Oxidation, purification and practical techniques

Reading

- ***A Level Chemistry for OCR textbook – Read pages 226 – 227***

Notes

- ***Copy the notes below into your exercise book.***

Oxidation of alcohols

Oxidation reactions require an oxidising agent such as acidified potassium dichromate:
Dilute H_2SO_4 / $K_2Cr_2O_7$ (can write $H^+/Cr_2O_7^{2-}$)
If the alcohol is oxidised a colour change from orange to green occurs.

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

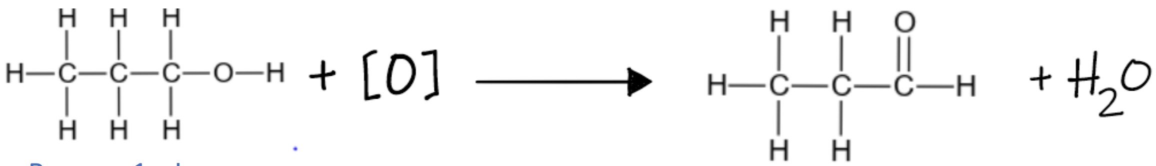
1° alcohols are oxidised to either aldehydes or carboxylic acids.
2° alcohols are oxidised to ketones.
3° alcohols **<u>DO NOT</u>** undergo oxidation reactions (No colour change).

This oxidation can test for the presence of 1° and 2° alcohols.

<u>Forming aldehydes</u>

Gentle heating of a primary alcohol with acidified potassium dichromate will produce an aldehyde. The product must be distilled off as it is being formed – this prevents the carboxylic acid forming.

E.g.



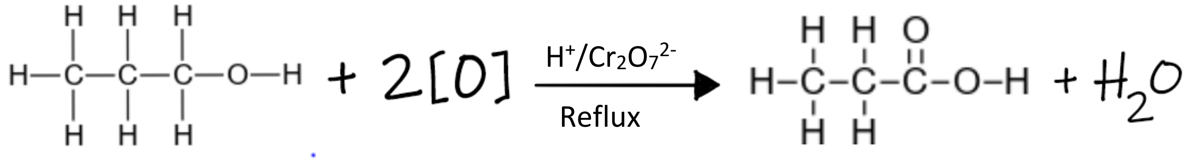
Propan-1-ol (balance as a single 'O' atom) Propanal

E.g. $CH_3CH(CH_3)CH_2OH + [O] \rightarrow CH_3CH(CH_3)CHO + H_2O$

<u>Forming carboxylic acids</u>

Primary alcohol is heated strongly under reflux with excess acidified potassium dichromate.

E.g.



Propanoic acid

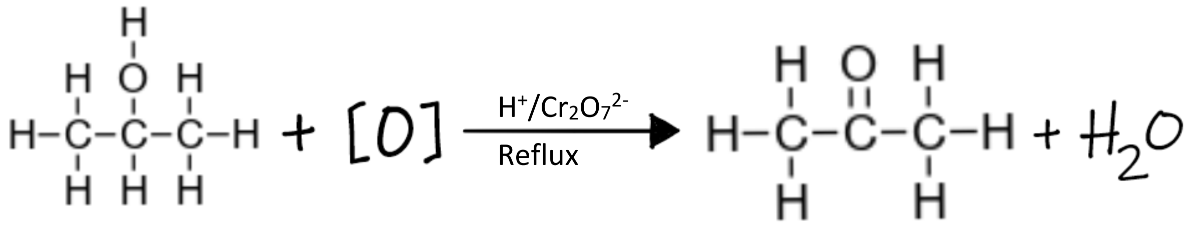
E.g. $CH_3(CH_2)_2C(CH_3)_2CH_2OH + 2[O]\ CH_3(CH_2)_2C(CH_3)_2COOH + H_2O$

Reflux – Continuous boiling and condensing of a reaction mixture to ensure that the reaction takes place without the contents boiling away.

<u>Forming ketones</u>

Secondary alcohols are oxidised to form ketones. This is done under reflux with acidified potassium dichromate.

