FACTFILE:
GCE CHEMISTRY
4.7 ALDEHYDES AND KETONES

Learning Outcomes

Students should be able to:

4.7.1 recall the molecular and structural formulae of aldehydes and ketones, including branched structures, with up to six carbon atoms in the main chain;

4.7.2 explain the boiling points and solubility of aldehydes and ketones by making reference to intermolecular forces;

4.7.3 recall that aldehydes and ketones can be prepared from the corresponding primary or secondary alcohol using a suitable oxidising agent

4.7.4 recall the reaction of aldehydes and ketones with hydrogen cyanide;

4.7.5 describe the mechanism for the nucleophilic addition reaction of hydrogen cyanide and propanone;

4.7.6 explain why racemic mixtures can be produced when hydrogen cyanide reacts with aldehydes and ketones;

4.7.7 recall the reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine;

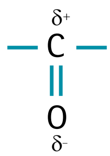
4.7.8 recall the preparation of 2,4-dinitrophenylhydrazones for identification purposes with reference to melting point determination;

4.7.9 recall that aldehydes and ketones can be distinguished using acidified potassium dichromate(VI), Fehling's solution and Tollens' reagent (with Fehling's solution and Tollens' reagent viewed as Cu^{2+} and Ag^{+} respectively);

4.7.10 recall that aldehydes and ketones can be reduced using lithium tetrahydridoaluminate(III) (lithal);

Nomenclature

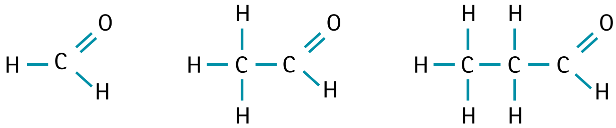
The functional group present in both aldehydes and ketones is the carbonyl group C=O which is polar.

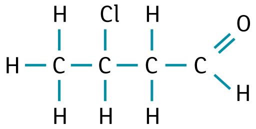


Aldehydes

The carbonyl group is always at the end of the chain in aldehydes and so a positional number is not needed. The names of aldehydes are based on the carbon skeleton, with the ending changed to –anal.

methanal ethanal propanal



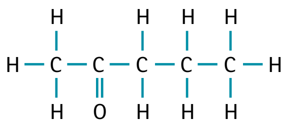


This is 3-chlorobutanal, the C=O is at the end of the chain in position1,hence it is an aldehyde the chloro group is on position 3

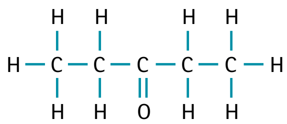
Ketones

The names of ketones are based on the carbon skeleton, with the ending changed **to –anone**. The carbonyl group can be at any position on the chain, except for the end hence propanone is the simplest ketone. A number for the position of the CO group is needed from 5 carbon atoms upwards.

pentan-2-one



pentan-3-one



Physical properties

1. The smaller aldehydes and ketones are soluble in water. This is due to hydrogen bonding between polar H of water and the lone pair on the oxygen of the carbonyl group.

   Solubility decreases as chain lengths increase as the longer hydrocarbon parts of the molecules start to get in the way. By forcing themselves between water molecules, they break the relatively strong hydrogen bonds between water molecules and so solubility decreases.

2 Aldehydes and ketones have van der Waals' forces and dipole dipole attractions between the molecules. This means that the boiling points will be higher than those of similarly sized hydrocarbons - which only have van der Waals' forces between the molecules. Boiling points increase as the molecules get bigger – this is because the bigger the molecule, the greater the number of electrons and the stronger the van der Waals' forces between the molecules .

Oxidation

Aldehydes and ketones are the products of the oxidation of alcohols. Aldehydes can be oxidised into carboxylic acids, and ketones cannot be oxidised.

primary alcohol $\xrightarrow{[O]}$ aldehyde $\xrightarrow{[O]}$ carboxylic acid

secondary alcohol $\xrightarrow{[O]}$ ketone $\xrightarrow{[O]}$ no further oxidation

1. Oxidation using acidified potassium dichromate(VI)
   The **orange** dichromate(VI) ion is reduced to the **green** chromium(III) ion, Cr^{3+} by the aldehyde:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The oxidising agent is represented by [O]

Example: Oxidation of an aldehyde
Condition: warm with acidified potassium dichromate(VI) solution.

