

AS Chemistry – Revision Notes
Unit 3 – Introduction To Organic Chemistry

Nomenclature And Isomerism

- There are two types of organic compounds:
 - Aliphatic – has a functional group attached to an alkyl group.
 - Aromatic – has a functional group attached to an aryl group (containing benzene).
- A functional group is an atom or group of atoms which, when present in different molecules, causes them to have similar chemical properties.
- Each functional group will have a homologous series, with the main carbon chain increasing by one carbon atom in each successive member (they differ by a CH₂ unit):

Homologous Series	Prefix / Suffix	Functional Group
Alkane	-ane	C – C
Alkene	-ene	C = C
Haloalkane	halo-	- Cl, - Br, - I
Alcohol	-ol, hydroxy-	- OH
Ether	alkoxy-	- O -
Aldehyde	-al	
Ketone	-one, oxo-	C = O
Carboxylic acid	-oic acid	
Amine	amino-, -amine	- NH ₂
Amide	-amide	
Nitrile	-nitrile	- C ≡ N

- There are three types of formula:
 - Molecular – shows the actual number of atoms in a single molecule.
 - Structural – shows how the atoms are grouped in the molecule.
 - Displayed – shows all the atoms and all the bonds (drawn out).
- To name an hydrocarbon from the displayed formula:
 - Look for the longest carbon chain containing the functional group – this gives the stem.
 - Add the position of the functional group (lowest number) to the stem (e.g. hex-2-ene).
 - For any side-chains, write down the chain position (using the same numbering as for the functional group) followed by a dash, followed by the name (e.g. 2-ethyl...).
 - For more than one of the same alkyl, use the di- and tri- prefixes (e.g. 2,3-dimethyl...).
- To draw a hydrocarbon from the name:
 - Draw the longest carbon chain as shown in the stem – number it from the right.
 - Add the functional group (if any) in the correct position.
 - Add the side-chains in the correct positions.
 - Fill in the rest of the bonds with hydrogens.
- Isomers are compounds that have the same molecular formula but different structures:
 - Structural isomers – have the same molecular formula but different structural formulae.
 - Stereoisomers – have the same structural formula, but different arrangements of the bonds in space.
- There are three types of structural isomer:
 - Chain isomers – the carbon chain can be arranged in different formations of chains and side chains, i.e. the carbon skeleton is different (e.g. butane and 2-methylpropane).
 - Positional isomers – the functional groups are in different positions (e.g. but-1-ene and but-2-ene).
 - Functional group isomers – these have different functional groups, and belong to different homologous series' (e.g. ethanol and methoxymethane – CH₃OCH₃).
- There are two types of stereoisomer:
 - Geometric isomers – there is no rotation about the double bond in an alkene, so two different groups at each end of the double bond can either be on the same side, i.e. *cis*, or on opposite sides, i.e. *trans* (e.g. *cis*-but-2-ene and *trans*-but-2-ene).

- b. Optical isomers – have the same geometric and structural formula, but cannot be superimposed onto one another, i.e. they are mirror images (e.g. 2-bromobutane).

Petroleum And Alkanes

- The general formula of an alkane is C_nH_{2n+2} .
- Alkanes are unreactive with acids, alkalis, nucleophiles and electrophiles and are non-polar.
- The boiling points of alkanes increase as the chain length increases, because there are more Van der Waals forces holding the longer molecules together, which require more energy to break.
- Alkanes can be extracted from crude oil (a mixture of hydrocarbons) using fractional distillation:
 - The crude oil is heated until vaporised, and passed into the fractionating column.
 - The temperature decreases going up the fractionating column.
 - Hydrocarbons will pass up the column until they reach their boiling point, at which they condense and can be tapped off. The bubble caps aid this by causing the vapour to bubble through the liquid at each fraction, and for the larger hydrocarbons to condense.
- The following fractions are obtained from fractional distillation (increasing boiling points):

Fraction	Carbon Atoms	Uses
LPG (liquefied petroleum gas)	1-4	calor gas, camping gas
Petrol (gasoline)	4-12	petrol
Naphtha	7-14	petrochemicals
Kerosine (paraffin)	11-15	jet fuel, petrochemicals
Gas oil (diesel)	15-19	central heating fuel
Mineral oil (lubricating oil)	20-30	lubricating oil, petrochemicals
Fuel oil	30-40	fuel for ships / power stations
Wax / grease	40-50	candles, grease, polish
Bitumen	>50	roofing, road surfacing

