- write equations, state conditions, and predict products to represent the reactions of alcohols, including but not limited to:
  – combustion
  – dehydration
  – substitution with HX
  – oxidation

- investigate the products of the oxidation of primary and secondary alcohols

Alcohol Reactions

- Alcohols can undergo a variety of chemical reactions including combustion, dehydration, substitution, and oxidation.

COMBUSTION OF ALCOHOLS

- Alcohols can react with oxygen to produce carbon dioxide and water in a complete combustion reaction.

  - For example, here is the complete combustion of ethanol in an exothermic reaction. The molar enthalpy of combustion of ethanol is $1370\ kJ/mol$ – familiarise yourself with this value as it will come up frequently in exams.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 3H_2O_{(g)} + 2CO_{2(g)}$$

- If there is insufficient oxygen present, incomplete combustion occurs which results in a lower energy produced per mole and unwanted products such as soot (carbon) and carbon monoxide.

  - For example, the incomplete combustion of ethanol may produce both soot and carbon monoxide:

$$2C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 6H_2O_{(l)} + 2CO_{(g)} + 2C_{(s)}$$

DEHYDRATION OF ALCOHOLS

- Alcohols can undergo dehydration when heated with **concentrated** sulfuric acid to produce an *alkene*.
- This involves chemically removing water from the alcohol molecule.
  - For example, the butan-2-ol is dehydrated to form but-1-ene:

$$C_4H_9OH_{(l)} \xrightarrow{\text{conc. } H_2SO_4} C_4H_{8(g)} + H_2O_{(l)}$$

- Covered later in this module are hydration reactions, such as the hydration of ethene (C_2H_4) to form ethanol (C_2H_5OH). Such reactions also the require the use of a catalyst such as **dilute** sulfuric acid.
- An easy acronym to memorise the catalyst for each of these two reactions is:
  - CD – Concentrated / Dehydration
  - HD – Hydration / Dilute

SUBSTITUTION OF ALCOHOLS WITH HYDROGEN HALIDES

- Alcohols can undergo substitution reactions with hydrogen halides, such as hydrogen chloride or hydrogen bromide, to form alkyl halide and water.

$$R-OH + H-X \rightarrow R-X + H_2O$$

**An alkyl halide is commonly referred to as a halogenated alkane.*

- For example, propan-2-ol reacts with hydrogen chloride to form 2-chloropropane and water:

$$C_3H_7OH_{(l)} + HCl_{(g)} \rightarrow C_3H_7Cl_{(l)} + H_2O_{(l)}$$

OXIDATION OF ALCOHOLS

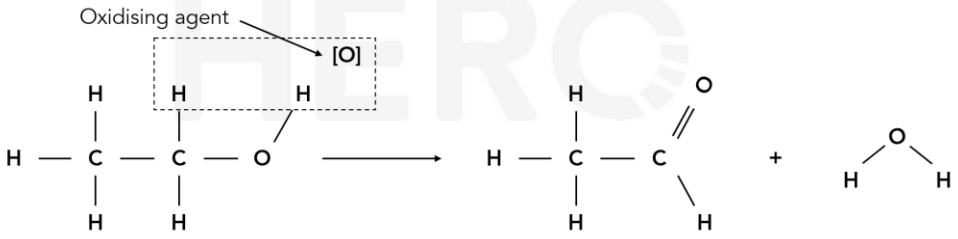
- Alcohols readily undergo oxidation with strong oxidising agents such as *acidified* potassium permanganate ($KMnO_4^-$) or sodium dichromate ($Na_2Cr_2O_7$) solutions.
    - The oxidising agents are acidified to provide a source of H^+ ions that are required for the oxidation reaction to take place. The H^+ *must* be included on top of the reaction arrow for an oxidation reaction.
- This occurs in a redox reaction where the alcohol undergoes oxidation (loses electrons) and the oxidising agent undergoes reduction (gains electrons).
- While complicated half reactions can be written for oxidation reactions, in organic chemistry, simplified versions are often used which concentrate on what is happening to the organic substances (in this case, the alcohol).
- Notably, a shorthand used to represent the oxygen atom from the oxidising agent is $[O]$.

COLOUR CHANGE DURING OXIDATION

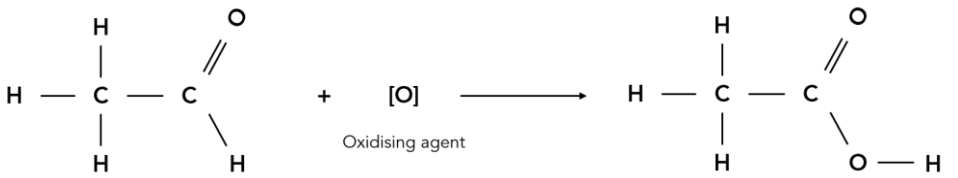
- The oxidation of each type of alcohol will be covered in detail over the following pages, but it is important to note the colour changes that you can expect to observe during such a reaction.
- The colour change will vary depending on the oxidising agent that is selected. You can be expected to be examined on this or require this knowledge for problem solving.
- For potassium permanganate ($KMnO_4^-$), the initially purple colour will become colourless when it oxidises.
- For sodium dichromate ($Na_2Cr_2O_7$), the initially orange colour will become green when it oxidises.

