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CUET · CHEMISTRY · CLASS XII · CODE 306

Aldehydes, Ketones and Carboxylic Acids

CUET unit: Aldehydes, Ketones and Carboxylic Acids

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Establishes the chemistry of the carbonyl group (>C=O) in three families: aldehydes (RCHO), ketones (RCOR') and carboxylic acids (RCOOH).
- Develops nomenclature (common + IUPAC), structure (sp^2 carbon, planar, ~120°, polar C=O), and a wide menu of preparations from alcohols, hydrocarbons, acyl chlorides, nitriles, esters and arenes.
- Builds the central reaction theme — nucleophilic addition / addition-elimination at C=O — with reactivity order aldehyde > ketone (steric + electronic).
- Covers oxidation tests that distinguish aldehydes from ketones (Tollens', Fehling's, haloform) and α-hydrogen reactions (aldol, Cannizzaro).
- Closes with acidity of carboxylic acids (pKa values, effect of EWG/EDG), and reactions at O–H, C–OH, –COOH and α-position (HVZ); ring substitution in benzoic acid is meta-directing & deactivating.

📖 Detailed Notes

2.1 Core concepts

- In aldehydes the carbonyl carbon is bonded to one H (and one C/H), while in ketones it is bonded to two carbons; carboxylic acids have the carboxyl group –COOH, a carbonyl fused with hydroxyl (NCERT §8.0, p. 227).
- Common names of aldehydes are derived from common names of the parent carboxylic acid by replacing "–ic acid" with "aldehyde"; positions are marked with Greek letters α, β, γ (NCERT §8.1.1, p. 228).
- IUPAC: aliphatic aldehydes end in "–al" (chain numbered from CHO), ketones in "–one" (numbering begins from end nearer the carbonyl); ring-attached CHO uses suffix "carbaldehyde" (NCERT §8.1.1, p. 229).
- The carbonyl carbon is sp^2-hybridised, trigonal planar with ~120° bond angles; oxygen carries two lone pairs and the C=O bond is polar due to oxygen's higher electronegativity, making C electrophilic and O nucleophilic (NCERT §8.1.2, p. 231).
- Aldehydes & ketones are prepared by (i) oxidation of 1°/2° alcohols, (ii) dehydrogenation of alcohols over Ag/Cu, (iii) ozonolysis of alkenes, and (iv) acid-catalysed hydration of alkynes (ethyne → ethanal; higher alkynes → methyl ketones) (NCERT §8.2.1, p. 231-232).

