4.1.1 Basic concepts of organic chemistry

Definitions

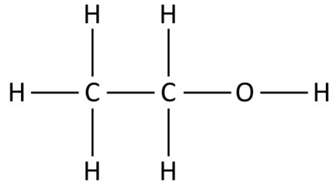
Term	**Definition**
Functional group	A group of atoms responsible for the characteristic reactions of a compound
Homologous series	A series of organic compounds having the **same functional group** but with **each successive member differing by CH_2**
Saturated	All carbon to carbon bonds are single bonds
Unsaturated	Contain carbon to carbon multiple bonds ($C=C$ or $C\equiv C$)
Hydrocarbons	Substances containing carbon and hydrogen atoms only
Isomerism	Compounds with the same molecular formula but different arrangements of atoms in space
Structural isomers	Compounds with the **same molecular formula** but **different structural formulae**

Basic definitions

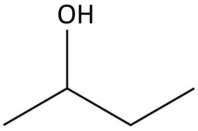
- Alkyl group
    - General formula C_nH_{2n+1}
    - Found on side chains of organic molecules
- Types of hydrocarbons
    - Aliphatic
        - A compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings
    - Alicyclic
        - An aliphatic compound arranged in non-aromatic rings with or without side chains
    - Aromatic
        - A compound containing **a benzene ring**
- Stem prefix

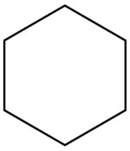
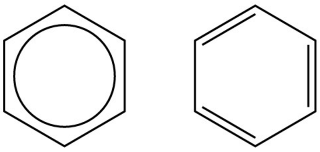
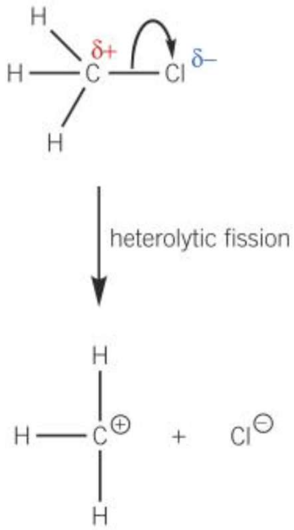
Number of carbon atoms	**Prefix**
1	Meth-
2	Eth-
3	Prop-
4	But-
5	Pen-
6	Hex-
7	Hept-
8	Oct-
9	Non-
10	Dec-

- Types of formulae (definition not required)
    - General formula
        - The simplest algebraic formula of a member of a homologous series
        - e.g. for an alkane: C_nH_{2n+2}
    - Structural formula
        - The minimal detail that shows the arrangement of atoms in a molecule
        - e.g. for butane: $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

  - Displayed formula
    - Shows the relative positioning of atoms and the bonds between them
    - e.g. for ethanol
      - 

$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

  - Skeletal formula
    - The simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups
    - e.g. for butan-2-ol
      - 

    - Cyclohexane
      - 
    - Benzene
      - 
- Types of covalent bond fission
  - Homolytic fission
    - **Each bonding atom receiving one electron** from the bonded pair forming 2 radicals
  - Heterolytic fission
    - **One bonding atom receiving both electrons** from the bonded pair
    - The atom that takes both electrons becomes a negative ion
    - The atom that does not take the electrons becomes a positive ion
    - e.g. $H_3C\text{-}Cl \rightarrow H_3C^+ + Cl^-$
- Radical
  - A species with **an unpaired electron**
  - Represented with a dot (•)
  - e.g. $H_3C\text{-}CH_3 \rightarrow H_3C\bullet + \bullet CH_3$
- Curly arrows
  - Showing the **movement of an electron pair**
  - Showing either heterolytic fission or formation of a covalent bond
  - 

- Types of reaction

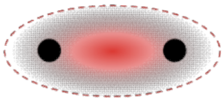
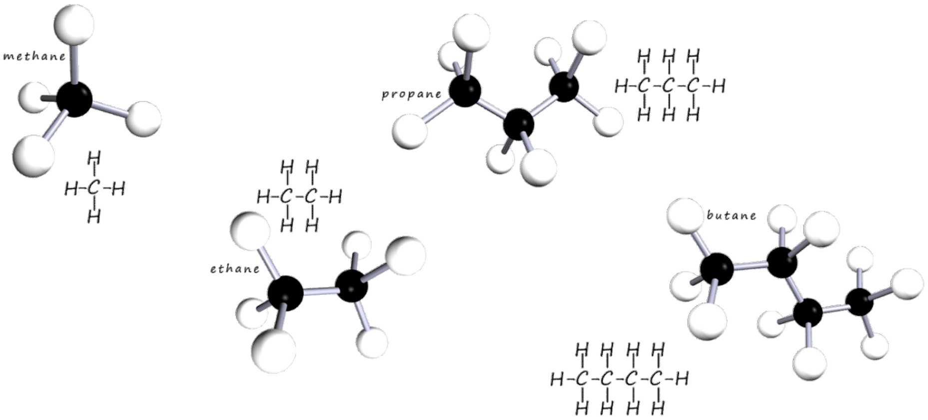
- Addition reaction
    - Two or more reactants join together to form one product
- Substitution reaction
    - An atom or group of atoms is replaced by a different atom or group of atoms
- Elimination reaction
    - Involves the removal of a small molecule from a larger one
    - One reactant molecule forms two products

4.1.2 Alkanes

Definitions

Term	Definition
Free radical	A species with an unpaired electron
Chain reaction	A reaction in which the propagation steps release new radicals that continue the reaction
Initiation	The first stage in a radical reaction in which radicals form when a covalent bond is broken by homolytic fission
Propagation	The steps that continue a free radical reaction, in which a radical reacts with a reactant molecule to form a new molecule and another radical, causing a chain reaction
Termination	The step at the end of a radical substitution when two radicals combine to form a molecule