OXIDATION OF PRIMARY ALCOHOLS

- Primary alcohols are first oxidised to form aldehydes which is then further oxidised to form carboxylic acids.
    - Aldehydes contain the carbonyl functional group ($C = O$)
    - Carboxylic acids contain the carboxyl functional group ($-COOH$)
- The final product of the oxidation of primary alcohol depends on the reaction conditions.
- The partial oxidation to form aldehydes is only possible in an excess of alcohol, where the aldehyde is distilled off as soon as it forms (otherwise it will further oxidise to form carboxylic acid).
    - Excess of alcohol means there is not enough oxidising agent to carry out the second stage of oxidation to form carboxylic acids.
    - Distilling the aldehydes removes it from the reaction system to prevent further oxidation.
- As an example, consider the oxidation of ethanol:
    - First stage: $C_2H_5OH_{(l)} + [O] \xrightarrow{H^+/MnO_4^-} CH_3CHO_{(l)} + H_2O_{(l)}$

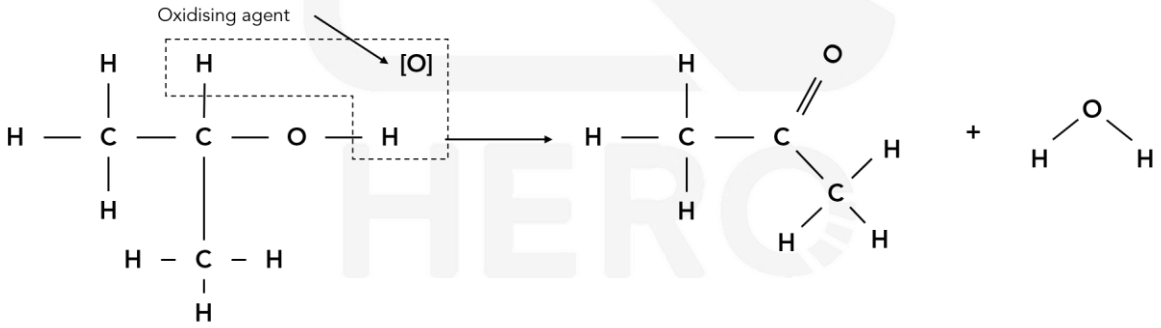


    - Second stage: $CH_3CHO_{(l)} + [O] \xrightarrow{H^+/MnO_4^-} CH_3COOH_{(aq)}$



OXIDATION OF SECONDARY ALCOHOLS

- Secondary alcohols are oxidised to form ketones which cannot be further oxidised, unlike aldehydes.
    - Ketones contain the carbonyl functional group ($C = O$), just like aldehydes.
    - For aldehydes, the $C = O$ group is positioned on the terminal carbon while for a ketone, the $C = O$ group is positioned in the middle of the carbon chain.
    - Aldehydes and ketones will be covered in more detail in the next submodule.
- The reaction conditions, therefore, have no effect on the product formed.
- As an example, consider the oxidation of propan-2-ol:
    - $C_3H_7OH_{(l)} + [O] \xrightarrow{H^+/MnO_4^-} CH_3COCH_{3(aq)} + H_2O_{(l)}$



Explain why secondary alcohols do not undergo further oxidation.

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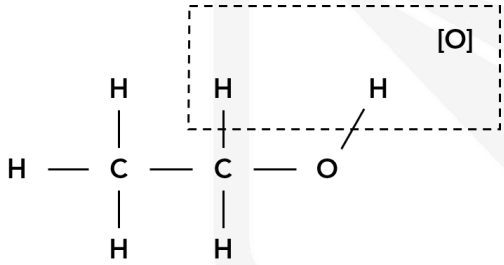
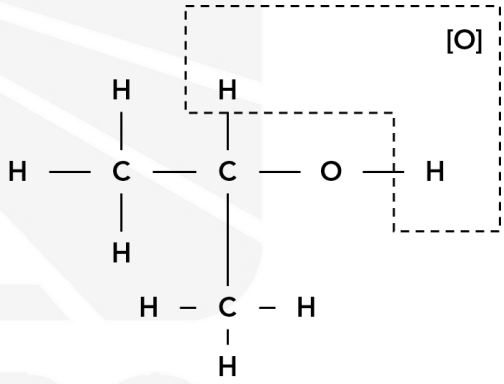
OXIDATION OF TERTIARY ALCOHOLS

- Tertiary alcohols do not undergo oxidation.
- As per the dotted outline in the oxidation of primary and secondary alcohols, the oxidising agent removes the H atom from the $-OH$ group and another H atom from the carbon atom attached to the hydroxyl group.
- Those two hydrogens must be removed in order to set up a $C = O$ double bond.
- However, tertiary alcohols do not have the H atom attached to the carbon atom with the hydroxyl group. Hence, oxidation cannot occur.
- Below is the structural formulae for different types of alcohol for a comparison:

