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CHAPTER NOTES

Aldehydes, Ketones and Carboxylic Acids Class 12 Notes — CBSE Chemistry Chapter 12

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Aldehydes, Ketones and Carboxylic Acids Class 12 Notes — CBSE Chemistry Chapter 12

Chapter 12 — **Aldehydes, Ketones and Carboxylic Acids** — is one of the most reaction-rich and important chapters for **8-10 marks** in Board exams. This chapter covers the carbonyl group (C=O), its reactions, and the chemistry of carboxylic acids. Focus on nucleophilic addition, named reactions (Aldol, Cannizzaro, Clemmensen), and distinction tests.

Key Concepts

Aldehydes and Ketones

Preparation

1. Oxidation of Alcohols:

1° alcohol + PCC → Aldehyde (mild, stops at aldehyde)

1° alcohol + $K_2Cr_2O_7/H^+$ → Carboxylic acid (strong, goes all the way)

2° alcohol + $K_2Cr_2O_7/H^+$ → Ketone

2. Ozonolysis of Alkenes: $R_2C{=}CR_2 + O_3$ → ozonide →(Zn/H_2O) aldehydes + ketones

3. Rosenmund Reduction: RCOCl + H_2/Pd-$BaSO_4$ → RCHO + HCl (acyl chloride → aldehyde)

4. Stephen Reduction: RCN + $SnCl_2$/HCl → RCHO (nitrile → aldehyde)

5. Gattermann-Koch: C_6H_6 + CO + HCl →($AlCl_3$) C_6H_5CHO (benzaldehyde)

6. Friedel-Crafts Acylation: C_6H_6 + RCOCl →($AlCl_3$) C_6H_5COR (aromatic ketone)

Nucleophilic Addition Reactions

The C=O group is polar (C^δ^+=O^δ^-). Nucleophiles attack the electrophilic carbon.

Nucleophile	Reagent	Product
HCN	HCN/KCN	Cyanohydrin (R–CH(OH)CN)
$NaHSO_3$	Sodium bisulphite	Bisulphite adduct (used for purification)
NH_2OH	Hydroxylamine	Oxime (C=NOH)
$NH_2–NH_2$	Hydrazine	Hydrazone ($C=N–NH_2$)
$C_6H_5NH–NH_2$	Phenylhydrazine	Phenylhydrazone
2,4-DNP	2,4-dinitrophenylhydrazine	2,4-DNP derivative (yellow/orange ppt — TEST!)
$NH_2–CO–NH–NH_2$	Semicarbazide	Semicarbazone

2,4-DNP Test: Both aldehydes AND ketones give yellow/orange precipitate with 2,4-dinitrophenylhydrazine. This confirms the presence of C=O group.

Reactivity order for nucleophilic addition:
$HCHO > CH_3CHO > C_2H_5CHO > (CH_3)_2CO$
(More alkyl groups → more steric hindrance + electron donation → less electrophilic carbon → slower)

Oxidation Reactions

Tollen's Test (Silver Mirror Test): $RCHO + 2[Ag(NH_3)_2]^+ + 2OH^- \rightarrow RCOO^- + 2Ag\downarrow + 4NH_3 + H_2O$
(Silver mirror deposited — works for aldehydes ONLY, not ketones)

Fehling's Test: $RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + Cu_2O\downarrow$(red ppt) $+ 3H_2O$
(Works for aliphatic aldehydes; aromatic aldehydes don't respond)

Reduction Reactions

To Alcohol: R–CHO + $NaBH_4$ or $LiAlH_4$ → $R–CH_2OH$
Clemmensen Reduction: R–CO–R' + Zn-Hg/conc. HCl → $R–CH_2–R'$ (C=O → CH_2, acidic)
Wolff-Kishner Reduction: R–CO–R' + NH_2NH_2/KOH/ethylene glycol → $R–CH_2–R'$ (C=O → CH_2, basic)