Properties of alkanes

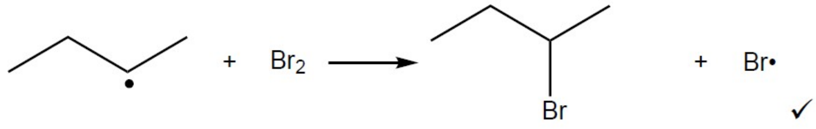
- Bonding in alkanes
  - Saturated hydrocarbons
  - Only carbon and hydrogen atoms joined together by single covalent bonds
  - Bond type = σ-bond (sigma bond)
    - σ-bond = **heads on** overlap of orbitals directly between the bonding atoms
    - One orbital from each bonding atom, each containing one electron
    - Positioned on a line directly between bonding atoms
    - 
  - Atoms can rotate freely around the σ-bond
- Shape of alkanes
  - Tetrahedral shape around each carbon atom, bond angle 109.5°
  - Each carbon atom surrounded by 4 bonded pairs in four σ-bonds
  - The electron pairs repel each other as far away as possible
  - 

- Effect of chain length on boiling points
  - Longer chain length = higher boiling point
  - Increased chain length = **greater surface area of contact** + more electrons
  - Stronger London forces
  - More energy is required to overcome the London forces
- Effect of branching on boiling points
  - More branching = lower boiling point
  - More branches = fewer surface area of contact → weaker London forces

  - The branches prevent the branched molecules getting as close together as straight-chain molecules → further decrease intermolecular forces
  - Less energy is required to overcome the London forces

Alkane reactions

- Reactivity of alkanes
  - Low reactivity
  - C-C and C-H σ-bonds are strong as they have a high bond enthalpy
  - C-C bonds are non-polar
  - C-H bond can be considered non-polar as the electronegativities of C and H are very similar
- Combustion of alkanes
  - Complete combustion (sufficient oxygen present)
    - Equation: $C_xH_{2x+2} + \left(\frac{3x+1}{2}\right)O_2 \rightarrow xCO_2 + (x+1)H_2O$
  - Incomplete combustion (insufficient oxygen present)
    - Hydrogen atom always oxidised to water
    - Combustion of carbon may be incomplete so carbon (soot) or carbon monoxide is formed instead of CO_2
    - Carbon monoxide is toxic + colorless and odorless so it is difficult to spot
    - CO combines irreversibly to haemoglobin and replace oxygen so oxygen cannot pass round the body and the person can suffocate
  - Alkane is a good source of fuel
    - Release large amounts of energy when burned
    - Easy to transport
- Methane and chlorine reaction
  - Equation: $R\text{-}CH_3 + X_2 \rightarrow R\text{-}CH_2X + HX$
  - Type: free radical substitution
  - Step 1: initiation
    - The halogen-halogen bond is broken by **homolytic fission** to form 2 free radicals
    - Energy for bond fission is provided by UV radiation
    - e.g. $Cl_2 \xrightarrow{\text{u.v.}} 2Cl\bullet$
  - Step 2: propagation (halogen radical intermediate react with original reactants)
    - One free radical reacts to produce another different free radical
    - Always in 2 steps
    - First propagation step: $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$
    - Second propagation step: $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
    - A halogen radical **acts as an catalyst and is recreated**
  - Step 3: termination
    - Two free radicals combine and their unpaired electrons pair up to form a covalent bond between the 2 species
    - $Cl\bullet + \bullet Cl \rightarrow Cl_2$ / $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$ / $\bullet CH_3 + \bullet Cl \rightarrow CH_3Cl$
    - Both radicals are removed from the reaction mixture so the reaction stops
  - (Same equation for bromine atoms)
- Skeletal formulae for free radical substitution

  - 

  - Dot on the carbon atom with hydrogen atom removed
- Limitations of radical substitution in synthesis
  - Further substitution
    - The propagation step can continue many times as it is a chain reaction
    - Conditions can be altered to favour the termination step and limit the number of

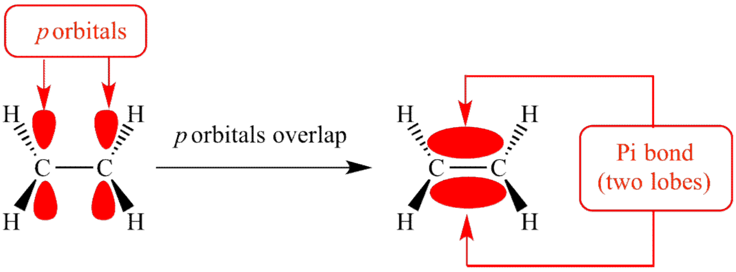
    substitutions
- Substitution at different positions in a carbon chain
    - Longer chain = a mixture of monosubstituted isomers formed by substitution at different positions of the chain
    - Different chains can also undergo further substitution
- Produces different termination products (more than one possible termination step)

4.1.3 Alkenes

Definitions

Term	Definition
Electrophile	An atom or group of atoms which is attracted to an electron-rich centre of atom, where it **accepts a pair of electrons** to form a new covalent bond, usually a cation or an atom or molecule with δ+ dipole
Electrophilic addition	An addition reaction in which the first step is attack by an electrophile on a region of high electron density
Addition polymerisation	Formation of a very long molecular chain, by repeated addition reactions of many **unsaturated alkene molecules** (monomers)

Properties of alkene

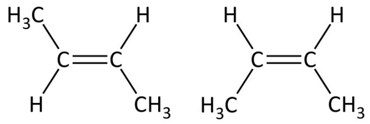
- Structure of C=C bond
    - Comprised of
        - A σ-bond: **head on overlap** of orbitals directly between the bonding atoms
        - A π-bond: **sideways overlap** of **adjacent p-orbitals** above and below the bonding carbon atoms
        - The π-bond locks the two carbon atoms in position and prevents them from rotating around the double bond (restrict rotation)
        - ★ 

    - **Trigonal planar** shape around each carbon atom in the C=C bond (120° bond angle)
        - 3 regions of electron density around each carbon atom (3 bonding regions)
        - The 3 regions repel each other as far apart as possible
- σ and π-bond difference

	σ-bond	π-bond
Position of electron density	Between bonding atoms	Above and below bonding atoms
Overlap of orbitals	Head on overlap of orbitals	Sideways overlap of orbitals
Bond enthalpy / strength	**Higher**	**Lower**
Size	**Larger**	**Smaller**

