

Carbonyl compounds

A-Level Chemistry

Aldehydes and ketones

Aldehydes and ketones are **carbonyl compounds** 羰基化合物—they contain the $\text{C}=\text{O}$ **carbonyl** 羰基 group.

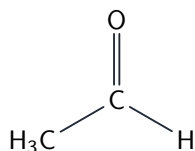
- in an **aldehyde** 醛 the carbonyl carbon is on the end of the chain (it also carries an H), written $-\text{CHO}$.
- in a **ketone** 酮 the carbonyl carbon is in the middle, between two other carbons.



Propanone (acetone), the simplest ketone, is the solvent in nail-polish remover

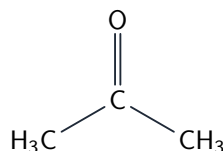
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aldehyde



$\text{C}=\text{O}$ carbon on the end
(also carries an H): $-\text{CHO}$

ketone



$\text{C}=\text{O}$ carbon in the middle,
between two carbons

Both have the $\text{C}=\text{O}$ carbonyl group: in an aldehyde it is on the end of the chain ($-\text{CHO}$), in a ketone it is in the middle

Making aldehydes and ketones

Both are made by the **oxidation** 氧化 of an **alcohol** 醇 with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 :

- a **primary** alcohol, with **distillation** 蒸馏, gives an aldehyde.
- a **secondary** alcohol gives a ketone.

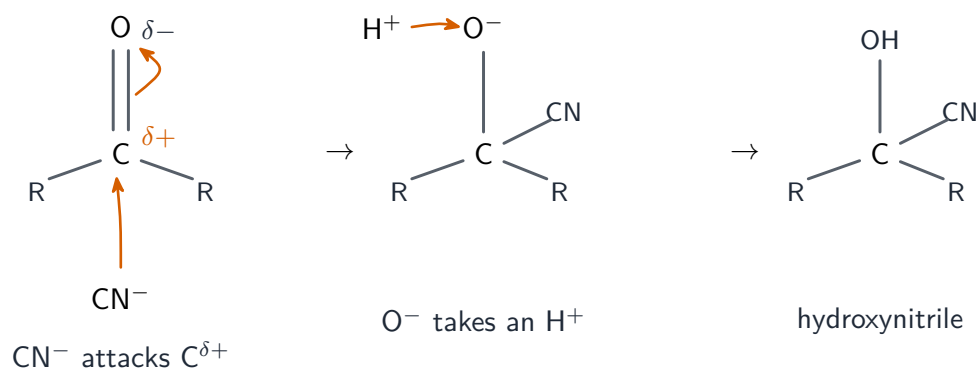
Reactions

- **reduction** 还原 with NaBH_4 or LiAlH_4 turns a carbonyl compound back into an alcohol (an aldehyde gives a primary alcohol; a ketone gives a secondary alcohol).
- reaction with **hydrogen cyanide** 氰化氢 (HCN), with KCN as catalyst and heat, adds H and CN across the $\text{C}=\text{O}$ to make a **hydroxynitrile** 羟基腈. This adds one carbon to the chain.

The mechanism: nucleophilic addition

The reaction with HCN is a **nucleophilic addition** 亲核加成. The carbonyl carbon is slightly positive (oxygen pulls the electrons away). So:

1. the CN^- ion (a nucleophile) attacks the slightly positive carbon.
2. this breaks the $\text{C}=\text{O}$ double bond, leaving a negative oxygen (O^-).
3. the O^- takes an H^+ (from HCN) to finish the hydroxynitrile.



Nucleophilic addition of HCN : CN^- attacks the $\delta+$ carbonyl carbon, the $\text{C}=\text{O}$ breaks to O^- , then O^- takes an H^+

Tests for carbonyl compounds

Detecting any carbonyl

Add **2,4-DNPH** reagent (2,4-dinitrophenylhydrazine). An orange precipitate confirms that the compound is an aldehyde or a ketone.

Telling an aldehyde from a ketone

Aldehydes are easily oxidised to carboxylic acids, but ketones are not. Two tests use this difference:

Test	Aldehyde	Ketone
Fehling's reagent 斐林试剂 (blue solution)	turns to a brick-red precipitate	no change
Tollens' reagent 托伦试剂 (colourless)	gives a silver mirror	no change

tell an aldehyde from a ketone



Fehling's
(blue)

→ brick-red ppt



Tollens'
(colourless)

→ silver mirror

a ketone gives **no change** with either test

Telling an aldehyde from a ketone: an aldehyde gives a brick-red precipitate with Fehling's and a silver mirror with Tollens'; a ketone gives no change



A positive Tollens' test: an aldehyde coats the tube with a shiny silver mirror

Image: Tmv23, CC BY-SA 3.0 (commons.wikimedia.org)

The iodoform test

If the compound has the $\text{CH}_3\text{CO}-$ group, warming it with alkaline aqueous iodine gives a pale yellow precipitate of **tri-iodomethane** 三碘甲烷 (CHI_3) and the ion RCO_2^- .

Worked example. A liquid gives an orange precipitate with 2,4-DNPH, gives **no** silver mirror with Tollens' reagent, and gives a yellow precipitate with alkaline aqueous iodine. Identify it. Take the tests one at a time, using each for exactly what it proves. The orange precipitate with **2,4-DNPH** proves a **carbonyl** group is present - an aldehyde or a ketone, nothing else. **No** silver mirror with Tollens' rules out an **aldehyde**, so it must be a **ketone**. The yellow precipitate in the **iodoform** test proves a $\text{CH}_3\text{CO}-$ group next to the carbonyl. The simplest compound satisfying all three is **propanone**, CH_3COCH_3 . Keep the roles straight: 2,4-DNPH finds **any** carbonyl, Tollens' separates aldehyde from ketone, and iodoform detects the **methyl group beside the $\text{C}=\text{O}$** .

Exam tips

- **2,4-DNPH** gives an orange precipitate with **any** carbonyl —it tests for $\text{C}=\text{O}$.
- **Tollens' (silver mirror)** and **Fehling's (brick-red)** are positive for **aldehydes only** —this is how you tell aldehydes from ketones.
- Nucleophilic addition of HCN adds **one carbon** ($\rightarrow$ hydroxynitrile); show the curly arrows.
- The **iodoform (tri-iodomethane)** test is positive for $\text{CH}_3\text{CO}-$ groups.