Important Named Reactions

Aldol Condensation: $2CH_3CHO \rightarrow$(dilute NaOH) $CH_3CH(OH)CH_2CHO$ (β-hydroxy aldehyde)

On heating: $\rightarrow CH_3CH{=}CHCHO + H_2O$ (α,β-unsaturated aldehyde)

Requires: α-hydrogen on the aldehyde/ketone

Cross Aldol: $HCHO + CH_3CHO \rightarrow HOCH_2CH_2CHO$

Cannizzaro Reaction: $2HCHO \rightarrow$(conc. NaOH) $HCOO^-Na^+ + CH_3OH$

(Self-oxidation-reduction — one molecule oxidised to acid, one reduced to alcohol)

Requires: NO α-hydrogen ($HCHO$, C_6H_5CHO, $(CH_3)_3CCHO$)

Key Rule: If α-H present → Aldol; If no α-H → Cannizzaro

Haloform Reaction: $CH_3CO{-}R + 3X_2 + 4NaOH \rightarrow RCOONa + CHX_3$

With I_2/NaOH: gives yellow precipitate of CHI_3 (iodoform) — **Iodoform Test**

Works for: CH_3CHO, methyl ketones (CH_3COR), ethanol, 2° alcohols ($CH_3CHOH{-}R$)

Carboxylic Acids (R–COOH)

Preparation

1. Oxidation: 1° alcohol/aldehyde + $KMnO_4$ or $K_2Cr_2O_7/H^+ \rightarrow RCOOH$

2. From Grignard: $RMgX + CO_2 \rightarrow$(dry ether) $RCOOMgX \rightarrow$(H_3O^+) $RCOOH$

3. Hydrolysis of Nitriles: $RCN + H_3O^+ \rightarrow RCOOH + NH_4^+$

4. Hydrolysis of Esters: RCOOR' + NaOH → RCOONa + R'OH (saponification)

Acidity of Carboxylic Acids

Carboxylic acids > Phenols > Alcohols > Water (in acidity)

Reason: $RCOO^-$ is stabilised by **resonance** — negative charge delocalised over two equivalent oxygen atoms. This makes it exceptionally stable compared to alkoxide or phenoxide.

Test: Carboxylic acids react with $NaHCO_3 \rightarrow CO_2\uparrow$ (effervescence)

Phenols do NOT give this test!

Effect of Substituents on Acidity

- **Electron-withdrawing groups (–Cl, $–NO_2$, $–CF_3$):** Increase acidity (stabilise COO^-)
- **Electron-donating groups ($–CH_3$, $–OCH_3$, $–NH_2$):** Decrease acidity (destabilise COO^-)
- $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$ (more Cl → more acidic)

Reactions of Carboxylic Acids

With $SOCl_2$: $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$ (acyl chloride)
With NH_3: $RCOOH + NH_3 \rightarrow RCOONH_4 \rightarrow(\Delta)\ RCONH_2$ (amide)
Esterification: $RCOOH + R'OH \rightarrow(H_2SO_4)\ RCOOR' + H_2O$
Decarboxylation: $RCOONa + NaOH \rightarrow(CaO, \Delta)\ RH + Na_2CO_3$ (loses CO_2)
Hell-Volhard-Zelinsky (HVZ): $RCOOH + Br_2/P \rightarrow$ α-bromoacid (halogenation at α-carbon)

Important Definitions

Term	Definition
Nucleophilic Addition	Addition of a nucleophile to the electrophilic C of C=O
Aldol Condensation	Self-condensation of aldehydes/ketones with α-H in dilute base
Cannizzaro Reaction	Self-redox of aldehydes without α-H in conc. NaOH
Iodoform Test	Yellow ppt of CHI_3 with I_2/NaOH — tests for $CH_3CO–$ or $CH_3CHOH–$
Tollen's Test	Silver mirror test for aldehydes using ammoniacal $AgNO_3$
Saponification	Alkaline hydrolysis of ester to give soap (sodium carboxylate)

Solved Examples — NCERT Based

Example 1: Distinguishing Aldehyde from Ketone

Q: How do you distinguish between ethanal and propanone?

