

# **CAIE Chemistry A-level**

# 17: Carbonyl Compounds Notes

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# Aldehydes and Ketones

Aldehydes and ketones both contain the carbonyl group, C=O.

The **position** of the **carbonyl** group in the carbon chain is **different** in aldehydes and ketones.

The carbonyl group is at the end of the carbon chain in aldehydes and in the middle in ketones. The suffix for aldehydes is **-al** and the suffix for ketones is **-one**.



### Formation of Aldehydes and Ketones

Aldehydes and ketones are formed when alcohols are **oxidised** using **acidified potassium dichromate(VI)** ( $Cr_2O_7^{2-}/H^+$ ).

Aldehydes are formed from **primary** alcohols, whereas ketones are formed from **secondary** alcohols.

#### Primary alcohols

Primary alcohols can be partially oxidised to aldehydes.

 $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$ 

If the aldehyde undergoes further oxidation, carboxylic acids are produced.

$$\rm CH_3CHO + [O] \rightarrow \rm CH_3COOH + \rm H_2O$$

The full oxidation reaction can be written as:

 $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + 2H_2O$ 

If you are only collecting the aldehyde, carry out the reaction with excess alcohol and distill off the aldehyde as soon as it forms to prevent further oxidation.

Secondary alcohols

Secondary alcohols are oxidised to ketones. No further oxidation can take place.

$$CH_{3}C(OH)HCH_{3} + [O] \rightarrow CH_{3}COCH_{3} + H_{2}O$$

#### **Reduction of Aldehydes and Ketones**

A **reducing agent** can be used to reverse the reactions above and convert aldehydes and ketones back to primary and secondary alcohols.

Typically  $LiAIH_4$  or  $NaBH_4$  (dissolved in water with methanol) are used as reducing agents for this reaction.

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#### **Reduction of Aldehydes**

 $RCHO + 2[H] \rightarrow RCH_2OH$ 

For example, the reduction of ethanal to ethanol:



#### Reduction of Ketones

 $R_1COR_2 + 2[H] \rightarrow RC(OH)HR_2$ 

For example, the reduction of propanone to propanal:

#### **Reaction with HCN and KCN**

Hydrogen cyanide reacts with aldehydes and ketones to produce **hydroxynitrile compounds** by removing the C=O double bond. The reaction is called **nucleophilic addition** (see the mechanism on the following page).

#### Naming:

When naming a hydroxynitrile, the **carbon in the nitrile group (C=N)** is referred to as the **first carbon** so the position of groups (including the alcohol group) is counted from there. In the equations below, the product of the first reaction is **2-hydroxypropanenitrile** and the product of the second reaction is **2-hydroxy-2-methylpropanenitrile**.



HCN is a very **poisonous gas**. Often **KCN** or **NaCN** are reacted with acid to form HCN in situ.





#### **Nucleophilic Addition Reactions**

When aldehydes and ketones react with HCN to form hydroxynitriles, a nucleophilic addition reaction occurs. A nucleophile is an electron pair donor.

#### The Mechanism:

The **carbonyl bond** (C=O) is **highly polar**. The negative **cyanide ion** acts as a **nucleophile** and attacks the slightly positive carbon atom. The C=O bond breaks, leaving only a **single bond** between the **carbon and oxygen** atoms.

The negatively charged oxygen then bonds to a **hydrogen ion** (from HCN or any added acid).



#### **Detecting Carbonyl Compounds**

The carbonyl group can be detected using 2,4-dinitrophenylhydrazine (2,4-DNPH). When 2,4-DNPH is added to a solution of aldehyde or ketone, a **yellow/ orange precipitate** is produced. The formation of this coloured precipitate indicates the presence of a **C=O carbonyl group**.

### **Distinguishing between Aldehydes and Ketones**

Simple tests can be carried out to detect whether a compound is an aldehyde or a ketone. **Ketones** are **not easily oxidised** whereas **aldehydes** are **easily oxidised** to carboxylic acids.

After identifying a solution as a carbonyl using 2,4-DNPH, certain reactions can be carried out using **oxidising agents**. A **positive result** indicates that an **aldehyde** is present while a **negative result** suggests a **ketone** is present.

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<u>Acidified potassium dichromate(VI)</u> <u>Aldehyde</u> - orange solution turns green. <u>Ketone</u> - no visible change / solution remains orange.

<u>Tollen's reagent</u> Aldehyde - silver mirror forms on the walls of the test tube. Ketone - no visible change.

<u>Fehling's reagent</u> <u>Aldehyde</u> - blue solution gives a brick red precipitate. <u>Ketone</u> - no visible change / solution remains blue.





## Deducing the Presence of CH<sub>3</sub>CO- Group

A CH<sub>3</sub>CO- group can be detected using alkaline aqueous iodine,  $I_2$ .

**lodine** is added to the carbonyl, followed by **sodium hydroxide** (to make the solution alkaline). If the  $CH_3CO$ - group is present, a **yellow precipitate** of **tri-iodomethane** (CHI<sub>3</sub>) will form.

 $\mathrm{CH_3COR} + \mathrm{3I_2} + \mathrm{4NaOH} \rightarrow \mathrm{RCOONa} + \mathrm{CHI_3} + \mathrm{3NaI} + \mathrm{3H_2O}$ 

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