Stereoisomerism in alkenes

- Stereoisomer
    - Compounds with the **same structural formula** but with a **different arrangement in space**
- E/Z isomerism / geometrical isomerism
    - An type of stereoisomerism
    - Different groups attached to each carbon atom of a C=C double bond may be arranged differently in space because of the restricted rotation about the C=C bond
    - Rotation about a double bond is restricted (due to the π-bond) so the groups attached to each carbon atom are fixed relative to each other
- Conditions for E/Z isomerism
    - A C=C double bond
    - **Two different groups** to be attached to **each carbon atom** of the double bond

- *Cis–trans* isomerism
    - A special case of E/Z isomerism
    - **One of the attached groups on each carbon atom of the double bond must be the same**
    - Same group on same side = cis, same group on different sides = trans (only works if there is a hydrogen atom bonded to both carbon atoms)
    - 
      E-but-2-ene (*trans*) *Z*-but-2-ene (*cis*)
- Identify E/Z isomers by Cahn-Ingold-Prelog (CIP) priority rules
    - Assigning priority
        - Examine the atomic number of the atoms directly attached to the carbon atoms of the double bond
        - Higher atomic number = higher priority
        - Two same atoms attached to the carbon atom
            - Find the first point of difference
            - Higher atomic number at first point of difference = higher priority
    - The groups of higher priority are on the **same side = Z isomer**
    - The groups of higher priority are **diagonally placed across the double bond = E isomer**

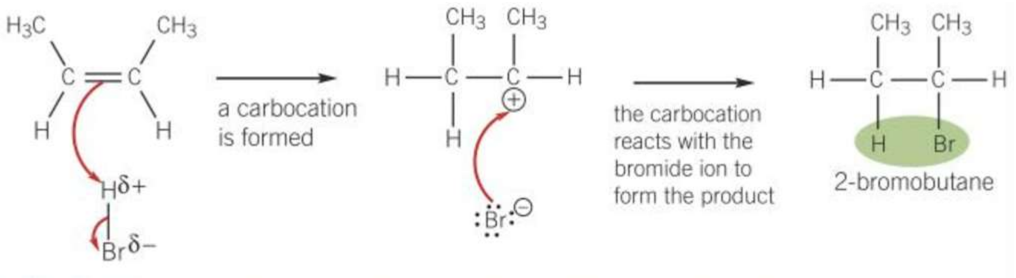
Addition reactions of alkenes

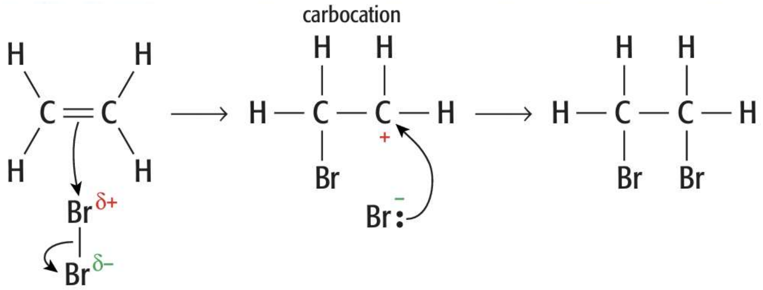
- Reactivity of alkenes
    - Much more reactive than alkanes
    - Relative low bond enthalpy of the π-bond so it is broken more readily
        - It is on the outside of the σ-bond so its electrons are more exposed
- Addition reactions of alkanes

Reaction	Condition	Detail
Hydrogenation	• Nickel catalyst • 423 K (150°C) • High pressure	• Alkene + hydrogen → alkene / $R\text{-}CH{=}CH_2 + H_2 \rightarrow R\text{-}CH_2\text{-}CH_3$ • Type: hydrogenation / addition

Halogenation	• RTP	• Alkene + halogen → dihaloalkane e.g. $R\text{-}CH{=}CH_2 + Br_2 \rightarrow R\text{-}CHBr\text{-}CH_2Br$
		• Type: electrophilic addition (see below for mechanism)
		• Reaction of alkenes with bromine can be used to test if the organic compound is unsaturated
		  • Bromine water added dropwise to alkene
		  • Bromine adds across the double bond
		  • The orange colour of bromine water disappears
		  • Added to an saturated compound: no addition reaction so no colour change

Addition with (gaseous) halogen halides	• RTP	• Alkene + halogen halide → haloalkane e.g. $R\text{-}CH{=}CH_2 + HBr \rightarrow R\text{-}CHBr\text{-}CH_3$ • Type: electrophilic addition (see below for mechanism) • Alkene is a gas: reaction takes place when the two gases are mixed • Alkene is a liquid: hydrogen halide bubbled through it • Can also react with concentrated hydrochloric or hydrobromic acid * **Two possible products**
Hydration	• Steam • **Phosphoric acid (H_3PO_4) catalyst**	• Alkene + $H_2O_{(g)}$ → alcohol • Type: hydration • $R\text{-}CH{=}CH_2 + H_2O \rightarrow R\text{-}CH(OH)\text{-}CH_3$ * **Two possible products**

- Electrophilic addition mechanisms
    - Electrophile = δ+ atom (accepts the π-electrons from the double bond)
    - Electron pair in the π -bond is attracted to the δ+ atom → double bond breaks
    - A bond forms between the δ+ atom and a carbon atom from the double bond
    - The bond in the molecule breaks by heterolytic fission, electron pair goes to the δ- atom
    - An anion and a carbocation (positively charged carbon atom) are formed
    - They react to form the addition product
    - 

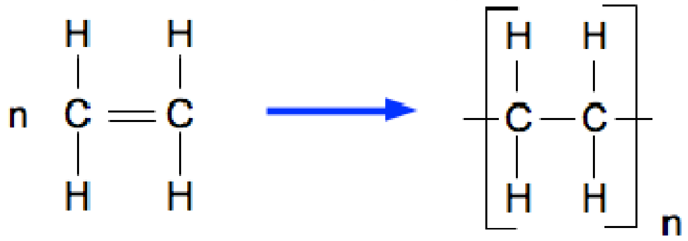
    - 

- Types of carbocations

Type	Definition
Primary	**1 alkyl group** attached to the positively charged carbon atom
Secondary	**2 alkyl groups** attached to the positively charged carbon atom
Tertiary	**3 alkyl groups** attached to the positively charged carbon atom