- Rosenmund reduction: acyl chloride + H_2 on $Pd/BaSO_4$ → aldehyde; Stephen reaction ($RCN + SnCl_2/HCl$ → imine → RCHO) and DIBAL-H reduce nitriles and esters to aldehydes (NCERT §8.2.2, p. 232).
- Aromatic aldehyde preparations: Etard reaction (toluene + CrO_2Cl_2 → benzaldehyde via chromium complex); CrO_3 in acetic anhydride (via benzylidene diacetate); side-chain chlorination then hydrolysis; Gattermann–Koch (C_6H_6 + CO + HCl with anhydrous $AlCl_3/CuCl$) (NCERT §8.2.2, p. 232-233).
- Ketones: acyl chloride + R_2Cd (R_2Cd from $CdCl_2$ + RMgX) → ketone; nitrile + RMgX then hydrolysis → ketone; Friedel–Crafts acylation (arene + acyl chloride / anhydrous $AlCl_3$) → aryl ketone (NCERT §8.2.3, p. 233-234).
- Physical properties: methanal is gas, ethanal a volatile liquid; bp of aldehydes/ ketones is higher than hydrocarbons & ethers (dipole–dipole) but lower than alcohols (no intermolecular H-bonding); lower members are miscible with water through H-bonding (NCERT §8.3, p. 235).
- Nucleophilic addition mechanism: Nu attacks the electrophilic carbonyl C perpendicular to the sp^2 plane; hybridisation changes sp^2 → sp^3, giving a tetrahedral alkoxide intermediate that picks up H^+ — net addition of Nu^- and H^+ across C=O (NCERT §8.4(1), p. 236).
- Reactivity in nucleophilic addition: aldehyde > ketone because (a) ketones have two bulky groups (steric hindrance) and (b) the two alkyl groups donate electrons and reduce electrophilicity of the carbonyl carbon (NCERT §8.4(1)(ii), p. 236).
- Important nucleophilic additions: HCN (base-catalysed) → cyanohydrin; $NaHSO_3$ → bisulphite addition product (equilibrium favours aldehydes; useful for purification); alcohols/HCl-dry → hemiacetal → acetal (gem-dialkoxy); ethylene glycol with ketone → cyclic ketal (NCERT §8.4(1)(iii), p. 237-238).
- Addition–elimination with $H_2N–Z$ gives >C=N–Z: ammonia → imine, RNH_2 → Schiff's base, NH_2OH → oxime, NH_2NH_2 → hydrazone, $PhNHNH_2$ → phenylhydrazone, 2,4-DNP → 2,4-dinitrophenylhydrazone (yellow/orange/red solids — useful for characterisation), $H_2N-NHCONH_2$ → semicarbazone (NCERT Table 8.2, p. 238).
- Reduction: $NaBH_4$ / $LiAlH_4$ / catalytic H_2 reduce C=O to alcohol; Clemmensen (Zn-Hg/ conc. HCl) and Wolff-Kishner (NH_2NH_2 then NaOH/KOH in ethylene glycol) reduce C=O all the way to CH_2 (NCERT §8.4(2), p. 238-239).
- Oxidation: aldehydes → carboxylic acids easily (HNO_3, $KMnO_4$, $K_2Cr_2O_7$, and even mild Tollens' & Fehling's); ketones resist oxidation and only break C–C bonds under harsh conditions; Tollens' (ammoniacal $AgNO_3$) gives silver mirror; Fehling's (Cu^{2+} in alkaline Rochelle salt) gives reddish-brown Cu_2O ppt (aromatic aldehydes don't respond to Fehling's) (NCERT §8.4(3), p. 239).
- Haloform: methyl ketones ($CH_3CO–$) and $CH_3CH(OH)–$ compounds + NaOX → sodium carboxylate (one C less) + CHX_3 (iodoform test); the reaction does not affect C=C double bonds (NCERT §8.4(3)(iii), p. 240).

