Aldehydes, Ketones and Carboxylic Acids Class 12 Key Points

CBSE Class 12 Chemistry · NCERT · for boards, NEET and JEE revision

ChapterNotes

The Carbonyl Group >C=O

C^δ+ = O^δ⁻ · sp^2 carbon · trigonal planar · ∠ ≈ 120°

Oxygen is more electronegative, so the carbon is electron-poor (δ+).

- Aldehyde R–CHO (carbonyl at chain end); ketone R–CO–R′ (in the middle); acid R–COOH
- δ+ carbon is electrophilic → open to nucleophiles; oxygen is mildly basic
- This single tilt drives nearly every reaction ahead

IUPAC & Common Names

–al (aldehyde) · –one (ketone) · –oic acid (acid) · –CHO & –COOH are always C-1

Seniority for suffix: carboxylic acid > ester > amide > aldehyde > ketone > alcohol.

- Trivial names: HCHO formaldehyde, CH_3CHO acetaldehyde, CH_3COCH_3 acetone
- HCOOH formic acid, CH_3COOH acetic acid
- Winner of seniority becomes the suffix; the rest become prefixes

Making Aldehydes, Ketones & Acids

Rosenmund: $RCOCl + H_2/Pd\text{-}BaSO_4 \rightarrow RCHO$ · Stephen: $RCN + SnCl_2/HCl \rightarrow RCHO$

Rosenmund uses POISONED $Pd/BaSO_4$; plain Pd over-reduces to the alcohol.

- Etard: toluene + CrO_2Cl_2 → benzaldehyde; Gattermann–Koch: C_6H_6 + $CO/HCl/AlCl_3$ → benzaldehyde
- Ketones: Friedel–Crafts acylation ($RCOCl/AlCl_3$); nitrile + Grignard then hydrolysis
- Ethyne is the ONLY alkyne giving an aldehyde on hydration (→ acetaldehyde)

Nucleophilic Addition to C=O

+HCN → cyanohydrin · $+NaHSO_3$ → bisulphite adduct · +R′OH/HCl → acetal · +RMgX → alcohol

NH_2–G derivatives: hydroxylamine → oxime, hydrazine → hydrazone, 2,4-DNP → orange ppt.

- 2,4-DNP confirms a carbonyl but CANNOT tell aldehyde from ketone
- $NaHSO_3$ purifies aldehydes & small/methyl ketones; bulky ketones fail
- Flat C=O becomes a tetrahedral carbon carrying two new groups

Aldehydes > Ketones

$HCHO > CH_3CHO > CH_3COCH_3$

Benzaldehyde is sluggish: the ring donates electrons by resonance, cutting the δ+.

- Two +I alkyl groups in ketones shrink the δ+ on carbon
- Alkyl groups also cause steric hindrance, blocking the nucleophile
- Electron-withdrawing groups raise reactivity; donating groups lower it

Aldol, Cannizzaro & Haloform

α-H present → Aldol & Iodoform · NO α-H → Cannizzaro (disproportionation)

Aldol gives a β-hydroxy carbonyl first; on heating it dehydrates to an α,β-unsaturated carbonyl.

- Cannizzaro needs NO α-H (HCHO, C_6H_5CHO): one oxidised to acid, one reduced to alcohol
- Iodoform (CHI_3, yellow): $CH_3CO–$ groups, plus $CH_3CH(OH)–$ → tests methyl ketones, acetaldehyde, ethanol
- 2 CH_3CHO aldol → 3-hydroxybutanal, then → but-2-enal (crotonaldehyde)

Tollens & Fehling

Tollens $[Ag(NH_3)_2]^+$ → silver mirror (aldehydes) · Fehling → red Cu_2O (aliphatic aldehydes)

NEET trap: benzaldehyde gives Tollens but does NOT give Fehling's.

- Ketones give neither Tollens nor Fehling
- Aromatic aldehydes do not respond to Fehling's
- Aldehydes are easily oxidised to acids; ketones cleave only under strong oxidation

Why Carboxylic Acids Are Acidic

R–C(=O)–O⁻ ↔ R–C(–O⁻)=O · resonance-stabilised $RCOO^-$ · lower pKa = stronger acid

Stronger than phenol: phenoxide spreads charge onto less electronegative carbons.

- EWG (–Cl, –F, $–NO_2$) stabilise the anion → stronger: Cl_3CCOOH > $Cl_2CHCOOH$ > $ClCH_2COOH$ > CH_3COOH
- Effect fades with distance: 2-chloro > 3-chloro > 4-chloro acid
- HCOOH > CH_3COOH (formic has no electron-donating +I alkyl group)

Reactions of –COOH

$+SOCl_2$ → acyl chloride · +R′OH/H_2SO_4 → ester · $+NH_3,\Delta$ → amide · $+P_2O_5$ → anhydride

$SOCl_2$ is preferred - its byproducts SO_2 and HCl are gases that escape, leaving a clean product.

- $LiAlH_4$ (or B_2H_6) reduces –COOH → 1° alcohol; $NaBH_4$ does NOT reduce acids
- HVZ: acid with α-H + X_2/red P → α-halo acid; HCOOH & benzoic acid (no α-H) fail
- Decarboxylation: RCOONa + soda lime → alkane ($CH_3COONa \rightarrow CH_4$, loses one carbon)

Quick revision

- Nucleophilic addition: HCHO > other aldehydes > ketones (steric + electronic)
- Tollens' 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