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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:

$1^\circ \text{ alcohol} + \text{PCC} \rightarrow \text{Aldehyde (mild, stops at aldehyde)}$

$1^\circ \text{ alcohol} + \text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+ \rightarrow \text{Carboxylic acid (strong, goes all the way)}$

$2^\circ \text{ alcohol} + \text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+ \rightarrow \text{Ketone}$

**2. Ozonolysis of Alkenes:**  $\text{R}_2\text{C}=\text{CR}_2 + \text{O}_3 \rightarrow \text{ozonide} \xrightarrow{(\text{Zn}/\text{H}_2\text{O})} \text{aldehydes} + \text{ketones}$

**3. Rosenmund Reduction:**  $\text{RCOCl} + \text{H}_2/\text{Pd-BaSO}_4 \rightarrow \text{RCHO} + \text{HCl}$  (acyl chloride  $\rightarrow$  aldehyde)

**4. Stephen Reduction:**  $\text{RCN} + \text{SnCl}_2/\text{HCl} \rightarrow \text{RCHO}$  (nitrile  $\rightarrow$  aldehyde)

**5. Gattermann-Koch:**  $\text{C}_6\text{H}_6 + \text{CO} + \text{HCl} \xrightarrow{(\text{AlCl}_3)} \text{C}_6\text{H}_5\text{CHO}$  (benzaldehyde)

**6. Friedel-Crafts Acylation:**  $\text{C}_6\text{H}_6 + \text{RCOCl} \xrightarrow{(\text{AlCl}_3)} \text{C}_6\text{H}_5\text{COR}$  (aromatic ketone)

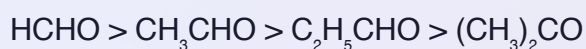
#### Nucleophilic Addition Reactions

The  $C=O$  group is polar ( $C^{\delta+}=O^{\delta-}$ ). 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:

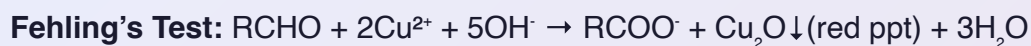


(More alkyl groups  $\rightarrow$  more steric hindrance + electron donation  $\rightarrow$  less electrophilic carbon  $\rightarrow$  slower)

## Oxidation Reactions

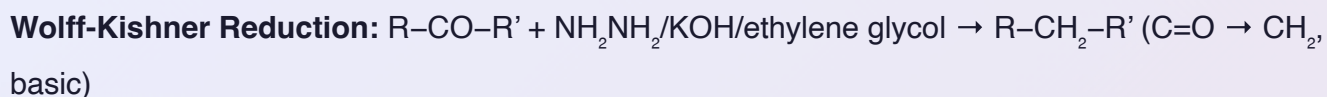
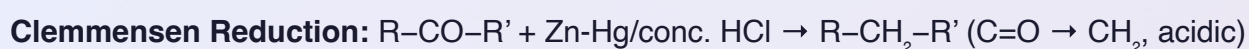
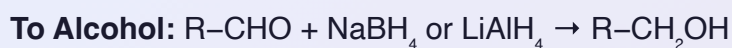


(Silver mirror deposited — works for aldehydes ONLY, not ketones)



(Works for aliphatic aldehydes; aromatic aldehydes don't respond)

## Reduction Reactions



## Important Named Reactions

**Aldol Condensation:**  $2\text{CH}_3\text{CHO} \rightarrow (\text{dilute NaOH}) \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$  ( $\beta$ -hydroxy aldehyde)

On heating:  $\rightarrow \text{CH}_3\text{CH}=\text{CHCHO} + \text{H}_2\text{O}$  ( $\alpha,\beta$ -unsaturated aldehyde)

Requires:  $\alpha$ -hydrogen on the aldehyde/ketone

**Cross Aldol:**  $\text{HCHO} + \text{CH}_3\text{CHO} \rightarrow \text{HOCH}_2\text{CH}_2\text{CHO}$

**Cannizzaro Reaction:**  $2\text{HCHO} \rightarrow (\text{conc. NaOH}) \text{HCOO}^-\text{Na}^+ + \text{CH}_3\text{OH}$

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

Requires: NO  $\alpha$ -hydrogen ( $\text{HCHO}$ ,  $\text{C}_6\text{H}_5\text{CHO}$ ,  $(\text{CH}_3)_3\text{CCHO}$ )