- α-Hydrogen acidity → Aldol condensation: with dilute alkali, aldehydes/ketones with α-H give β-hydroxy carbonyl (aldol/ketol) that loses water to give α,β-unsaturated carbonyl; cross-aldol with two different α-H carbonyls gives four products (NCERT §8.4(4), p. 241-242).
- Cannizzaro reaction: aldehydes with NO α-H (HCHO, PhCHO) undergo disproportionation with concentrated alkali — one molecule is oxidised to the carboxylate salt, the other is reduced to alcohol (NCERT §8.4(5)(i), p. 242).
- Aromatic aldehydes/ketones undergo electrophilic substitution at the ring with the C=O group acting as a deactivating, meta-directing group (NCERT §8.4(5)(ii), p. 243).
- Carboxylic acids: common names end in "–ic acid" (formic from ants, acetic from vinegar, butyric from rancid butter); IUPAC names use "–oic acid" with COOH carbon numbered one; –COOH on a ring uses "carboxylic acid" suffix (NCERT §8.6.1, p. 244-245).
- Carboxyl carbon is less electrophilic than carbonyl carbon because of resonance donation from the –OH oxygen (NCERT §8.6.2, p. 245).
- Preparations of carboxylic acids: (1) $KMnO_4/K_2Cr_2O_7/CrO_3$ (Jones) oxidation of 1° alcohol or aldehyde; (2) vigorous oxidation of alkyl benzenes (any 1°/2° alkyl side chain → COOH, but 3° unaffected); (3) hydrolysis of nitriles → amide → acid (mild conditions stop at amide); (4) RMgX + dry CO_2 then H^+ → RCOOH (one C extra); (5) hydrolysis of acid chlorides, anhydrides and esters (NCERT §8.7, p. 245-247).
- Acidity: RCOOH + active metal → H_2; RCOOH + $NaHCO_3$ / Na_2CO_3 → CO_2 (this CO_2 test distinguishes –COOH from phenols, which do not react with hydrogencarbonate); carboxylate anion is stabilised by two equivalent resonance structures placing –ve charge on two O atoms — hence RCOOH > phenol > alcohol in acidity (NCERT §8.9.1, p. 249-250).
- pKa values (NCERT lists): HCl pKa = –7.0; CF_3COOH (strongest carboxylic acid here) 0.23; benzoic acid 4.19; acetic acid 4.76; smaller pKa = stronger acid (NCERT §8.9.1, p. 250).
- Substituent effect on acidity — EWG ($-NO_2$, –CN, halogens, $-CF_3$) stabilise carboxylate and increase acidity; EDG ($-OCH_3$, $-CH_3$) decrease it. Order: Ph < I < Br < Cl < F < CN < NO_2 < CF_3. On aromatic ring, p-OMe-C_6H_4-COOH (pKa 4.46) < benzoic (4.19) < p-NO_2-C_6H_4-COOH (3.41) (NCERT §8.9.1, p. 250-251).
- C–OH cleavage reactions: (1) heating with H_2SO_4 or P_2O_5 → anhydride; (2) Fischer esterification with alcohol + conc. H_2SO_4/HCl gas (nucleophilic acyl substitution: protonation → addition of alcohol → loss of H_2O); (3) $PCl_5/PCl_3/SOCl_2$ → acid chloride ($SOCl_2$ preferred — by-products SO_2 + HCl are gases); (4) NH_3 → ammonium salt → on heating → amide (NCERT §8.9.2, p. 251-252).
- –COOH group reactions: $LiAlH_4$ or B_2H_6 reduce –COOH to 1° alcohol ($NaBH_4$ does NOT reduce –COOH; diborane is selective and does not touch ester/nitro/halo); decarboxylation of sodium salt with sodalime (NaOH + CaO, 3:1) → R–H + CO_2; Kolbe

electrolysis of carboxylate salts gives hydrocarbons with double the C atoms (NCERT §8.9.3, p. 252-253).

- Hell–Volhard–Zelinsky (HVZ): RCH_2COOH with Cl_2 or Br_2 + small amount of red P → α-halocarboxylic acid; aromatic acids — ring electrophilic substitution gives meta product because –COOH is deactivating and meta-directing; benzoic acid does NOT undergo Friedel–Crafts ($AlCl_3$ binds to –COOH) (NCERT §8.9.4, p. 253-254).

2.2 Definitions to memorise

Term	Definition	Page
Carbonyl group	>C=O functional group; sp² C, trigonal planar, polarised C^δ+=O^δ−	231
Cyanohydrin	Addition product of HCN with aldehyde/ketone, $R_2C(OH)(CN)$; base-catalysed	237
Hemiacetal / Acetal	RCH(OH)(OR') (hemi) and $RCH(OR')_2$ (gem-dialkoxy, acetal) from RCHO + 2 R'OH/HCl	237
2,4-DNP-derivative	Coloured (yellow/orange/red) solid from C=O + 2,4-dinitrophenylhydrazine; characterises aldehydes/ketones	238
Schiff's base	Substituted imine $R_2C{=}NR'$ from carbonyl + 1° amine	238
Tollens' reagent	Ammoniacal $AgNO_3$; oxidises –CHO and deposits silver mirror (Ag)	239
Fehling's reagent	Cu^{2+} in alkaline Rochelle salt (A + B); gives reddish-brown Cu_2O ppt with aliphatic aldehydes (aromatic aldehydes do NOT respond)	239
Haloform reaction	Methyl ketone or $CH_3CH(OH)$– + NaOX → carboxylate (one C less) + CHX_3	240
Aldol	β-hydroxy aldehyde/ketone from base-catalysed self-condensation of α-H carbonyl	241
Cannizzaro reaction	Disproportionation of α-H-less aldehyde with conc. alkali → alcohol + carboxylate	242
Clemmensen reduction	Zn-Hg / conc. HCl: C=O → CH_2	238
Wolff-Kishner reduction	NH_2NH_2 then NaOH/KOH in ethylene glycol: C=O → CH_2	239
Rosenmund reduction	RCOCl + H_2 / Pd-$BaSO_4$ → RCHO	232
Stephen reaction	RCN + $SnCl_2$/HCl, then hydrolysis → RCHO	232
Etard reaction	$C_6H_5CH_3$ + CrO_2Cl_2, then hydrolysis → C_6H_5CHO	232
Gattermann–Koch	Benzene + CO + HCl / anhydrous $AlCl_3$ (or CuCl) → benzaldehyde	233