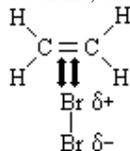
- After primary distillation, vacuum distillation can be used to separate the fractions further, particularly the residue (the last four in the above table are from the residue).
- Larger fractions that are not in high demand can be cracked into smaller fractions that are in much higher demand by cracking:
 - Cracking will result in a long alkane being broken into a shorter alkane, and an alkene (e.g. ethene) being produced. Hydrogen may also be produced.
 - Thermal cracking – temperatures from 400°C to 900°C and pressures of up to 7000kPa are used to cause the cracking to take place as a free radical mechanism (the conditions will initiate the homolytic fission).
 - Catalytic cracking – a zeolite catalyst is used (acts as a Lewis acid and involves carbocation formation), at a temperature of about 450°C and a slight excess pressure. This produces more branched hydrocarbons, and also some cyclic and aromatic hydrocarbons.
- Alkanes undergo complete combustion to form CO_2 and H_2O (g), which are both greenhouse gases. The enthalpy of combustion increases as the carbon chain length increases.
- In a limited supply of oxygen, incomplete combustion of alkanes will take place, producing carbon as soot, or carbon monoxide gas, which is toxic and causes carbon monoxide poisoning.
- Impurities in petrol can result in the formation of SO_2 gases in car engines. Also the high temperature causes the oxidation of nitrogen gas to form NO_x gases. These gases cause acid rain.
- Catalytic converters are used to reduce the emissions of these gases, using a platinum, rhodium and palladium mixture spread in a thin layer – $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$
- There are two ways in which a covalent bond can break:
 - Homolytic fission – one electron goes to each atom to form free radicals.
 - Heterolytic fission – one atom takes both electrons, forming ions.
- A free radical is a highly reactive species with an unpaired electron, signified with a \bullet next to the atom that contains the unpaired electron.
- The chlorination of methane is a substitution reaction and a free radical mechanism:
 - Initiation (requires UV light): $Cl_2 \xrightarrow{UV\ light} 2Cl\bullet$
 - Propagation (chain reaction): $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$
 $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
 - Termination (free radicals react): $2Cl\bullet \rightarrow Cl_2$
 $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$
 $2\bullet CH_3 \rightarrow C_2H_6$

- In an excess of chlorine, further substitution can occur to form CH_2Cl_2 , CHCl_3 and CCl_4 .
- The reaction will occur between all alkanes and all halogens, but the rate will decrease going down the group. Fluorine doesn't require UV light, as it is so reactive.

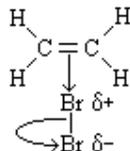
Alkenes And Epoxyethane

- The general formula of an alkene is C_nH_{2n} .
- In naming alkenes, the number signifies the first carbon atom in the chain that forms the double bond. If there is more than one double bond, then add "a" to the end of the stem, and use the prefixes di-, tri- etc. in front of the -ene ending (e.g. hexa-1,2-diene).
- An alkene has strong single covalent bonds between all the carbon atoms (σ bonds), with an extra weaker covalent bond between the two carbons held by the double bond (π bond). A π bond is formed due to the overlapping of two p orbitals parallel to one another, so that the delocalised π bond electrons lie above and below the σ bond and are therefore held less strongly.
- Tests for alkenes:
 - Shake with bromine water; alkenes decolourise the mixture.
 - Shake with acidified potassium manganate (VII) (aq); alkenes decolourise the mixture.
- Alkenes combust in the same way as alkanes, but are more likely to undergo incomplete combustion. They are not used as fuels because of this, and because they are so important in the manufacture of other chemicals.
- An electrophile is an electron-deficient compound that can form a new covalent bond, using an electron pair provided by the carbon compound. This can be either a positive ion (e.g. H^+) or a polar molecule with a δ^+ charge (e.g. BF_3).
- Ethene reacts with bromine in the dark (not free radical), and is an electrophilic addition reaction. This must take place dissolved in an organic solvent:

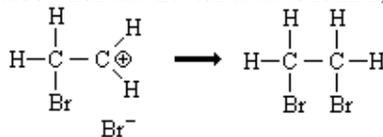
- Initiation (dipole induced by π electrons, and electrophile approaches double bond):



- Formation of intermediate (the electrophile attacks the bond, forming a covalent bond and resulting in the formation of a carbocation or carbonium ion and a Br^- ion):



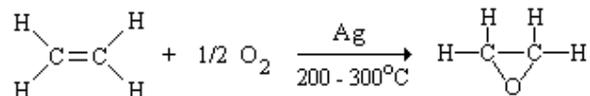
- Termination (the carbocation and Br^- ion react to form 1,2-dibromoethane):