CH_3CHO	+ [O] →	CH_3COOH
ethanal		ethanoic acid
(aldehyde)		(carboxylic acid)

Observation: orange solution changes to green solution.

2. Oxidation by Fehling's solution and Tollens' reagent.

Fehling's solution and Tollens' reagent are mild oxidising agents which are used to distinguish between aldehydes and ketones. Aldehydes are oxidised and ketones are not.

Solution	Method	Result	Equation
Fehling's solution	Add a few drops of the unknown solution to 1cm^3 of freshly prepared Fehling's solution reagent in a test tube. *Warm* in a water bath	If the unknown is an aldehyde a red ppt occurs. Solution remains blue for a ketone.	$Cu^{2+} + e^- \rightarrow Cu^+$
Tollens' reagent	Add a few drops of the unknown solution to 1 cm^3 of freshly prepared Tollens' reagent in a clean test tube. *Warm* in a water bath.	If the unknown is an aldehyde a silver mirror occurs on the inside surface of the test tube. Solution remains colourless for a ketone.	$Ag^+ + e^- \rightarrow Ag$

Tollens' reagent produces a silver mirror on

warming with an aldehyde.
Fehling's solution produces a red ppt when warmed with an aldehyde.

Preparation of aldehydes and ketones.

Aldehydes can be prepared by oxidation of the primary alcohol. When oxidising the primary alcohol it is important that the apparatus used is that of distillation. When ethanol is heated with the acidified dichromate oxidising agent it is oxidised into ethanal (aldehyde) which vaporises and moves into the condenser. If reflux was used the aldehyde would still be in contact with the oxidising agent and would be oxidised further to the carboxylic acid.

Ketones are prepared by the oxidation of a secondary alcohol.

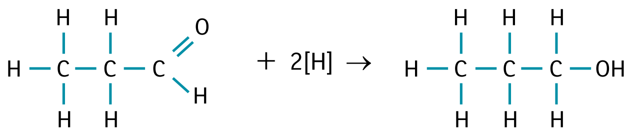
Reduction

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols, using the reducing agent using lithium tetrahydridoaluminate(III) (lithal) $LiAlH_4$. In equations the reducing agent is represented by [H]

aldehyde $\xrightarrow{[H]}$ **primary alcohol**

$$CH_3CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2OH$$

propanal aldehyde → propan-1-ol primary alcohol



Conditions: $LiAlH_4$ in dry ether.

ketone $\xrightarrow{[H]}$ **secondary alcohol**

$$CH_3COCH_2CH_3 + 2[H] \rightarrow H_3CCH(OH)CH_2CH_3$$

propanone ketone → propan-2-ol secondary alcohol

Conditions: $LiAlH_4$ in dry ether as opposed tgo just in ether.

Nucleophilic addition reactions

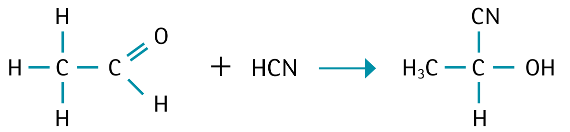
The carbonyl group is unsaturated and can undergo addition reactions The carbonyl group is also polar and the carbon δ+ is susceptible to attack by nucleophiles. Hence aldehydes and ketones take part in nucleophilic addition reactions.

A nucleophile is a lone pair donor. It is an atom or group which is attracted to an electron deficient centre, where it donates the lone pair to form a new covalent bond.