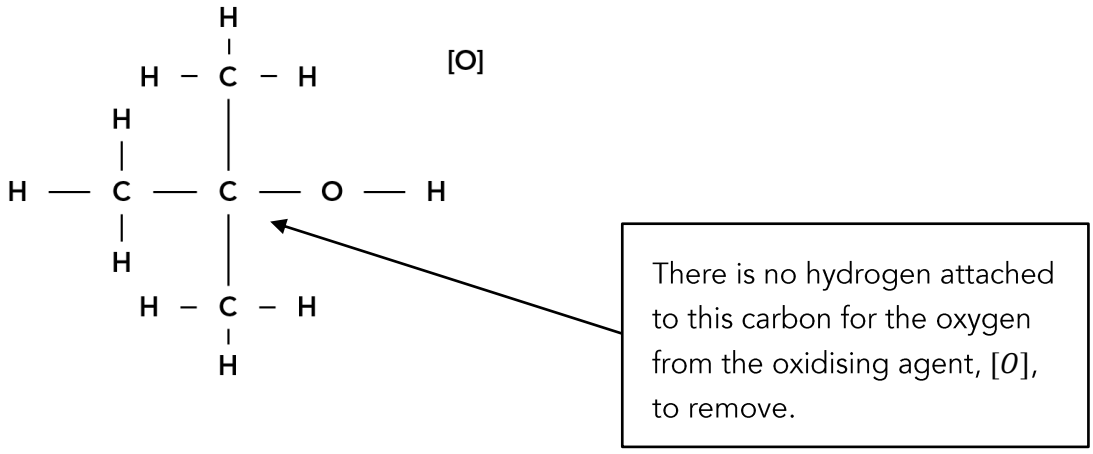
Primary alcohol



Secondary alcohol



Tertiary alcohol

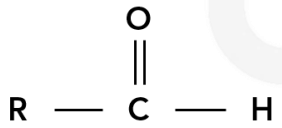


OXIDATION: PRIMARY ALCOHOL VS. SECONDARY ALCOHOL

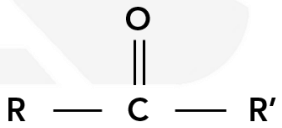
- This section is to deepen student's understanding for **why** primary alcohols will oxidise to form aldehydes while secondary alcohols will oxidise to form ketones.
- The study of the naming, functional group and structural arrangement of aldehydes and ketones will be studied in much greater detail in OC Theory Booklet 3.
- However, for illustrative purposes, it is necessary to have a basic understanding for the difference between the two.
- While they both possess the carbonyl functional group ($C = O$) the difference is:
  - Aldehydes: $C = O$ is positioned at the **end** of the carbon chain
  - Ketones: $C = O$ is positioned in the **middle** of the carbon chain

General Formula

Aldehyde:

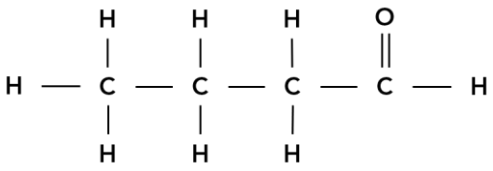


Ketone:

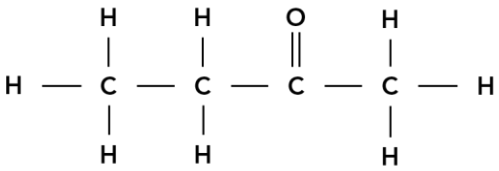


Example

Butanal:

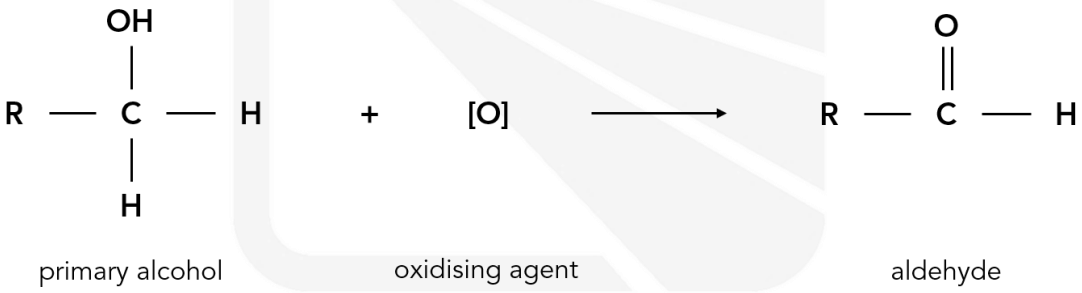


Butan-2-one:



- Similarly, when we consider the position of the functional $-\boldsymbol{OH}$ group in a primary and secondary alcohol we should recall that:
  - Primary: $-\boldsymbol{OH}$ is positioned at the **end** of the carbon chain
  - Secondary: $-\boldsymbol{OH}$ is positioned at the **middle** of the carbon chain
- During oxidation, the oxidising agent $[O]$ will form the carbonyl group at the same carbon that is attached to the $-OH$ group.
- Structurally, we can now understand why primary alcohols will only oxidise to form aldehydes while secondary alcohols will only oxidise to form ketones.

Oxidation of Primary Alcohol to Form Aldehyde



Oxidation of Secondary Alcohol to Form Ketone