- Using Markownikoff's rule to predict formation of major organic product
    - For **unsymmetrical alkanes**
    - **Major product is formed from the most stable carbocation intermediate**
    - Stability: tertiary carbocation > secondary carbocation > primary carbocation
    - Halide / OH^- ion attached to the carbon atom attached to the carbon atom with the **least hydrogens attached / most alkyl groups attached**
    - The hydrogen attaches itself to the carbon atom with the **most hydrogens attached**

Polymers

- Addition polymerisation of alkenes
    - Short chain monomers join together to form long chain polymers **under high pressure**
    - Double bond of the alkene is replaced by single bonds to form a repeating unit + bond with other monomers to form the polymer
    - Addition polymers as the short chains join together to form **a single product**
        - 

- Problems of waste polymers
    - Benefits of cheap oil-derived plastics are counteracted by problems for the environment of landfill
    - They are unreactive so they are non-biodegradable and cannot be broken down by species in nature
    - Non-biodegradable waste polymers can become a threat to wildlife

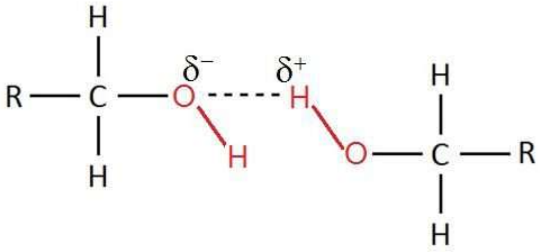
- Reducing the effect of waste polymers
  - Choose plastic items that are made from polymers that can be recycled
  - Re-use plastic items at many time as possible
  - Try to recycle plastic items
- Ways of processing waste polymers
  - Recycle
    - High cost of collection and re-processing
    - The different types of polymer have to be separated
  - Combustion to **release heat energy for generating electricity**
    - Toxic fumes produced from burning halogenated polymers
      - HCl is removed during the combustion of chlorine containing haloalkanes
      - CO produced during incomplete combustion
      - Can be removed by scrubbing in the chimney
    - Greenhouse gases can be released which causes global warming
  - Organic feedstock
    - Use the waste for the production of useful organic compounds
    - New technology can convert waste into hydrocarbons
    - Hydrocarbons can then be turned back into polymers
- New types of polymers
  - Biodegradable polymers
    - Broken down by microorganisms into water, CO_2 and organic compounds
    - Compostable polymer degrade and leave no visible or toxic residues
    - e.g. can be used as bin liners for food waste
  - Photodegradable polymers
    - Contain weak bonds that break when they absorb light energy
  - Benefits
    - Conserve fossil fuel reserves
    - Reduce pollution from disposing polymers

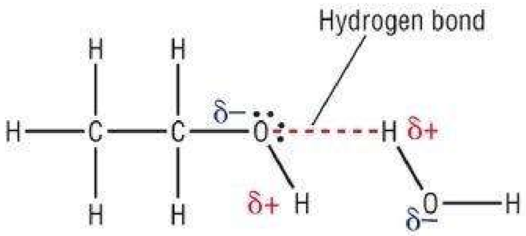
4.2.1 Alcohols

Definitions

Term	Definition
Dehydration	A **water molecule** is removed from the starting material

Properties of alcohols

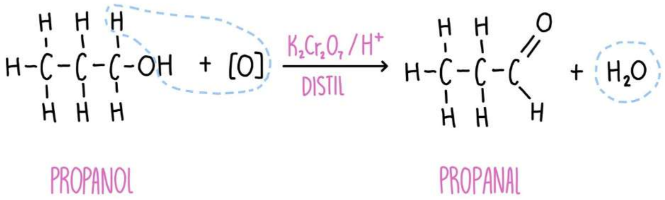
- Alcohol structure
  - Functional group = -OH (hydroxyl group)
  - Has **polar and non-polar** parts
    - The O-H bond is **polar** (oxygen is more electronegative than hydrogen)
    - The side chain is **non-polar**
    - so alcohol can mix with both polar and non-polar liquids
- Alcohol properties
  - Higher melting & boiling point than alkanes
    - Induced dipole-dipole interactions between the non-polar side chains
    - **Strong hydrogen bonds** + permanent dipole-dipole interactions between alcohol molecules hold them together (stronger than London forces)
    - Extra heat energy is required to break the strong hydrogen bonds
    - 

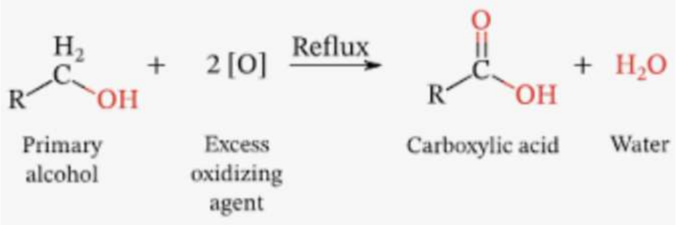
  - Greater water solubility than alkenes
    - Alkanes are non-polar so they cannot form **hydrogen bonds / PDD** with water
    - O-H bond in alcohol is polar and forms **hydrogen bond with water**
      - 

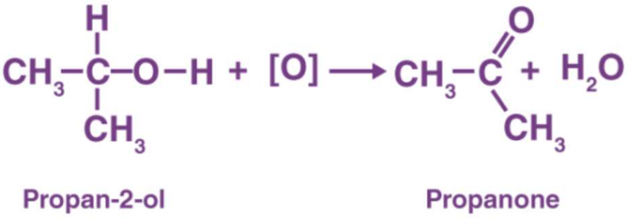
    - Longer carbon chain = less miscible in water
    - More -OH groups = more miscible in water
- Classifying alcohols
  - Primary: -OH group attached to a carbon atom attached to **2 hydrogen atoms + 1 alkyl group**
  - Secondary: -OH group attached to a carbon atom attached to **1 hydrogen atom + 2 alkyl groups**
  - Tertiary: -OH group attached to a carbon atom attached to **no hydrogen atoms + 3 alkyl groups**