**Key Rule:** If  $\alpha$ -H present  $\rightarrow$  Aldol; If no  $\alpha$ -H  $\rightarrow$  Cannizzaro

**Haloform Reaction:**  $\text{CH}_3\text{CO-R} + 3\text{X}_2 + 4\text{NaOH} \rightarrow \text{RCOONa} + \text{CHX}_3$

With  $\text{I}_2/\text{NaOH}$ : gives yellow precipitate of  $\text{CHI}_3$  (iodoform) — **Iodoform Test**

Works for:  $\text{CH}_3\text{CHO}$ , methyl ketones ( $\text{CH}_3\text{COR}$ ), ethanol,  $2^\circ$  alcohols ( $\text{CH}_3\text{CHOH-R}$ )

## Carboxylic Acids ( $\text{R-COOH}$ )

### Preparation

1. **Oxidation:**  $1^\circ$  alcohol/aldehyde +  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+ \rightarrow \text{RCOOH}$

2. **From Grignard:**  $\text{RMgX} + \text{CO}_2 \rightarrow (\text{dry ether}) \text{RCOOMgX} \rightarrow (\text{H}_3\text{O}^+) \text{RCOOH}$

3. **Hydrolysis of Nitriles:**  $\text{RCN} + \text{H}_3\text{O}^+ \rightarrow \text{RCOOH} + \text{NH}_4^+$

4. **Hydrolysis of Esters:**  $\text{RCOOR}' + \text{NaOH} \rightarrow \text{RCOONa} + \text{R}'\text{OH}$  (saponification)

### Acidity of Carboxylic Acids

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

Reason:  $\text{RCOO}^-$  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  $\text{NaHCO}_3 \rightarrow \text{CO}_2 \uparrow$  (effervescence)

Phenols do NOT give this test!

## Effect of Substituents on Acidity

- **Electron-withdrawing groups** ( $-\text{Cl}$ ,  $-\text{NO}_2$ ,  $-\text{CF}_3$ ): Increase acidity (stabilise  $\text{COO}^-$ )
- **Electron-donating groups** ( $-\text{CH}_3$ ,  $-\text{OCH}_3$ ,  $-\text{NH}_2$ ): Decrease acidity (destabilise  $\text{COO}^-$ )
- $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$  (more Cl  $\rightarrow$  more acidic)

## Reactions of Carboxylic Acids

**With  $\text{SOCl}_2$ :**  $\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$  (acyl chloride)

**With  $\text{NH}_3$ :**  $\text{RCOOH} + \text{NH}_3 \rightarrow \text{RCOONH}_4 \xrightarrow{(\Delta)} \text{RCONH}_2$  (amide)

**Esterification:**  $\text{RCOOH} + \text{R}'\text{OH} \xrightarrow{(\text{H}_2\text{SO}_4)} \text{RCOOR}' + \text{H}_2\text{O}$

**Decarboxylation:**  $\text{RCOONa} + \text{NaOH} \xrightarrow{(\text{CaO}, \Delta)} \text{RH} + \text{Na}_2\text{CO}_3$  (loses  $\text{CO}_2$ )

**Hell-Volhard-Zelinsky (HVZ):**  $\text{RCOOH} + \text{Br}_2/\text{P} \rightarrow \alpha\text{-bromoacid}$  (halogenation at  $\alpha$ -carbon)

## Important Definitions

| Term                  | Definition                                                                                                                  |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------|
| Nucleophilic Addition | Addition of a nucleophile to the electrophilic C of $\text{C}=\text{O}$                                                     |
| Aldol Condensation    | Self-condensation of aldehydes/ketones with $\alpha\text{-H}$ in dilute base                                                |
| Cannizzaro Reaction   | Self-redox of aldehydes without $\alpha\text{-H}$ in conc. $\text{NaOH}$                                                    |
| Iodoform Test         | Yellow ppt of $\text{CHI}_3$ with $\text{I}_2/\text{NaOH}$ — tests for $\text{CH}_3\text{CO}-$ or $\text{CH}_3\text{CHOH}-$ |
| Tollen's Test         | Silver mirror test for aldehydes using ammoniacal $\text{AgNO}_3$                                                           |
| 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 ( $\text{CH}_3\text{CHO}$ ) gives silver mirror. Propanone ( $\text{CH}_3\text{COCH}_3$ ) does not.