E.g.



E.g. $CH_3CHOHCH_2C(CH_3)_3 + [O] \rightarrow CH_3COCH_2C(CH_3)_3 + H_2O$

Textbook work

- ***Write down any additional notes from pages 226 - 227***
- ***Answer the summary questions on page 228***
- ***Check your answers using the mark scheme on page 571***

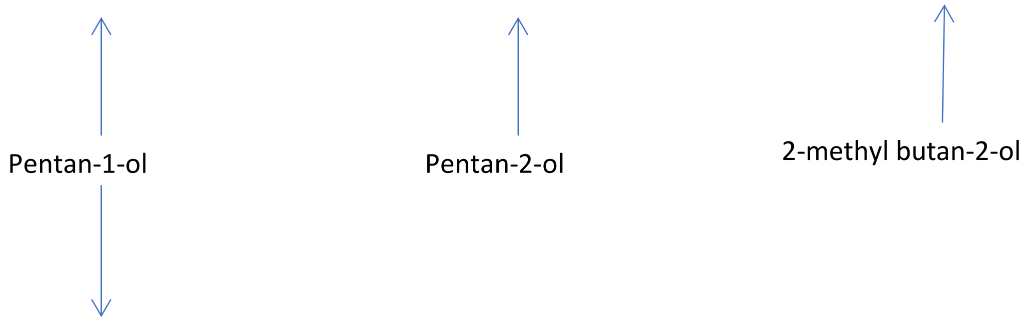
Worksheet

- ***Complete the worksheet – 'Oxidation of alcohols' (I gave this to you last lesson but I have inserted it below for those of you who weren't present last lesson or have lost it…!)***
- ***Using a green pen, mark the worksheet with the mark scheme below.***

Oxidation of alcohols

Primary, secondary and tertiary alcohols

Complete the diagram showing the different products of oxidation: Include the reagents, conditions, and products.



Equations of oxidation

Write balanced equations for the **full** oxidation of…

Pentan-2-ol: ____

Butan-2-ol: ____

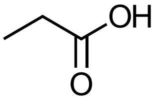
Propan-1-ol: ____

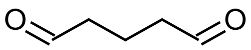
Propan-2-ol: ____

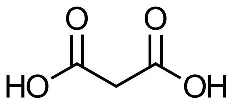
Methanol: ____

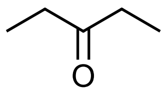
Hexane-1,6-diol: ____

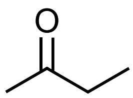
Identify the original alcohol used to make…











Oxidation methods

- How do the conditions of oxidising affect the chemical produced?

  ____

  ____

- Why do the conditions of oxidising affect the chemical produced?

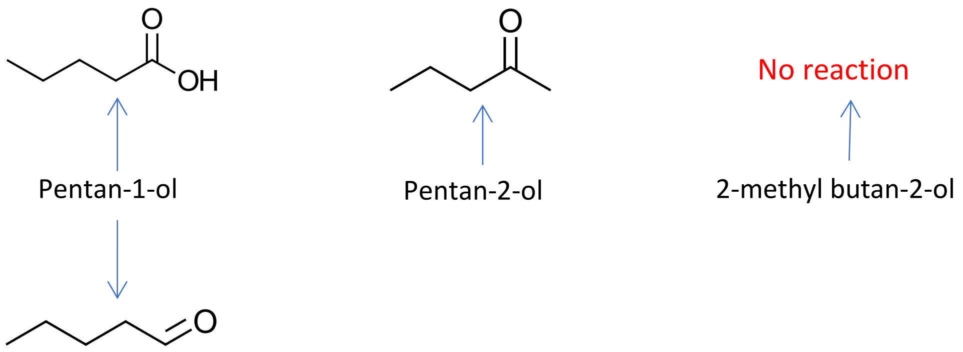
  ____

  ____

Oxidation of alcohols Mark Scheme

Primary, secondary and tertiary alcohols

Complete the diagram showing the different products of oxidation: Include the reagents, conditions, and products.



