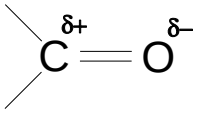
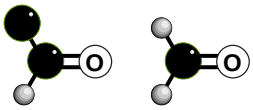
CARBONYL COMPOUNDS - Aldehydes and Ketones

Structure

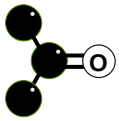
- carbonyl groups consists of a **carbon-oxygen double bond**
- the bond is **polar** due to the difference in electronegativity
- aldehydes and ketones differ in what is attached to the carbon.



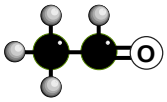
ALDEHYDES - at least one H attached



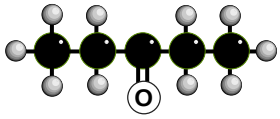
KETONES - two carbons attached



Structures can be written in shortened form such as CH_3CHO for ethanal and $C_2H_5COC_2H_5$ or $CH_3CH_2COCH_2CH_3$ for pentan-3-one or in a form showing all the bonds;



CH_3CHO



$C_2H_5COC_2H_5$

Nomenclature

Aldehydes

- look for the longest chain of C atoms containing the carbonyl group
- **remove E** from the equivalent alkane name and **add AL**
- substituents are numbered based on the C with the O being number 1

Ketones

- look for the longest chain of C atoms containing the carbonyl group
- **remove E** from the equivalent alkane name and **add ONE**
- if necessary, the position of the C=O is given (lower number counting from one end)
- substituents are numbered based on the number allocated to the C in the C=O

Trivial names Before a systematic naming system was introduced, many aldehydes and ketones were named from the carboxylic acid they could be oxidised to.

	systematic name	*old name*	*derived from*
HCHO	methanal	*formaldehyde*	formic acid - HCOOH
CH_3CHO	ethanal	*acetaldehyde*	acetic acid - CH_3COOH
CH_3COCH_3	propanone	*acetone*	acetic acid
C_6H_5CHO	benzenecarbaldehyde	*benzaldehyde*	benzoic acid - C_6H_5COOH

Q.1 *How many carbonyl compounds have the formula $C_5H_{10}O$? Draw their structures, classify them as aldehydes or ketones and name them.*

Bonding

- the carbonyl carbon is sp^2 hybridised and three sigma (σ) bonds are planar
- the unhybridised 2p orbital of carbon is at 90° to these
- it overlaps with a 2p orbital of oxygen to form a pi (π) bond
- as oxygen is more electronegative than carbon the bond is polar

PHYSICAL PROPERTIES

Boiling point **Increases as the molecular size increases** due to increased van der Waals' forces.

More branching = lower inter-molecular forces = lower boiling point

- aldehydes and ketones have slightly higher boiling points than similar mass alkanes
- due to inter-molecular dipole-dipole interactions between polar C=O bonds
- more energy is required to separate the molecules.

Solubility Soluble in organic solvents. Only the very short chain compounds are water soluble.

PREPARATION

Aldehydes

- Oxidation of primary (1°) alcohols - **beware of further oxidation to acids**
- Reduction of carboxylic acids

Ketones

- Oxidation of secondary (2°) alcohols.

Q.2 *Give the name and draw the structure of the alcohols used to make*

- CH_3CHO
- $C_2H_5COCH_3$
- *hexanal*
- *3-methylhexan-2-one*

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

OXIDATION

- provides a way of differentiating between aldehydes and ketones
- mild oxidising agents are best
- aldehydes are easier to oxidise
- powerful oxidising agents can oxidise ketones to a mixture of carboxylic acids

ALDEHYDES **easily oxidised to acids** *e.g.* $RCHO_{(l)} + [O] \longrightarrow RCOOH_{(l)}$

$CH_3CHO_{(l)} + [O] \longrightarrow CH_3COOH_{(l)}$

KETONES **only oxidised under vigorous conditions** to acids with fewer carbon atoms.

e.g. $C_2H_5COCH_2CH_{3(l)} + 3\,[O] \longrightarrow C_2H_5COOH_{(l)} + CH_3COOH_{(l)}$

Differentiation

- to tell an aldehyde from a ketone you need a mild oxidising agent ...

Tollen's Reagent

- **ammoniacal silver nitrate** - contains the diammine silver(I) ion - $[Ag(NH_3)_2]^+$
- acts as a mild oxidising agent and will oxidise aldehydes but not ketones
- the silver(I) ion is reduced to silver

  $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$
- the test is known as THE SILVER MIRROR TEST

Fehling's Solution

- **contains copper(II) ions** complexed with tartrate ions giving a blue solution
- on warming, it will oxidise aliphatic (but not aromatic) aldehydes
- copper(II) is reduced and a **red precipitate** of copper(I) oxide, Cu_2O, is formed

The silver mirror test is the better alternative as it works with all aldehydes.

IDENTIFICATION

Theory Identifying an aldehyde or a ketone needs a two-step test ...

1 prove it is a carbonyl compound
2 test with Tollen's Reagent ; aldehydes produce a silver mirror, ketones don't.

Carbonyl

- a characteristically strong peak around 1400-1600 cm^{-1} in the **infra red spectrum**

then

Aldehyde

- Silver mirror with ammoniacal silver nitrate - Tollen's Reagent
- Red precipitate with Fehling's Solution - aliphatic aldehydes only

Ketones

- No reaction with Tollen's Reagent or Fehling's Solution.

REDUCTION

Method 1

Reagent sodium tetrahydridoborate(III) (sodium borohydride), $NaBH_4$

Conditions aqueous or alcoholic solution

Mechanism Nucleophilic Addition (also reduction as it is addition of H^-)

Nucleophile H^- (hydride ion)

Product(s) Alcohols :- Aldehydes are REDUCED to primary (1°) alcohols.
Ketones are REDUCED to secondary (2°) alcohols.

Equation(s)

$$CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$$

$$CH_3COCH_3 + 2[H] \longrightarrow CH_3CHOHCH_3$$

Note $NaBH_4$ doesn't reduce C=C bonds

e.g. $CH_2=CHCHO + 2[H] \longrightarrow CH_2=CHCH_2OH$

Q.3 *Draw a diagram to indicate the bonding in $NaBH_4$. What shape is it ?*

Method 2

Reagent hydrogen

Conditions catalyst - nickel or platinum

Reaction type Hydrogenation

Product(s) Alcohols :- Aldehydes are REDUCED to primary (1°) alcohols.
Ketones are REDUCED to secondary (2°) alcohols.

Equation(s)

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

$$CH_3COCH_3 + H_2 \longrightarrow CH_3CHOHCH_3$$

Note Hydrogen also reduces C=C bonds

e.g. $CH_2=CHCHO + 2H_2 \longrightarrow CH_3CH_2CH_2OH$