litmus red. React with metals (Na, K), alkalies ($NaOH$), and weak bases like carbonates/bicarbonates ($NaHCO_3$) to evolve CO_2 (a distinguishing test for the $-COOH$ group).
    - **Effect of Substituents:** Electron-withdrawing groups (EWG) stabilize the carboxylate anion through the -I effect, increasing acidity (e.g., $FCH_2COOH > ClCH_2COOH > Cl$). Electron-donating groups (EDG) destabilize the anion, decreasing acidity.
2. **Reactions Involving Cleavage of C-OH Bond:**
    - **Formation of Anhydrides:** Heating with mineral acids (H_2SO_4) or P_2O_5.
    - **Esterification:** Heating with alcohols or phenols in the presence of concentrated H_2SO_4. $R-COOH + R'-OH \rightleftharpoons R-COC$
    - **Reactions with PCl_5, PCl_3, and $SOCl_2$:** Replaces $-OH$ with $-Cl$ to form acyl chlorides. $SOCl_2$ is preferred because byproducts (SO_2 and HCl) are gases.
    - **Reaction with Ammonia:** Yields amides upon strong heating.
3. **Reactions Involving Cleavage of -COOH Group:**
    - **Reduction:** Reduced to primary alcohols using $LiAlH_4$ or B_2H_6. (Note: $NaBH_4$ does not reduce the carboxyl group).
    - **Decarboxylation:** Sodium salts of carboxylic acids heated with soda lime ($NaOH$ and CaO in 3:1 ratio) yield alkanes containing one carbon less than the acid.
4. **Substitution Reactions in the Hydrocarbon Part:**
    - **Hell-Volhard-Zelinsky (HVZ) Reaction:** Carboxylic acids with an α-hydrogen are halogenated at the α-position by reaction with chlorine or bromine in the presence of small amounts of red phosphorus.
5. **Ring Substitution in Aromatic Acids:**
    - The $-COOH$ group is a deactivating and **meta-directing** group. They undergo electrophilic substitution (nitration, halogenation) but do not undergo Friedel-Crafts reaction because the carboxyl group acts as an acid and reacts with the Lewis acid catalyst ($AlCl_3$).

10. Uses of Aldehydes, Ketones, and Carboxylic Acids

- **Methanal (Formaldehyde):** A 40% aqueous solution (formalin) is used to preserve biological specimens and to prepare Bakelite.
- **Ethanal (Acetaldehyde):** Used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, and polymers.
- **Propanone (Acetone) & Butanone:** Common industrial solvents.

- **Benzaldehyde:** Used in perfumery and dye industries.
- **Methanoic Acid (Formic Acid):** Used in rubber, textile, dyeing, and leather industries.
- **Ethanoic Acid (Acetic Acid):** Used as a solvent and as vinegar in the food industry.
- **Hexanedioic Acid (Adipic Acid):** Used in the manufacture of Nylon-6,6.
- **Esters of Benzoic Acid:** Used in perfumery. Sodium benzoate is widely used as a food preservative.