- Ethene reacts with hydrogen halides in the same way (electrophilic addition), except that the dipole is permanent, and therefore doesn't need to be induced. They react as aqueous solutions.
- For unsymmetrical hydrocarbons, Markownikoff's rule states which of the two possible products will be formed:
 - An alkyl group tends to donate electrons slightly to any carbon atom it is attached to – this is the inductive effect.
 - A primary carbocation will have one alkyl group doing this, whereas a secondary carbocation will have two, and a tertiary carbocation will have three.
 - As the inductive effect increases for increasing order of carbocation, so does stability.
 - The highest order carbocation will always be formed, as this is the most stable.
 - When a molecule adds across a double bond, the more electropositive atom or group (the electrophile) adds to the carbon atom with more hydrogen atoms already attached.
- Catalytic hydration of alkenes:
 - Generally $\text{C}_n\text{H}_{2n} + \text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH}$ – i.e. an alcohol is formed.
 - A phosphoric (V) acid (H_3PO_4) is used, along with a temperature of 300°C and a pressure of 60 atmospheres.

- c. This reaction is reversible, and so can also be used to produce alkenes from alcohols.
11. An alternative method for the production of alcohols uses concentrated sulphuric acid:
- Sulphuric acid should be thought of as:

$$\begin{array}{c} \text{H}-\text{O} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{S} \\ \quad \quad \quad \diagup \\ \text{H}-\text{O} \end{array} \begin{array}{l} \text{O} \\ \text{O} \end{array}$$
 - The reaction will be electrophilic addition, and will form an alkyl hydrogen sulphate. It takes place in the cold.
 - The alkyl hydrogen sulphate is then added to water and warmed, causing it to be hydrolysed to an alcohol and sulphuric acid.
 - The sulphuric acid is regenerated, and has therefore acted as a catalyst.
12. Catalytic hydrogenation of alkenes:
- Generally $\text{C}_n\text{H}_{2n} + \text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n+2}$ – i.e. an alkane is formed.
 - A nickel (Ni) catalyst is used, along with a temperature of 150°C to 300°C .
 - The mechanism for this reaction is not electrophilic addition; it is a catalytic reduction.
 - This reaction is used to convert polyunsaturated fatty acids in vegetable oils into more saturated fatty acids. This makes them less rigid, so they can pack closer together and the intermolecular forces increase, increasing the melting point. They will therefore be solid, and are used as margarine.
13. Polymerisation involves a large number of alkenes bonding together into addition polymers that are saturated, in the presence of a catalyst. This involves free radicals.
14. Epoxyethane (a cyclic ether) is produced by the direct partial oxidation of ethene:

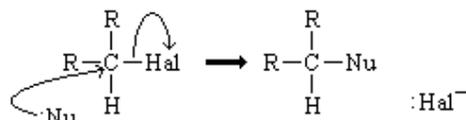


15. Epoxyethane has the following properties:
- It is a colourless gas at room temperature, with a boiling point of 10°C .
 - It is flammable and explosive, due to the instability of its structure so it will readily react.
 - It is highly reactive towards nucleophiles, due to the polar C–O bonds.
 - It has a strong tendency to polymerise, particularly in contact with an alkali.
 - It is highly toxic.
16. Epoxyethane is hydrolysed with a ten molar excess of water to produce ethane-1,2-diol:
- Steam is used at 200°C and a pressure of 14 atmospheres.
 - Alternatively concentrated sulphuric acid catalyst at 60°C is used.
 - Ethane-1,2-diol is used in antifreeze. It is 30% sweeter than sugar, but is very toxic.
17. Epoxyethane can be hydrated with less water to produce polyethylene glycols, that can be used as solvents and lubricants, and in the manufacture of plasticisers, polyurethanes and polyester resins.
18. Epoxyethane will react with alcohols to form monoalkyl ethers of ethane-1,2-diol. These can be used in paints, printing inks, plasticisers and surfactants.
19. An organic acid with two COOH groups will react with a diol to form a monomer with one ester linkage. These can then be polymerised to form a polyester.
20. Ethane-1,2-diol is used in the production of poly(ethyleneterephthalate), i.e. PET. Condensation reactions with benzene-1,4-dicarboxylic acid and two ethane-1,2-diol molecules form the monomer ($230\text{--}250^\circ\text{C}$, 3–4 atm) and this is then polymerised to form PET ($270\text{--}300^\circ\text{C}$, zero pressure, antimony catalyst).