Term	Definition	Page
Friedel–Crafts acylation	Arene + RCOCl / anhydrous $AlCl_3$ → aryl ketone	234
HVZ reaction	α-halogenation of carboxylic acid with Cl_2/Br_2 in presence of red P	253
Decarboxylation	RCOONa + NaOH/CaO (sodalime), Δ → RH + Na_2CO_3	253
pKa	–log Ka; smaller pKa = stronger acid	250

2.3 Diagrams / processes to remember

- Fig. 8.1 — Orbital diagram for the carbonyl group: sp^2 carbon, three σ bonds, π bond above and below the plane (p. 231).
- Resonance structures of C=O — neutral (A) and dipolar (B) explaining polarity and high dipole moment (p. 231).
- Fig. 8.2 — Nucleophilic attack on the carbonyl carbon perpendicular to the sp^2 plane, producing a tetrahedral alkoxide that captures H^+ (p. 236).
- Table 8.1 — Common vs IUPAC names of aldehydes & ketones (p. 230).
- Table 8.2 — N-substituted derivatives (>C=N–Z): imine, Schiff's base, oxime, hydrazone, phenylhydrazone, 2,4-DNP-hydrazone, semicarbazone (p. 238).
- Table 8.3 — Common vs IUPAC names of carboxylic acids (formic/methanoic … benzoic/benzenecarboxylic) (p. 244).
- Resonance pair stabilising carboxylate anion (two equivalent O bearing –ve charge) versus phenoxide (–ve charge on C atoms) — explains why RCOOH > PhOH in acidity (p. 250).
- Ranked bp comparison at MW ≈ 58–60: n-butane (273 K) < methoxyethane (281) < propanal (322) < acetone (329) < propan-1-ol (370) (p. 235).

2.4 Common confusions / NTA trap points

- Tollens' vs Fehling's: BOTH oxidise aldehydes, but Fehling's does NOT respond to AROMATIC aldehydes (benzaldehyde) — a favourite trap (p. 239).
- HVZ uses red phosphorus + Cl_2/Br_2 (not just Cl_2/Br_2 alone); also it acts at the α-C, not the ring (p. 253).
- Reactivity in nucleophilic addition is aldehyde > ketone — students sometimes invert this; remember both steric and electronic factors (p. 236).
- Cannizzaro requires NO α-H and conc. alkali (HCHO, PhCHO, $(CH_3)_3CCHO$, 2,2-dimethylpropanal qualify); aldehydes with α-H instead do aldol (p. 242).
- Iodoform test is given by methyl ketones AND $CH_3CH(OH)$–R (ethanol gives iodoform, methanol does not); iodoform does not affect C=C (p. 240).

- $NaBH_4$ does NOT reduce –COOH; use $LiAlH_4$ or diborane (B_2H_6). Diborane is selective — leaves nitro/halo/ester untouched (p. 252).
- Benzoic acid is deactivating and meta-directing despite the lone pairs on O — and it does NOT undergo Friedel–Crafts ($AlCl_3$ chelates with –COOH) (p. 253-254).
- Phenyl/vinyl directly attached to –COOH INCREASES acidity (against expectation from resonance) because sp^2-C is more electronegative than sp^3-C (p. 251).
- For ketone preparation from acyl chloride, use R_2Cd (dialkylcadmium), NOT RMgX directly (Grignard goes through to tertiary alcohol) (p. 233).
- Aromatic ring of toluene side-chain oxidation: $KMnO_4$/CrO_3 takes 1°/2° alkyl → –COOH; tertiary alkyl is NOT oxidised (p. 246).
- **Rosenmund vs Stephen** — Rosenmund reduces acyl chloride to aldehyde using H_2/Pd-$BaSO_4$; Stephen reduces nitrile via $SnCl_2$/HCl then hydrolysis (p. 230).
- **Etard reaction** uses CrO_2Cl_2 (chromyl chloride) on toluene to give benzaldehyde after hydrolysis (p. 231) — distractor names the wrong oxidant.