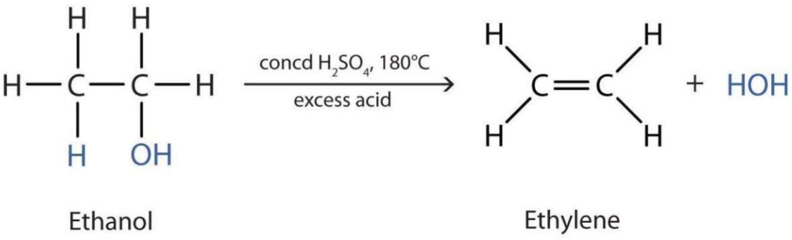
Reactions of alcohols

- (Complete) combustion of alcohols
  - Alcohol + oxygen → carbon dioxide + water
  - Exothermic reaction
    - A large quantity of energy released in the form of heat
    - Burn with a clear blue flame

    - More carbon atoms in the alcohol chain = more heat energy released per mole
    - Alcohols undergo complete combustion more often than alkanes due to the oxygen atom in the molecule
- Oxidation of alcohols
    - Heat with an oxidising agent ([O])
        - Normally acidified dichromate (VI) ($Cr_2O_7^{2-}$ / H^+)
        - e.g. acidified potassium dichromate (VI) ($K_2Cr_2O_7$ / H_2SO_4)
    - Observations
        - Cr will be reduced
        - Reaction mixture turn from orange (Cr^{6+} in $Cr_2O_7^{2-}$) to green (Cr^{3+})
- Oxidation of primary alcohols
    - Gentle heating + **distillation** = aldehyde formed
        - Aldehyde distilled out of the reaction mixture as it forms to prevent any further reaction (distil)
        - 

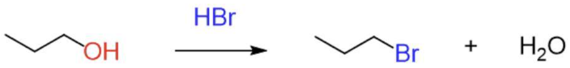
    - Heated strongly + **reflux** + **excess of acidified potassium dichromate (VI)** = carboxylic acid
        - Reflux = ensure that all aldehyde formed initially also oxidised to carboxylic acid
        - Excess of oxidising agent = ensure that all alcohol is oxidised
        - 

- Oxidation of secondary alcohols
    - Oxidised to ketones with an oxidising agent (acidified dichromate (VI) ions)
    - **Ketones cannot be further oxidised**
    - Heated under **reflux** with the oxidising agent to ensure that the reaction goes to completion
    - 

- Oxidation of tertiary alcohols
    - Do not undergo oxidation reactions
    - Acidified dichromate (VI) ions remain orange when added to a tertiary alcohol
- Dehydration of alcohols
    - Heated under **reflux** with **concentrated acid catalyst** (e.g. concentrated H_2SO_4 / H_3PO_4)
    - Product = an alkene
    - Type = elimination reaction
    - 

- Substitution reaction of alcohols
    - Alcohols react with halide ions to form haloalkanes
    - Heated under **reflux** with **concentrated acid catalyst** & halide ion e.g. H_2SO_4 + NaBr
        - Acid need to be concentrated to minimise back reactions

Alcohols can be converted to Alkyl Halides with HX acids

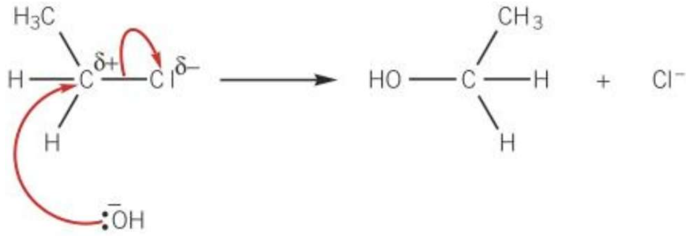
- 
- ★ $R{-}OH + NaX \xrightarrow{H_2SO_4} R{-}X + NaHSO_4 + H_2O$

4.2.2 Haloalkanes

Definitions

Term	Definition
Nucleophile	An atom or group of atoms which is attracted to an electron-deficient centre or atom, where it **donates a pair of electrons** to form a new covalent bond
Nucleophilic substitution	A reaction in which a nucleophile is attracted to an electron-deficient centre or atom, where it donates a pair of electrons to form a new covalent bond
Hydrolysis	A reaction with water that breaks a chemical compound into two compounds, the H and OH in a water molecule becomes incorporated into the two compounds

Haloalkane reactions

- Reactivity of haloalkanes
    - Reactivity: alkenes > haloalkanes > alkanes
    - Halogen atoms are more electronegative than carbon atoms so the carbon-halogen bond is polar
    - δ+ on carbon can attract nucleophiles (contain a lone pair of electrons)
    - The nucleophile replaces the halogen atom
    - A new compound with a different functional group is formed
- Hydrolysis mechanism
    - **Nucleophilic substitution**
    - OH^- normally from NaOH
    - OH^- (nucleophile) approaches the carbon atom attached to the halogen from the opposite side of halogen to minimise repulsion
    - A lone pair on OH attracted & donated to δ+ carbon atom
    - New bond formed between oxygen atom of OH and the carbon atom
    - **Carbon-halogen** bond breaks by **heterolytic fission**
    - Alcohol + halide ion formed
    - 

- Trend in reaction rates of hydrolysis of primary haloalkanes
    - C-F has the greatest bond enthalpy (strongest), C-I has the lowest bond enthalpy (weakest)
        - Going down the table = larger halogen atom = longer bond = bond becomes weaker
    - Rate: iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes
        - Rate increases as the **bond enthalpy** of carbon-halogen bond decreases
        - C-I bond is the **weakest (lowest bond enthalpy)**, C-F bond is the **strongest (highest bond enthalpy)**
        - Less energy is needed to break the carbon-halogen bond to start the reaction so the activation energy is lower
- Measuring rate of hydrolysis
    - Set up 3 test tubes of 1 cm^3 ethanol and couple drops of 1-chlorobutane / bromobutane / iodobutane
        - Slow down the reaction so we can measure the reaction time easier
    - Put the test tubes + a test tube with silver nitrate in water bath at 60°C
    - Allow them to reach constant temperature (60°C)
    - Add 1 cm^3 of silver nitrate to each test tube quickly + start stop watch
    - Observe time taken for precipitate to form
        - Chlorine = white, bromine = cream, iodine = yellow

