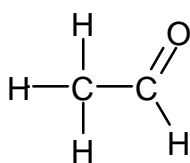


3.8 Aldehydes and Ketones

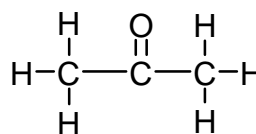
Carbonyls: Aldehydes and Ketones

Carbonyls are compounds with a C=O bond. They can be either aldehydes or ketones



If the C=O is on the end of the chain with an H attached it is an aldehyde.
The name will end in **-al**

CH₃CHO ethanal



If the C=O is in the middle of the chain it is a ketone.
The name will end in **-one**

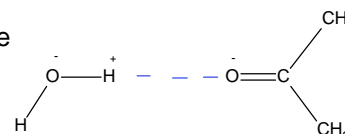
CH₃COCH₃ propanone

Intermolecular forces in carbonyls

Pure carbonyls cannot hydrogen bond to themselves, but are attracted instead by **permanent dipole forces**.

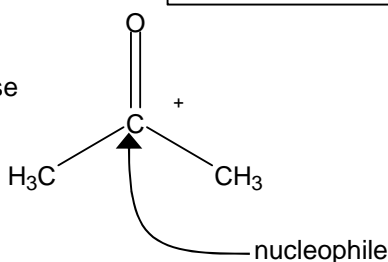
Solubility in water

The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.



Reactions of carbonyls

The C=O bond is polarised because O is more electronegative than carbon. The positive carbon atom attracts nucleophiles.



In comparison to the C=C bond in alkenes, the C=O is stronger and does not undergo addition reactions easily.

This is in contrast to the electrophiles that are attracted to the C=C.

Oxidation Reactions

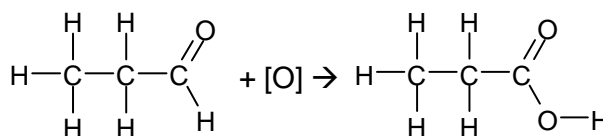
Potassium dichromate K₂Cr₂O₇ is an oxidising agent that causes alcohols and aldehydes to oxidise.

Primary alcohol → aldehydes → carboxylic acid
Secondary alcohol → ketones
Tertiary alcohols do not oxidise

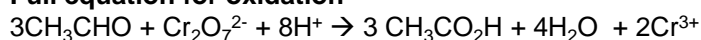
Key point: Aldehydes can be oxidised to carboxylic acids, but ketones cannot be oxidised.

Oxidation of Aldehydes

Reaction: aldehyde → carboxylic acid
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: heat under reflux



Full equation for oxidation



Observation: the orange dichromate ion (Cr₂O₇²⁻) reduces to the green Cr³⁺ ion

Aldehydes can also be oxidised using Fehling's solution or Tollen's reagent. These are used as tests for the presence of aldehyde groups

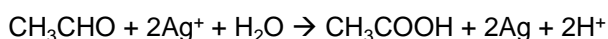
Tollens' Reagent

Reagent: Tollens' reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)₂]⁺.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollens' reagent into a carboxylic acid. The silver(I) ions are reduced to silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.



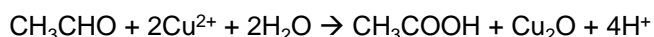
Fehling's solution

Reagent: Fehling's solution containing blue Cu²⁺ ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling's Solution into a carboxylic acid. The copper (II) ions are reduced to copper(I) oxide.