2.5 Quick reaction map — aldehydes, ketones and carboxylic acids

#	Reaction / reagent	Substrate → product	Page
1	Rosenmund (H_2/Pd-$BaSO_4$)	Acyl chloride → aldehyde	230
2	Stephen ($SnCl_2$/HCl, then H_3O^+)	Nitrile → aldehyde	230
3	DIBAL-H	Nitrile / ester → aldehyde	231
4	Etard (CrO_2Cl_2)	Toluene → benzaldehyde	231
5	Gattermann–Koch (CO+HCl/ $AlCl_3$-CuCl)	Benzene → benzaldehyde	232
6	Tollens' reagent	Aldehyde → silver mirror	239
7	Fehling's solution	Aliphatic aldehyde → red Cu_2O ppt	239
8	Iodoform (NaOI / I_2+NaOH)	Methyl ketone / $CH_3CH(OH)R$ → CHI_3	240
9	Aldol condensation (dilute NaOH)	Aldehyde/ketone with α-H → β-hydroxy carbonyl → α,β-unsat.	240
10	Cannizzaro (conc. NaOH)	Aldehyde without α-H → alcohol + acid	242
11	HVZ (X_2 + red P)	Carboxylic acid → α-halo acid	253
12	Clemmensen (Zn-Hg/HCl)	C=O → CH_2 (acid-stable substrate)	237
13	Wolff–Kishner (NH_2NH_2/KOH, glycol)	C=O → CH_2 (base-stable substrate)	237
14	Kolbe electrolysis	RCOONa → R–R + CO_2	(related, §10)
15	$LiAlH_4$	–COOH/ester/nitrile → 1° alcohol/amine	252

🎯 Practice MCQs

Q1. The hybridisation and approximate bond angle at the carbonyl carbon in an aldehyde are:

A. sp^3 and 109.5°

B. sp^2 and 120°

C. sp and 180°

D. sp^3d and 90°

Q2. Which reagent on reaction with an acyl chloride gives an aldehyde without over-reducing it to alcohol?

A. $LiAlH_4$ in dry ether

B. $NaBH_4$ in methanol

C. H_2 / Pd-$BaSO_4$

D. Zn-Hg and concentrated HCl

Q3. The conversion of toluene to benzaldehyde using chromyl chloride (CrO_2Cl_2) is called:

A. Gattermann–Koch reaction

B. Etard reaction

C. Stephen reaction

D. Rosenmund reduction

📊 PYQ Alignment

This chapter is among the heaviest in CUET Chemistry (typically 10–15 MCQs across the paper, often the single largest organic-chemistry contributor in the 306 paper). Recurring question types: (i) reagent identification — Tollens' / Fehling's / haloform / 2,4-DNP /

Rosenmund; (ii) reactivity orders in nucleophilic addition; (iii) named reactions — Cannizzaro, aldol, Etard, Gattermann–Koch, HVZ; (iv) pKa-based comparisons of carboxylic acid strength with EWG/EDG substituents; (v) product prediction (Grignard + nitrile, RMgBr + CO_2, Friedel–Crafts acylation); and (vi) compound-identification problems modelled on Example 8.4 (2,4-DNP + iodoform + Tollens' patterns).

CUET 2025 — Actual PYQs from this chapter

Q.27 (CUET 2025) Hell-Volhard-Zelinsky reaction forms:

- A) Alcohols B) Aldehydes C) Ketones D) α-halo carboxylic acids

Tests: α-halogenation of carboxylic acids (HVZ) Answer: Not in extracted key

Q.30 (CUET 2025) Which reagent distinguishes benzophenone from acetone?