  - Speed: iodobutane > bromobutane > chlorobutane

Organohalogen compounds and the ozone layer

- CFCs
  - Shorthand for chlorofluorocarbons
    - Compounds containing carbon with chlorine and fluorine atoms attached
- Uses of CFCs
  - CFCs are non-flammable and not very toxic so they have a lot of uses
    - Refrigerants
    - Propellants for aerosols
    - Generating foamed plastics
    - Solvents for dry cleaning and for general degreasing purposes
- Problems associated with CFCs
  - Global warming
  - Breakdown of ozone layers in the atmosphere
- Ozone layer
  - Ozone continually formed and broken down by the action of UV radiation
  - Initially very high energy UV breaks oxygen molecules into oxygen radicals: $O_2 \rightarrow 2O$
  - A steady state then set up where rate of ozone formation is the same as the rate of ozone

    being broken down: $O_2 + O \rightleftharpoons O_3$
  - Equilibrium disturbed by human activities e.g. production and use of CFCs
- How CFCs break down ozone
  - CFCs remain stable until they reach the stratosphere
  - In the stratosphere UV breaks carbon-halogen bond by homolytic fission to form radicals (initiates the breakdown of ozone)
    - Photodissociation (Initiation): e.g. $CF_2Cl_2 \rightarrow CF_2Cl\bullet + Cl\bullet$
  - Chlorine radical formed is a very reactive intermediate and can react with an ozone molecule
    - Propagation step 1: $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
    - Propagation step 2: $ClO\bullet + O \rightarrow Cl\bullet + O_2$
    - (Overall: $O_3 + O \rightarrow 2O_2$)
    - There is a significant amount of O_3 and free oxygen atoms in the upper atmosphere for reaction
  - Chlorine radical can go on in chain reaction to break down other ozone molecules
- How nitrogen oxide break down ozone
  - Reaction with NO
    - Initiation: $NO \rightarrow N\bullet + O\bullet$
    - Propagation step 1: $N\bullet + O_3 \rightarrow \bullet NO + O_2$
    - Propagation step 2: $\bullet NO + O \rightarrow N\bullet + O_2$
    - Overall: $O_3 + O \rightarrow 2O_2$
  - Reaction with NO_2
    - Initiation: $NO_2 \rightarrow NO\bullet + O\bullet$
    - Propagation step 1: $NO\bullet + O_3 \rightarrow NO_2\bullet + O_2$
    - Propagation step 2: $NO_2\bullet + O \rightarrow NO\bullet + O_2$
    - Overall: $O_3 + O \rightarrow 2O_2$
- Alternatives for CFCs
  - Replace the C-Cl bond with stronger C-F bond
    - Hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) can be used
    - Still volatile, non-toxic and non-flammable
    - Still damage the ozone layer
  - Replace the C-Cl bond with a C-H bond
    - Use hydrocarbons
    - The C-H bond is much weaker and the molecules don't persist until they reach the upper atmosphere
    - They are very flammable

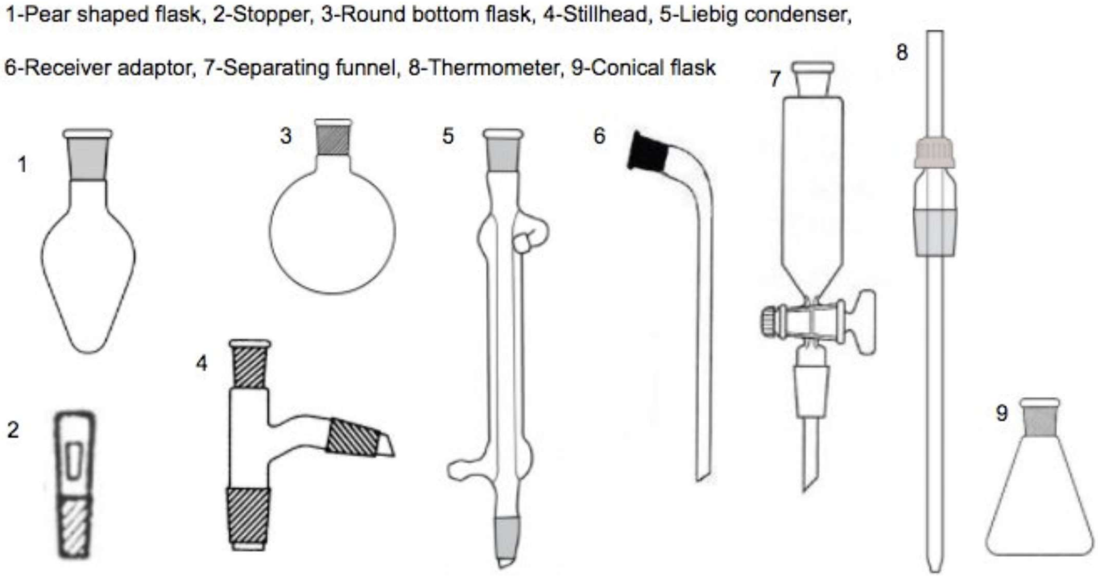
4.2.3 Organic synthesis

Definitions

Term	Definition
Fractional distillation	The separation of components in a liquid mixture by their different boiling points into fractions with different compositions
Drying agent	An **anhydrous solid** that readily absorbs water from the mixture to become hydrated