Observation: Aldehydes: Blue Cu²⁺ ions in solution change to a red precipitate of Cu₂O. **Ketones do not react.**



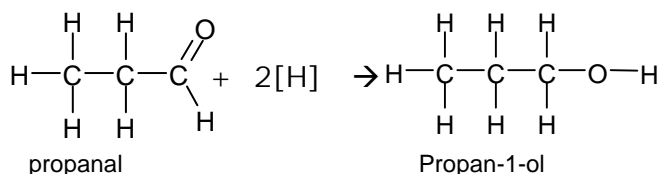
Reduction of carbonyls

Reagents: NaBH₄ in aqueous ethanol

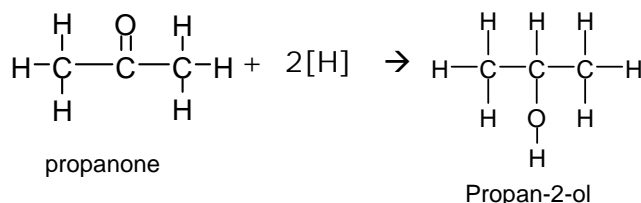
Conditions: Room temperature and pressure

Reducing agents such as NaBH₄ (sodium tetrahydridoborate) or LiAlH₄ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

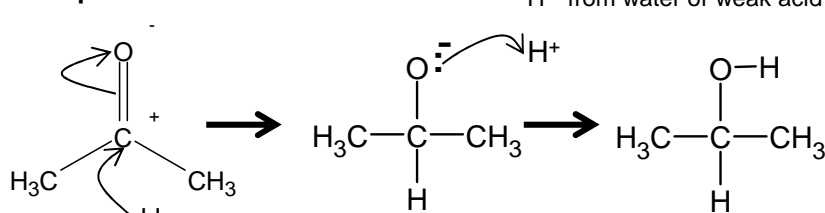
Aldehydes will be reduced to primary alcohols



Ketones will be reduced to secondary alcohols.



Nucleophilic Addition Mechanism



NaBH₄ contains a source of nucleophilic hydride ions (:H⁻) which are attracted to the positive carbon in the C=O bond.

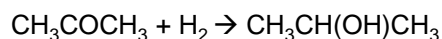
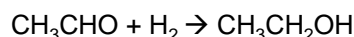
Catalytic Hydrogenation

Carbonyls can also be reduced using catalytic hydrogenation

Reagent: hydrogen and nickel catalyst

Conditions: high pressure

Example Equations



Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

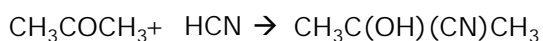
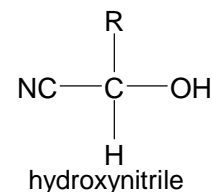
Reaction: carbonyl → hydroxynitrile

Reagent: sodium cyanide (NaCN) and dilute sulfuric acid.

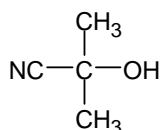
Conditions: Room temperature and pressure

Mechanism: nucleophilic addition

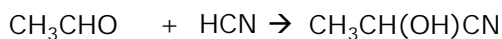
The NaCN supplies the nucleophilic CN⁻ ions. The H₂SO₄ acid supplies H⁺ ions needed in second step of the mechanism



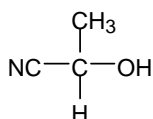
2-hydroxy-2-methylpropanenitrile



When naming hydroxy nitriles the CN becomes part of the main chain and carbon n^o 1

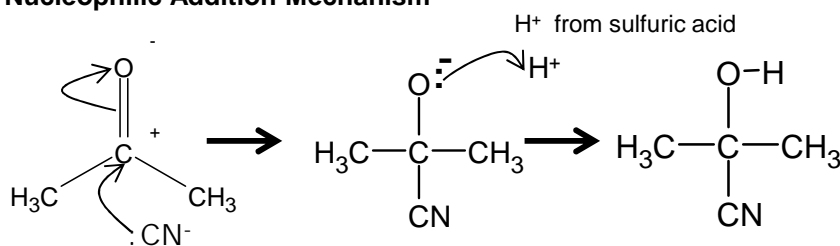


2-hydroxypropanenitrile



We could use HCN for this reaction but it is a toxic gas that is difficult to contain. KCN/NaCN are still, however, toxic, because of the cyanide ion.

Nucleophilic Addition Mechanism



Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate.

Mechanism for the reaction (drawn the same for both enantiomers)