- A) Fehling’s reagent B) Tollens reagent C) 2,4-DNP reagent D) I_2/NaOH

Tests: Distinguishing tests for carbonyls Answer: Not in extracted key

Q.31 (CUET 2025) Structural feature for Aldol condensation:

- A) At least one β-hydrogen B) At least one α-hydrogen C) Concentrated base D) Lack of α-hydrogen

Tests: Aldol condensation Answer: Not in extracted key

Q.28 (CUET 2025) Correct sequence of increasing reactivity towards nucleophilic addition: (A) Ethanal (B) Propanone (C) Propanal (D) Butanone

- A) — B) — C) — D) —

Tests: Nucleophilic addition reactivity ordering Answer: Not in extracted key

CUET 2024 — Actual PYQs from this chapter

Q.15 (CUET 2024) Which compound gives Hell-Volhard-Zelinsky reaction?

- A) $R\text{-}CH_2\text{-}COOH$ B) $R_3C\text{-}CHO$ C) R_2CO D) $H\text{-}COOH$

Tests: α-halogenation of carboxylic acids (HVZ) Answer: Not in extracted key

Q.16 (CUET 2024) Increasing order of acidic strength: $HCOOH$, FCH_2COOH, NO_2CH_2COOH, $ClCH_2COOH$ Options given.

- A) — B) — C) — D) —

Tests: Carboxylic acid acidity Answer: Not in extracted key

Q.17 (CUET 2024) Increasing order of reactivity toward nucleophilic addition: Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone Options given.

- A) — B) — C) — D) —

Tests: Aldehydes/ketones/acids Answer: Not in extracted key

Q.18 (CUET 2024) In Gattermann-Koch reaction, the electrophile is:

- A) CO^+ B) $HCl + CO_2 + AlCl_3$ C) HCO^+ D) $CO + AlCl_3$

Tests: Named reactions of aldehydes/ketones Answer: Not in extracted key

Q.19 (CUET 2024) Formaldehyde undergoes Cannizzaro reaction because: (A) It has α-hydrogen (B) It does not have α-hydrogen (C) It does not undergo self-oxidation reduction (D) It undergoes self-oxidation reduction Options given.

- A) — B) — C) — D) —

Tests: Named reactions of aldehydes/ketones Answer: Not in extracted key

Q.23 (CUET 2024) In Etard reaction, final product is:

- A) Aromatic aldehyde B) Aromatic chloride C) Aromatic amine D) Aromatic alcohol

Tests: Named reactions of aldehydes/ketones Answer: Not in extracted key

Q.25 (CUET 2024) Match reagents: (A) Tollens reagent (B) Jones reagent (C) Lucas reagent (D) Fehling solution With respective chemicals.

- A) — B) — C) — D) —

Tests: Distinguishing tests for carbonyls Answer: Not in extracted key

Q.30 (CUET 2024) Increasing order of acidity (pKa): (A) $BrCH_2COOH$ (B) $ClCH_2COOH$ (C) FCH_2COOH (D) HCOOH

- A) — B) — C) — D) —

Tests: Carboxylic acid pKa Answer: Not in extracted key

CUET 2023 — Actual PYQs from this chapter

Q.8 (CUET 2023) Basic hydrolysis of esters produces:

- A) Carboxylates B) Carboxylic acids C) Aldehydes D) Ketones

Tests: Aldehydes/ketones/acids Answer: Not in extracted key

Q.13 (CUET 2023) Acetaldehyde and benzaldehyde can be distinguished by:

- A) 2,4-DNP test B) Tollens' test C) Sodium bicarbonate test D) Fehling's test

Tests: Distinguishing tests for carbonyls Answer: Not in extracted key

Q.32 (CUET 2023) CH_3CHO does not give a silver mirror with Tollens' reagent but forms an oxime with hydroxylamine. It can give positive:

- A) Iodoform test B) Fehling's test C) Schiff's test D) Carbylamine test

Tests: Distinguishing tests for carbonyls Answer: Not in extracted key

Q.46 (CUET 2023) Aspirin is an acetylation product of:

- A) o-Dihydroxybenzoic acid B) p-Hydroxybenzoic acid C) m-Hydroxybenzoic acid D) Salicylic acid (o-hydroxybenzoic acid)

Tests: Aldehydes/ketones/acids Answer: Not in extracted key