Equations of oxidation

Write balanced equations for the **full** oxidation of…

Pentan-2-ol: $CH_3CH_2CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2CH_2COCH_3 + H_2O$

Butan-2-ol: $CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O$

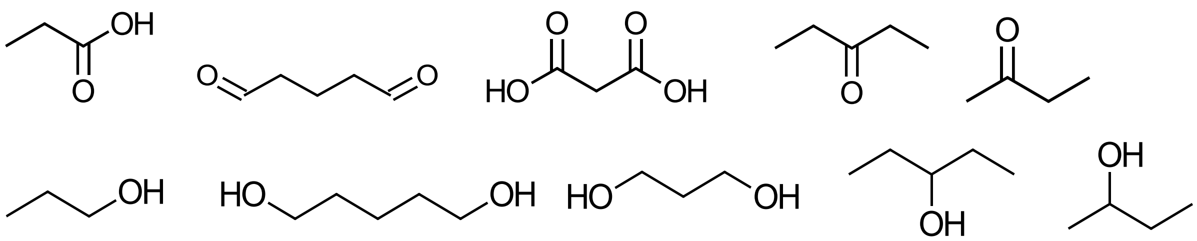
Propan-1-ol: $CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$

Propan-2-ol: $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$

Methanol: $CH_3OH + [O] \rightarrow HCOOH + H_2O$

Hexane-1,6-diol: $CH_2(OH)(CH_2)_4CH_2OH + 4[O] \rightarrow HOOC(CH_2)_4COOH + 2H_2O$

Identify the original alcohol used to make…



Oxidation methods

- How do the conditions of oxidising affect the chemical produced?

  Distillation produces aldehydes during oxidation of primary alcohols; reflux produces carboxylic acids.

- Why do the conditions of oxidising affect the chemical produced?

  Reflux prevents the aldehyde escaping the reaction mixture and so the reaction goes to completion.

Reading

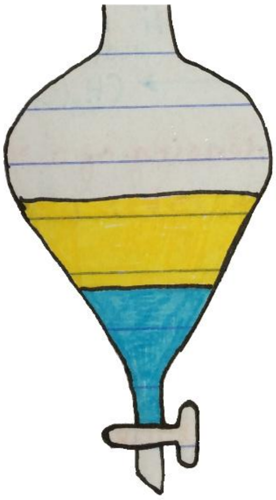
- ***A Level Chemistry for OCR textbook – Read pages 240 – 243***

Notes

- ***Copy the notes below into your exercise book.***

Purifying organic products and other practical basics

Immiscible: Not forming a homogeneous mixture when mixed.



When producing an organic substance, water may also be produced which may need to be removed. It is removed using a separation funnel.

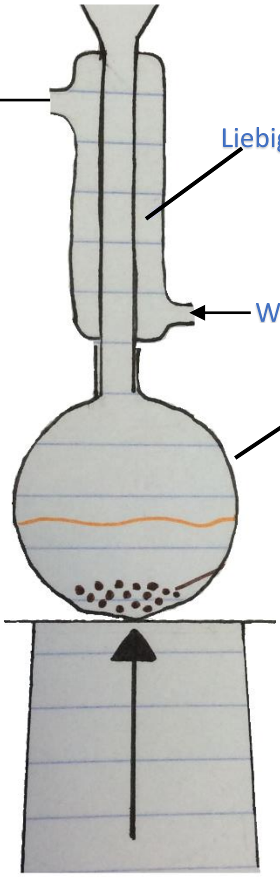
Identify the aqueous layer by adding water, this will cause the aqueous layer to get larger.

- Pour in liquids, place a stopper in the top and invert to mix.
- Layers settle, and identify aqueous layer.
- Remove stopper and turn tap to empty one layer out into conical flask.
- Empty out other layer into a different flask.

