

# Carbonyl compounds

## A-Level Chemistry

### Aldehydes and ketones

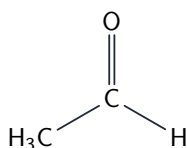
Aldehydes and ketones are **carbonyl compounds** – they contain the  $\text{C}=\text{O}$  **carbonyl** group.

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



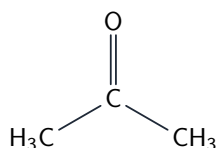
*Propanone (acetone), the simplest ketone, is the solvent in nail-polish remover*

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** of an **alcohol** with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{KMnO}_4$ :

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

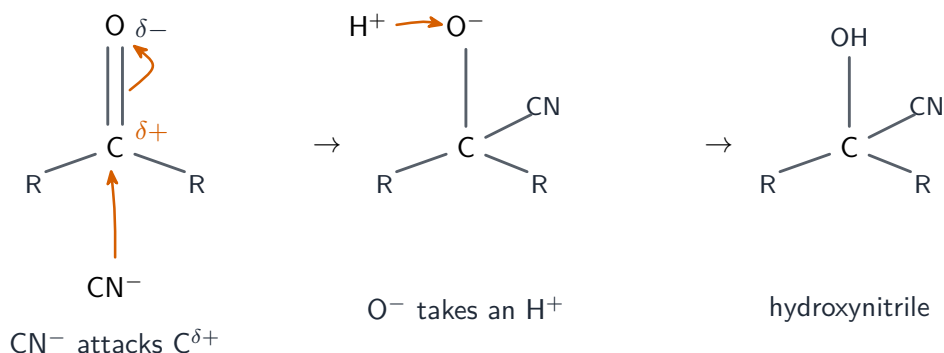
## ■ Reactions

- **reduction** with  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  turns a carbonyl compound back into an alcohol (an aldehyde gives a primary alcohol; a ketone gives a secondary alcohol).
- reaction with **hydrogen cyanide** ( $\text{HCN}$ ), with  $\text{KCN}$  as catalyst and heat, adds  $\text{H}$  and  $\text{CN}$  across the  $\text{C}=\text{O}$  to make a **hydroxynitrile**. This adds one carbon to the chain.

## ■ The mechanism: nucleophilic addition

The reaction with  $\text{HCN}$  is a **nucleophilic addition**. The carbonyl carbon is slightly positive (oxygen pulls the electrons away). So:

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



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

## 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    |
|-----------------------------------------|--------|----------------------------------|-----------|
| <b>Fehling's reagent</b><br>(solution)  | (blue) | turns to a brick-red precipitate | no change |
| <b>Tollens' reagent</b><br>(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*

## ■ 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** ( $\text{CHI}_3$ ) and the ion  $\text{RCO}_2^-$ .

**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**,  $\text{CH}_3\text{COCH}_3$ . 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  $\text{HCN}$  adds **one carbon** ( $\rightarrow$  hydroxynitrile); show the curly arrows.
- The **iodoform (tri-iodomethane)** test is positive for  $\text{CH}_3\text{CO}-$  groups.