Solution:

Tollen's test: Ethanal (CH_3CHO) gives silver mirror. Propanone (CH_3COCH_3) does not.

Fehling's test: Ethanal gives red precipitate of Cu_2O. Propanone does not.

Iodoform test: Both give positive iodoform test (both have CH_3CO-). So this test cannot distinguish them.

Example 2: Aldol Condensation

Q: Write the products of aldol condensation of acetaldehyde (CH_3CHO).

Solution:

$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal — aldol)

On heating: $CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$ (crotonaldehyde)

Example 3: Acidity Order

Q: Arrange in increasing acidity: CH_3COOH, $HCOOH$, $ClCH_2COOH$, FCH_2COOH

Solution:

–I effect: F > Cl (F is more electronegative). HCOOH has no alkyl group → more acidic than CH_3COOH.

Order: **$CH_3COOH < HCOOH < ClCH_2COOH < FCH_2COOH$**

Example 4: Identifying Reactions

Q: Which reaction will formaldehyde (HCHO) undergo: Aldol or Cannizzaro? Write the products.

Solution:

HCHO has **no α-hydrogen** → undergoes **Cannizzaro reaction**.

2HCHO + conc. NaOH → HCOONa (sodium formate) + CH_3OH (methanol)

One molecule is oxidised to formate, the other is reduced to methanol.

Important Questions for Board Exams

1 Mark Questions

1. What is the reagent for Tollen's test?
2. Which compound gives both Aldol and Cannizzaro? (None — they're mutually exclusive!)
3. Name the product when acetic acid reacts with $SOCl_2$.
4. Why is HCOOH stronger acid than CH_3COOH?

2 Mark Questions

1. Explain why aldehydes are more reactive than ketones towards nucleophilic addition.
2. Write the mechanism of Cannizzaro reaction of formaldehyde.
3. Give the iodoform test. What structural feature does it detect?
4. How do you convert: (a) benzaldehyde → benzoic acid (b) acetone → 2-propanol?

3 Mark Questions

1. What is aldol condensation? Give its mechanism. Can ketones undergo aldol condensation?
2. Distinguish between: (a) ethanal and propanal (b) acetaldehyde and benzaldehyde (c) pentan-2-one and pentan-3-one.
3. Compare the acidity of acetic acid, formic acid, chloroacetic acid and phenol with reasons.

5 Mark Questions

1. Discuss the nucleophilic addition reactions of aldehydes and ketones. Why are aldehydes more reactive? Explain with 5 reactions.
2. What are carboxylic acids? Discuss their preparation (any 3 methods), acidic character, and important reactions (esterification, $SOCl_2$, HVZ).

Quick Revision Points

- Nucleophilic addition: HCHO > other aldehydes > ketones (steric + electronic)
- Tollen's test: Ag mirror (aldehyde only); Fehling's: Cu_2O red ppt (aliphatic aldehyde only)
- 2,4-DNP test: confirms C=O group (both aldehyde and ketone)
- Iodoform: CH_3CHO, CH_3COR, CH_3CHOH-R give yellow CHI_3
- α-H present → Aldol; no α-H → Cannizzaro
- Clemmensen: Zn-Hg/HCl (acidic) | Wolff-Kishner: NH_2NH_2/KOH (basic) — both reduce C=O to CH_2
- Acidity: RCOOH > PhOH > H_2O > ROH

- EWG increases acidity (–Cl, –NO_2), EDG decreases (–CH_3)
- $NaHCO_3$ test: carboxylic acids give CO_2, phenols don't
- HVZ: α-halogenation of carboxylic acids using Br_2/P

← Previous: Alcohols, Phenols and Ethers **Next: Amines →**