An addition reaction is one in which the pi bond of the double bond is broken and species are added

Reaction of aldehydes and ketones with hydrogen cyanide

In this reaction a hydroxynitrile is produced.



ethanal (aldehyde) | hydrogen cyanide | 2-hydroxypropanenitrile (hydroxynitrile)

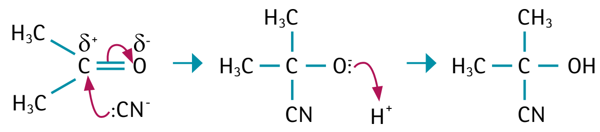
When naming hydroxynitriles, the carbon with nitrogen attached is always counted as the first carbon in the chain.

propanone (ketone) | hydrogen cyanide | 2-hydroxy-2-methylpropanenitrile (hydroxynitrile)

Condition: add dilute acid to an aqueous solution of potassium cyanide to generate hydrogen cyanide in the reaction mixture.

Mechanism

The mechanism is nucleophilc addition.
The cyanide ion is the nucleophile.



Remember that in the formation of a covalent bond the curly arrow starts from a lone pair or from another covalent bond. In the breaking of a covalent bond the curly arrow starts from the bond.

Aldehydes and unsymmetrical ketones form mixtures of enantiomers when they react with hydrogen cyanide.

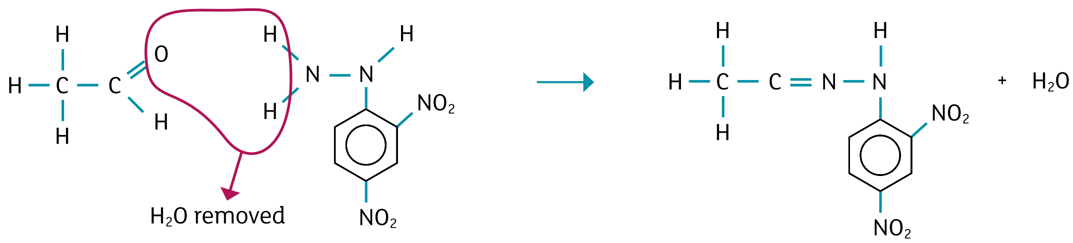
- All aldehydes produce a racemic mixture in this reaction. For example the reaction of ethanal with potassium cyanide produces 2-hydroxypropanenitrile which is optically inactive because a racemic mixture – a 50/50 mixture of the two optical isomers is formed. A racemic mixture occurs because the carbonyl bond is planar and the cyanide ion can attack the carbon atom equally from either side.
- Unsymmetrical ketones eg $CH_3COCH_2CH_3$ will produce a racemic mixture.
- Symmetrical ketones eg CH_3COCH_3 produce a product which does not have an asymmetric carbon and is optically inactive.

CONDENSATION REACTIONS with 2,4-dinitrophenylhydrazine

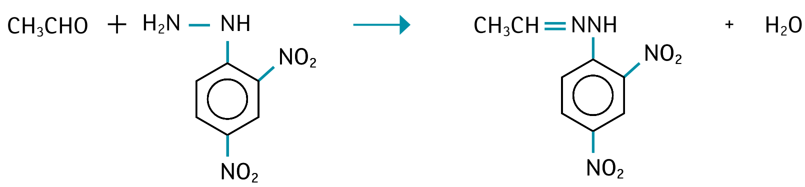
A condensation reaction is one in which the elements of water are removed.

In this reaction a 2,4-dinitrophenylhydrazone is produced.

eg. ethanal + 2,4-dinitrophenylhydrazine → ethanal-2,4-dinitrophenylhydrazone + water



A typical equation is shown below:



Condition: room temperature,
2,4-dinitrophenylhydrazine solution in acid

Observations: orange/ yellow precipitates are produced

This reaction produces a 2,4-dinitrophenylhydrazone which is named by putting the name of the organic compound in front. Aldehydes and ketones are often liquids and difficult to identify – so they are reacted with 2,4-dinitrophenylhydrazine. Solid crystals of the 2,4-dinitrophenylhydrazone are formed and the melting point can be found (after purification by recrystallisation) and compared to a data book to identify the original aldehyde and ketone.