<u>Impurities – removal</u>

- Acid impurities
  - Add Na_2CO_3(aq) to separating funnel containing organic layer.
  - Invert with stopper in; release CO_2 by inverting and turning tap.
  - Remove aqueous layer.
- Drying organic layer
  - Add an anhydrous inorganic salt (takes up water to become hydrated) to conical flask.
    e.g. $CaSO_4$/$MgSO_4$ – general drying
    $CaCl_2$ – drying hydrocarbons
  - Add organic layer and swirl contents.
  - Add stopper and leave for 10 minutes.
  - If clumped together – add more drying agent until dispersed to a fine powder.
  - Decant liquid out.

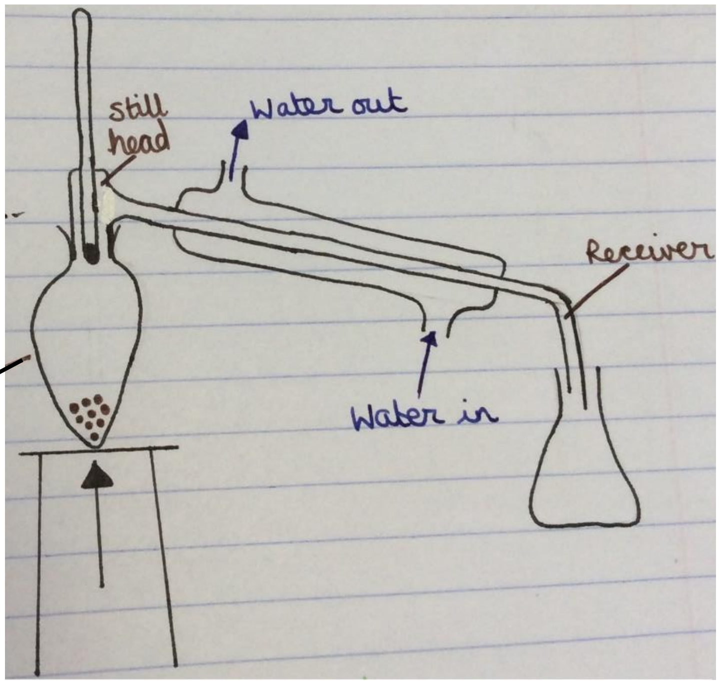
Reflux



A pear shaped flask is also used.

Distillation

Evaporation followed by condensation to allow the most volatile compound to be separated.



Redistillation can be performed to ensure a purer product. A second distillation is carried out with a narrower boiling range of the product – the narrower the range, the purer the product.

Textbook work

- ***Write down any additional notes from pages 240 - 243***
- ***Answer the summary questions on page 243***
- ***Check your answers using the mark scheme on page 572***

Worksheet

- ***Complete the worksheet – 'Separation anxiety' (I gave this to you last lesson but I have inserted it below for those of you who weren't present last lesson or have lost it…!)***
- ***Using a green pen, mark the worksheet with the mark scheme below.***
- ***Complete the worksheet – 'Distillation and Reflux' (I gave this to you last lesson but I have inserted it below for those of you who weren't present last lesson or have lost it…!)***
- ***Using a green pen, mark the worksheet with the mark scheme below.***

Separation anxiety

1. A student has made an alcohol, hexan-2-ol, from an alkene. The student mixed sulfuric acid catalyst with the alkene, and then added water in excess. Hexan-2-ol is relatively insoluble in water.
    a. In which phase (aqueous or organic) of the reaction mixture will you find:
        i. Sulfuric acid? ____
        ii. Hexan-2-ol? ____
        iii. Excess water? ____
    b. The density of hexan-2-ol is 0.81 g cm^{-1}. The density of water is 1.00 g cm^{-1}. Which phase will be the upper phase in the separating funnel?

    ____
    c. How might the student wash all aqueous impurities from the hexan-2-ol?

    ____
    d. How might the student dry the organic substance?

    ____
2. In the production of esters, ethanoic acid is reacted with ethanol to make ethyl ethanoate. After separation, there is still ethanoic acid left in the product.
    a. How should the acid impurity be removed?

    ____
    b. What potential safety hazards are associated with this approach? Explain how this might be mitigated.

    ____

    ____
3. A student is synthesising 1-bromopropane from an alcohol.
    a. Suggest the reagents and conditions required, including the starting material.