Practical techniques

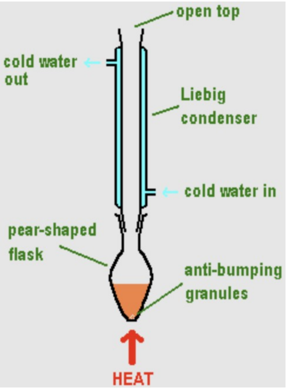
- Quickfit apparatus set



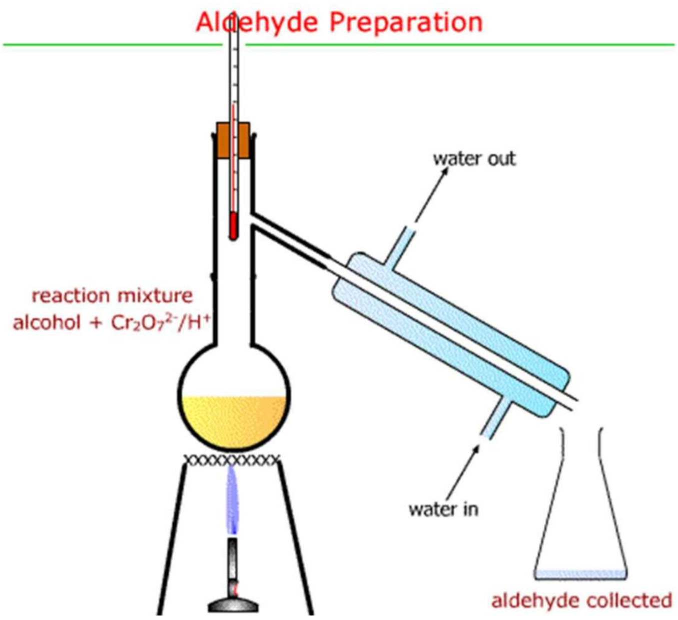
1-Pear shaped flask, 2-Stopper, 3-Round bottom flask, 4-Stillhead, 5-Liebig condenser,

6-Receiver adaptor, 7-Separating funnel, 8-Thermometer, 9-Conical flask

- Heating under reflux
  - To prepare organic products without boiling off solvent, reactants or products
  - Ensures that the reaction goes to completion
  - Water bath can be used rather than Bunsen if can be carried out below 100°C
  - Heating mantle can be used for flammable liquids
  - **Anti-bumping granules added to liquid so it boils smoothly**
    - Otherwise large bubbles will form at bottom so the glassware vibrate / jump
  - Glass joints greased lightly so apparatus comes apart easily after experiment
  - Condensers should be clamped loosely as the outer jacket is very fragile + kept in upright position
  - Never put stopper in top-closed system or pressure would build up and the apparatus would explode
  - Rubber tubing used to connect the inlet of condenser to tap and outlet to the sink (water always enters the condenser at the bottom and leaves at the top)