Laboratory preparation of 2,4-dinitrophenylhydrazones

1. Place 5 cm^3 of 2,4-dinitrophenylhydrazine solution (Brady's reagent) in a suitable container.
2. Add some drops of the test liquid eg. propanal or the test solid dissolved in ethanol.
3. If crystals do not form add some dilute sulfuric acid and warm the mixture.
4. Cool the mixture in iced water.
5. Filter off the crystals using suction filtration.
6. Recrystallise.
7. Determine the melting point.

Recrystallisation method

1. Dissolve the impure crystals in the minimum volume of hot solvent.
2. Filter when hot by gravity filtration, using a hot funnel, to remove insoluble impurities.
3. Cool and allow to crystallise - the impurities are left in the solution.
4. Dry the crystals between filter paper/in a cool oven/in a dessicator.

Suction filtration method

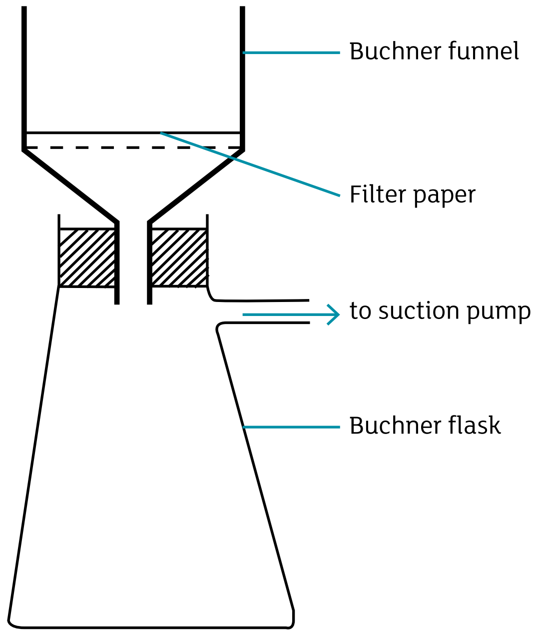
1. Place filter paper in a Buchner funnel.
2. Place Buchner funnel in a Buchner flask.
3. Attach the flask to a suction pump and suck air through the flask.

This is faster than normal filtration and the solid is left quite dry.

Melting point method

1. Place some solid in a capillary tube which is sealed at one end.
2. Heat slowly (using melting point apparatus).
3. Record the temperature at which the solid starts and finishes melting.
4. Compare the temperature to data book/tabulated values.

A solid which melts within a range of 1-2 °C indicates that the solid is pure.



Apparatus for suction filtration

Revision Questions

1 Which one of the following compounds produced a silver mirror when heated with Tollens' reagent?

A CH_3COCH_3

B CH_3CO_2H

C CH_3CHO

D $CH_3CO_2CH_3$ [1]

2 An organic compound, X, gives an orange crystalline product with 2,4-dinitrophenylhydrazine, but does not give a precipitate on heating with Fehling's solution. Which one of the following formulae is that of X?

A HCHO

B $C_6H_5CH_2CHO$

C CH_3COCH_3

D $CH_3CH_2CO_2H$ [1]

3 a) Name the compound CH_3CHO and state its functional group.

.... [1]

b) Name and outline a mechanism for the reaction of CH_3CH_2CHO with HCN.

.... [4]

c) State and explain how a racemic mixture is formed in this reaction.

....

....

.... [2]

4 Some Scotch whiskies have the fragrance of cut grass.
This smell is attributed to *cis* hex-3-enal, an unsaturated aldehyde

a) Suggest a structure for *cis* hex-3-enal.

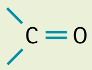
[2]

b) What would be observed if *cis* hex-3-enal is warmed with Fehling's solution?

....

.... [2]

c) Write the equation for the reaction between cis hex-3-enal and 2,4-dinitrophenylhydrazine.
Represent the structure of cis hex-3-enal as.



There is no requirement to draw the full structure.

[3]