    ____
    b. Write an equation to show…
        i. How HBr is made in situ in this reaction.

        ____
        ii. The reaction with the alcohol and the HBr

        ____
    c. The starting material is miscible with water. Explain why this is, including a diagram.

    d. The product has a lower boiling point than the reactant. Explain why this is, referring to intermolecular forces in your answer.

    ____

    ____

    ____

e. Explain why this reaction produces an organic phase and an aqueous phase as its reaction mixture.

____

____

f. Suggest the identity of all possible compounds found in the aqueous phase from this reaction. Assume that the alcohol is the limiting reagent.

____

____

g. The student wants to separate the mixture using a separating funnel, but is unsure of which layer contains the organic product. How could the student tell which layer is aqueous and which is organic?

____

____

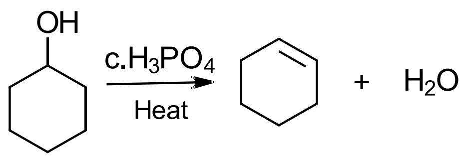
h. What further steps could be required to ensure that a pure dry organic product is isolated? Give the purpose of each step.

____

____

____

4. Study the reaction scheme below:



Boiling point of cyclohexanol: 161°C
Boiling point of cyclohexene: 83°C

Suggest a practical method to produce cyclohexene from cyclohexanol. Consider the following points.

- How you might set up any equipment to ensure completion of the reaction, and prevent loss of product.
- How you might separate the product from the reaction mixture.
- How you could ensure that the organic product is pure.

____

____

____

____

____

____

____

____

____

____

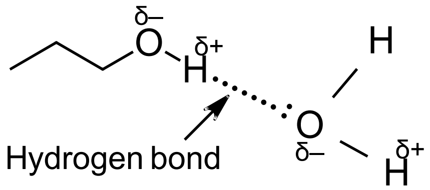
____

____

Separation anxiety- Answers

1.
    a.
        i. Aqueous
        ii. Organic
        iii. Aqueous
    b. Organic
    c. Remove the aqueous layer
       Add distilled water
       Stopper the flask and shake
       Remove the aqueous layer.
       Add organic layer to clean beaker.
    d. Shake with $CaSO_4$/$MgSO_4$

2.
    a. Add aqueous sodium carbonate
       Stopper the flask and shake
       Remove the aqueous layer
    b. Gas build-up could force the bung out. Open the tap every so often to release gas pressure.
3.
    a. Propan-1-ol, NaBr, H_2SO_4
    b.
        i. $NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$
        ii. $HBr + CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH_2Br + H_2O$
    c. Propan-1-ol forms hydrogen bonds



    d. Both molecules have **weak London forces**, however propan-1-ol forms **hydrogen bonds** which are much **stronger**, and these require **more energy** to overcome.

    e. The organic product does not form hydrogen bonds, and the other is water.

    f. NaBr (Ionic salt), HBr (acid), H_2SO_4 (Acid), H_2O, $NaHSO_4$ (Ionic salt). Alcohol is used up as it is limiting reagent.

    g. Add more distilled water and see which layer increases in size. This is the aqueous layer.

    h. Wash with distilled water.
       Remove aqueous layer.

Add organic layer to clean beaker.
Dry over $CaSO_4$/$MgSO_4$
Distil

4. The product and reactant are volatile, so a **reflux** will be required:
   Condenser inserted into round bottom flask.
   Phosphoric acid and cyclohexanol added to flask.
   Cold water supply to condenser.
   A suitable source of heat would be an **electric hotplate**, as alcohols and alkenes are flammable.
   i. Add the mixture to a separating funnel
      Remove the aqueous layer
      Shake with distilled water.
      Remove the aqueous layer.
      Add the organic layer to a clean beaker.
      Add $MgSO_4$/$CaSO_4$
      Filter
   ii. Using a clean flask, **distil** the product.
      Fix the condenser to a still head,
      Heat using a hotplate until the thermometer is close to the boiling point of the product.