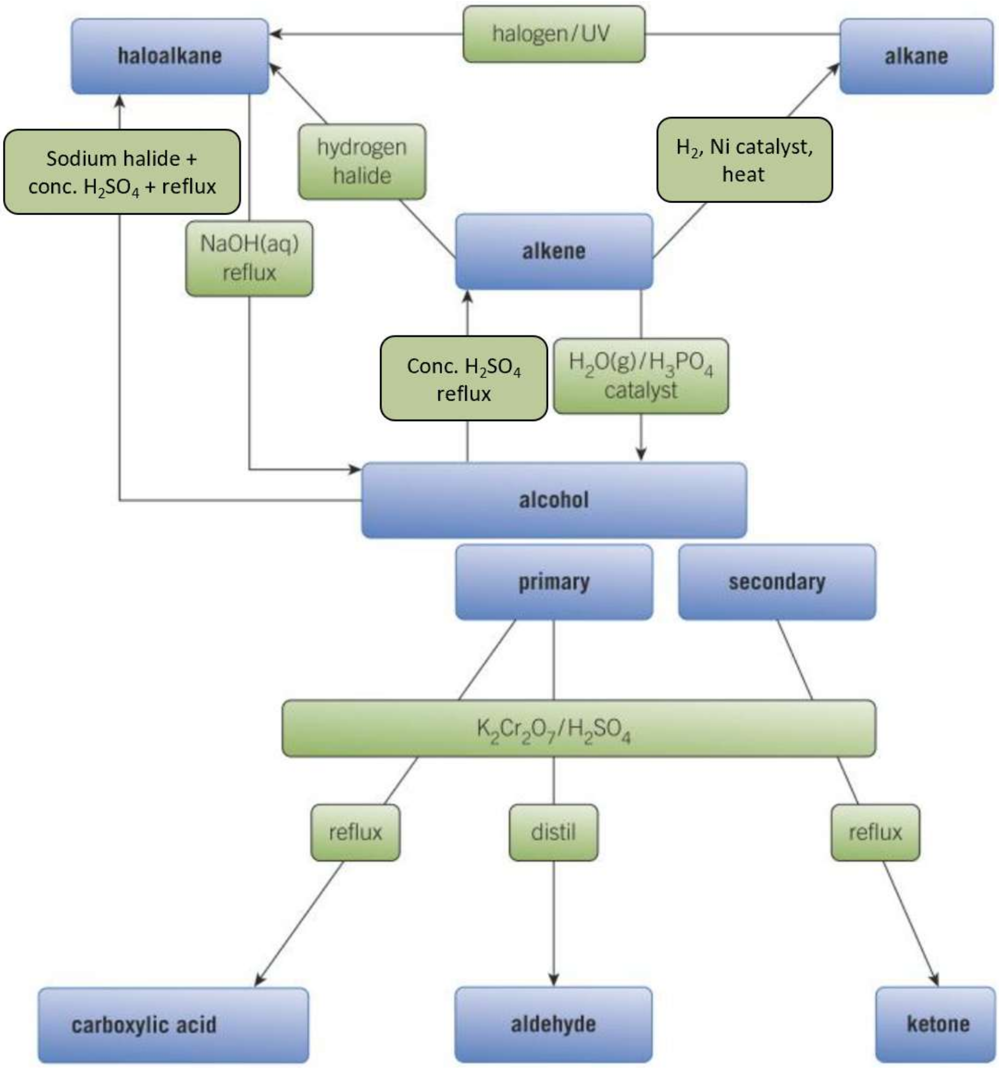


- Distillation

  - 

  - Separates a pure liquid from impurities
  - Flask clamped by neck
  - Still head connected to the flask
  - Condenser connected to rubber tubing for water (**water enters at the bottom**)
  - Flask used to collect the distillate so the apparatus is not airtight
  - Heat the mixture gently (make sure the temperature doesn't reach the boiling point of the less volatile compound)
- Purifying organic products using a separating funnel
  - When there are two layers inside the collection flask: one organic layer, one aqueous / water layer
  - Ensure tap of the separating funnel is closed
  - Pour in mixture and place a stopper in the top of the funnel + invert to mix the contents
  - Allow layers to settle
  - Can't tell the layers: add water to the mixture, the layer that increase in volume is the aqueous layer
  - Place conical flask under the separating funnel
  - Remove stopper + open the tap until whole lower layer has left the funnel
  - If the top layer is accidentally poured then pour the content in the first conical flask back into the separating funnel and restart
  - Repeat this several times until the bottom layer is almost completely removed
- Redistillation
  - Organic compounds may have relatively close boiling points so the sample may still have some impurities left over
  - Carry out a second distillation (or more)
  - Only collect product with the exact boiling point of the target compound
  - Try to not overheat the mixture
  - Narrower boiling point range = purer product
- Drying an organic product
  - There may be water left in the organic product
  - Add organic liquid to conical flask
  - Add some drying agent with spatula + swirl the contents
    - e.g. $CaCl_2$ for drying hydrocarbons, $CaSO_4$ / $MgSO_4$ for general drying
  - Put a stopper on to prevent product from evaporating away
  - Leave for about 10 minutes
  - If the solid stuck in a lump water is still present so add more drying agent until it becomes a fine powder
  - After all the water is absorbed the organic mixture can be separated by filtration / simply decanting the liquid

Synthetic routes



4.2.4 Analytical technique

Definitions

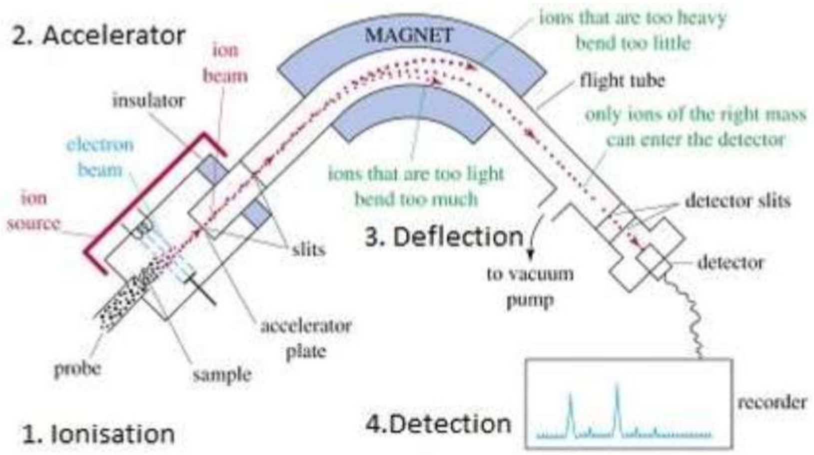
Term	Definition
Fragmentation	The process in mass spectrometry that causes a positive ion to split into smaller pieces, one of which is a positive fragment ion
Fragment ions	Ions formed from the breakdown of the molecular ion in a mass spectrometer

IR spectroscopy

- Vibrations in bonds
  - Bonds vibrate at a particular frequency
    - Stretch: moving along the line between atoms so the distance between them changes
    - Bend: results in change in bond angle
  - Bonds only absorb radiation with the same frequency as the natural frequency of the bond
    - The frequency of the light depends on bond strength, bond length and atomic masses at both ends of the bond
    - Most bonds absorb at a frequency of 300 - 4000 cm^{-1}, i.e. IR radiation
  - Absorbing IR radiation causes covalent bonds to absorb energy and vibrate more
- Greenhouse effect
  - Most of the Sun's radiation is **short wave** and is relatively unaffected by atmospheric gases
  - They pass through the atmosphere to the Earth's surface and some is reflected as **long wave** radiation
  - C=O, O-H and C-H bonds absorb radiation in the IR range which causes bond in gas molecules to vibrate
    - e.g. CO_2, H_2O and CH_4 molecules
  - The vibrating bonds eventually re-emit the energy as radiation that increases the temperature of the atmosphere close to the Earth's surface
  - This creates incentives to reduce CO_2 emission to reduce global warming
- Infrared spectroscopy
  - Determine the functional groups present
  - Sample placed in IR spectrometer
  - IR radiation beams with wavenumber 200-4000 cm^{-1} is passed through the sample
  - Molecules absorb some IR + emerging beam is analysed to identify frequencies absorbed
  - IR spectroscopy is usually connected to a computer that plots a graph of transmittance against wavenumber
  - The computer uses the fingerprint region to identify the compound
    - Fingerprint region: region **below 1500 cm^{-1}** with **unique peaks to identify particular molecule**
  - All organic compounds produce a peak 2850-3100 from C-H bond
  - Look at other peaks to identify other bonds present
- Uses of IR spectroscopy in real life
  - Remote sensors analyse IR spectra of vehicle emissions to detect pollutants
  - IR-based breathalysers pass beams of IR through breathed out gas + detect IR absorbance
    - Detecting C-O bonds in alcohol molecules
    - O-H bond is present in water vapour breathed out so it is not used
    - Blood test taken if the result suggests that the person is too drunk to drive safely

Mass spectroscopy

- Mass spectroscopy
  - Used to analyse **gaseous** samples
  - Consists of 4 basic regions



  - Some molecular ions break down into smaller fragments by fragmentation
- Analysing the structure from a mass spectrum
  - M_r = the m/z value of the **rightmost peak**
  - There might be a small peak after M^+ peak called the M+1 peak due to the presence of carbon-13 isotope
  - Other peaks are due to fragment ions
- Common m/z values for fragment ions

m/z value	**Ion (remember to include the + charge)**
15	CH_3^+
29	$CH_3CH_2^+$
31	CH_2OH^+
41	$C_3H_5^+$, $C_2H_3N^+$
43	$CH_3CH_2CH_2^+$ / CH_3CO / C_3H_7
45	$CH_3CH_2O^+$
49	$CH_3CH_2CH_2CH_2^+$

  - Specify: peak at m/z = … is due to …

Combining analytical skills

- Identifying the organic compound
  - Elemental analysis: empirical formula
  - Mass spectrometry: determine molecular mass + identify sections of the molecule
  - IR spectrometry: identify bonds + functional groups present