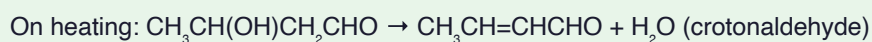
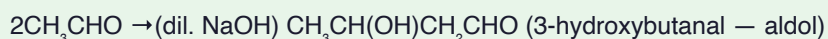
**Fehling's test:** Ethanal gives red precipitate of  $\text{Cu}_2\text{O}$ . Propanone does not.

**Iodoform test:** Both give positive iodoform test (both have  $\text{CH}_3\text{CO}-$ ). So this test cannot distinguish them.

## Example 2: Aldol Condensation

**Q:** Write the products of aldol condensation of acetaldehyde ( $\text{CH}_3\text{CHO}$ ).

**Solution:**



## Example 3: Acidity Order

**Q:** Arrange in increasing acidity:  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$ ,  $\text{ClCH}_2\text{COOH}$ ,  $\text{FCH}_2\text{COOH}$

**Solution:**

–I effect:  $\text{F} > \text{Cl}$  (F is more electronegative).  $\text{HCOOH}$  has no alkyl group  $\rightarrow$  more acidic than  $\text{CH}_3\text{COOH}$ .

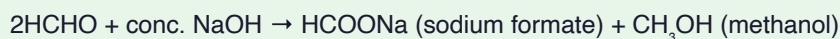
Order:  $\text{CH}_3\text{COOH} < \text{HCOOH} < \text{ClCH}_2\text{COOH} < \text{FCH}_2\text{COOH}$

## Example 4: Identifying Reactions

**Q:** Which reaction will formaldehyde ( $\text{HCHO}$ ) undergo: Aldol or Cannizzaro? Write the products.

**Solution:**

$\text{HCHO}$  has **no  $\alpha$ -hydrogen**  $\rightarrow$  undergoes **Cannizzaro reaction**.



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  $\text{SOCl}_2$ .
4. Why is  $\text{HCOOH}$  stronger acid than  $\text{CH}_3\text{COOH}$ ?

## 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  $\rightarrow$  benzoic acid (b) acetone  $\rightarrow$  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,  $\text{SOCl}_2$ , HVZ).

## Quick Revision Points

- Nucleophilic addition:  $\text{HCHO} > \text{other aldehydes} > \text{ketones}$  (steric + electronic)
- Tollen's test: Ag mirror (aldehyde only); Fehling's:  $\text{Cu}_2\text{O}$  red ppt (aliphatic aldehyde only)
- 2,4-DNP test: confirms  $\text{C=O}$  group (both aldehyde and ketone)
- Iodoform:  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COR}$ ,  $\text{CH}_3\text{CHOH-R}$  give yellow  $\text{CHI}_3$
- $\alpha\text{-H}$  present  $\rightarrow$  Aldol; no  $\alpha\text{-H}$   $\rightarrow$  Cannizzaro
- Clemmensen:  $\text{Zn-Hg/HCl}$  (acidic) | Wolff-Kishner:  $\text{NH}_2\text{NH}_2/\text{KOH}$  (basic) — both reduce  $\text{C=O}$  to  $\text{CH}_2$
- Acidity:  $\text{RCOOH} > \text{PhOH} > \text{H}_2\text{O} > \text{ROH}$

- EWG increases acidity ( $-\text{Cl}$ ,  $-\text{NO}_2$ ), EDG decreases ( $-\text{CH}_3$ )
- $\text{NaHCO}_3$  test: carboxylic acids give  $\text{CO}_2$ , phenols don't
- HVZ:  $\alpha$ -halogenation of carboxylic acids using  $\text{Br}_2/\text{P}$

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