Distillation and Reflux

1.
   a. Explain why alcohols generally have higher boiling points than aldehydes – Draw a diagram to support your answer.

   ____

   ____

   ____

   b. Explain why carboxylic acids have higher boiling points than aldehydes – Draw a diagram to support your answer.

   ____

   ____

   ____

   c. Explain why carboxylic acids have higher boiling points than alcohols.

   ____

   ____

   ____

2. Below are the boiling points of a selection of chemicals.

Molecule	Boiling point °C
Butan-1-ol	118
Butan-2-ol	74
Butanone	80
Butanoic acid	164
Butanal	75

In a reaction mixture containing butan-1-ol and $Cr_2O_7^{2-}/H^+$ there will be a mixture of reactants and products.

a. Identify **all** possible chemicals present in the mixture.

____

b. If the equipment was set up to distil the reaction mixture, what temperature would be set at the still head, and what would the first chemical to boil be?

____

c. What colour change would you observe?

____

d. Write an equation for the reaction.

____

e. What problems would you encounter using distillation to produce butanone?

____

3. What is the purpose of a reflux in the case of production of a carboxylic acid?

____

4. Explain, with the aid of a diagram where you would expect each of these chemicals in the reflux column, given that the water in the round bottom flask is *boiling* at ~100°C:

Ethanol (bp 86°C)

Ethanal (bp 20°C)

Ethanoic acid (bp 119°C)

Water (bp 100°C)

Potassium dichromate (bp 500°C)

____

____

____

____

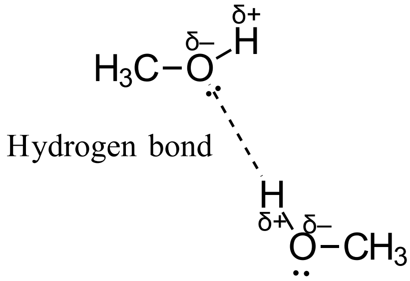
____

____

____

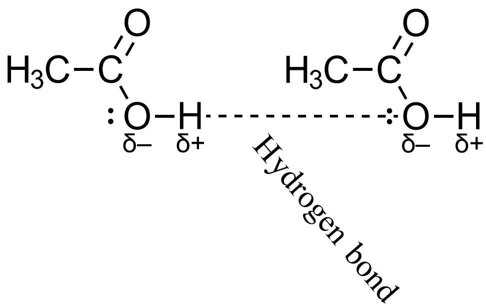
Distillation and Reflux- Answers

1.
    a. Alcohols form hydrogen bonds in addition to their London forces.



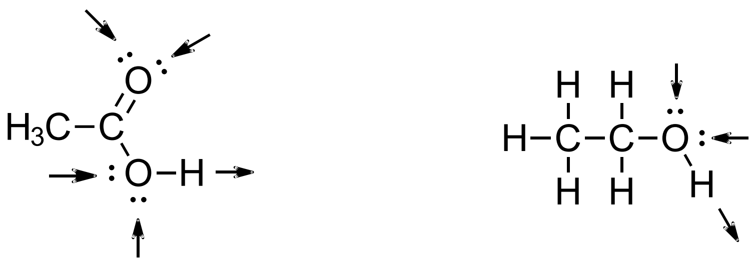
    Lone pairs, dipoles and dotted line required.

    b. Carboxylic acids form hydrogen bonds in addition to their London forces.



    Lone pairs, dipoles and dotted line required.

    c. Carboxylic acids have more sites that can hydrogen bond.



2.
    a. Butan-1-ol, butanal, butanoic acid, water, acidified potassium dichromate, Cr^{3+}
    b. 75°C. Butanal would be distilled first.
    c. Orange→green
    d. $CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2CHO + H_2O$
    e. Butanone and butan-2-ol have boiling points only 6°C apart. They may not separate well.
3. To ensure that the oxidation is complete.
4. The water, potassium dichromate and ethanoic acid will be mainly in the flask (Some ethanoic acid and water will evaporate). The higher up the column, the less ethanol there will be. The ethanal will be present throughout.