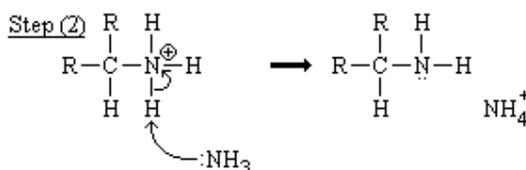
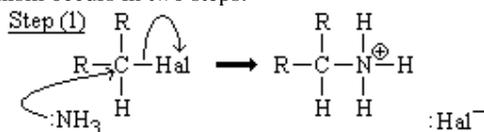
Halogenoalkanes

- In naming halogenoalkanes:
 - The name of the halogen (fluoro, chloro, bromo, iodo) precedes any alkyl groups.
 - The prefixes di, tri, tetra etc. are used for more than one of the same halogen.
- The boiling point of a halogenoalkane is affected by:
 - The chain length – longer chains have greater Van der Waals forces and will therefore have a higher boiling point.
 - The size of the halogen atom – the smaller the halogen atom, the lower the boiling point.
 - The number of halogen atoms – the more halogen atoms, the higher the boiling point.
- Chlorofluorocarbons are haloalkanes whereby every hydrogen atom has been replaced by either a chlorine or a fluorine atom. They are very stable, so persist in the atmosphere for many years.
- Halogenoalkanes have polar bonds, because the halogens are very electronegative, and so create a dipole. This leaves the δ^+ carbon atom open to nucleophilic attack.

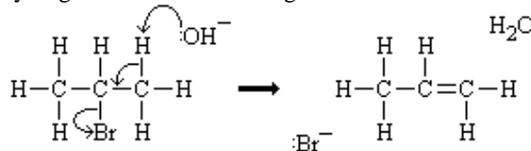
5. Increasing the size of the halogen atom:
 - a. Decreases the bond strength, as the reactivity decreases down the group.
 - b. Increases the reactivity of the haloalkane, as the weaker bond is easier to break.
 - c. Decreases the polarity of the bond, as the electronegativity decreases down the group.
6. A nucleophile is an electron-rich species with a lone pair of electrons. This attacks a carbon atom that is electron deficient by donating a pair of electrons.
7. Primary and secondary haloalkanes will undergo nucleophilic substitution in the following mechanism (S_N2):



8. Warming a halogenoalkane with an aqueous alkali will result in the formation of alcohols (S_N2), where the OH^- ion is the nucleophile.
9. Warming a halogenoalkane with an aqueous solution of potassium cyanide will result in the formation of nitriles (S_N2), where the CN^- ion is the nucleophile. This increases the length of the carbon chain by one carbon atom.
10. Nitriles can be hydrolysed to carboxylic acids by heating under reflux (a condenser is used to stop gases from escaping) with an aqueous alkali or with mineral acid:
 - a. Nitrile to amide – $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CONH}_2$.
 - b. Amide to carboxylic acid – $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_3$.
11. Warming a halogenoalkane in a sealed container with an excess of ammonia will result in the formation of primary amines (S_N2), where the NH_3 molecule is the nucleophile:
 - a. Generally – $\text{R-Hal} + \text{NH}_3 \rightarrow \text{R-NH}_2 + \text{H-Hal}$.
 - b. The H-Hal will immediately react with NH_3 to form NH_4Hal .
 - c. The mechanism occurs in two steps:



12. When a halogenoalkane reacts with OH^- ions, the hydroxide ions may function as a base rather than a nucleophile, causing an elimination reaction to take place. This results in the formation of an alkene, with one hydrogen atom and one halogen atom eliminated:

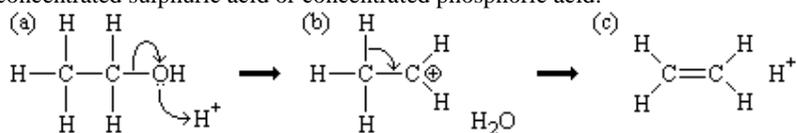


13. Primary haloalkanes tend to favour substitution reactions, whereas tertiary haloalkanes tend to favour elimination reactions. With secondary haloalkanes, both reactions occur concurrently.
14. In order to favour one reaction, the conditions need to be altered:
 - a. Elimination is favoured by hot ethanolic conditions, and a stronger base.
 - b. Substitution is favoured by warm aqueous conditions, and a weaker base.

Alcohols

1. When naming alcohols, use the prefixes di- and tri- to signify dihydric and trihydric alcohols respectively.
2. Alcohols are industrially produced for alcoholic drinks by fermentation:
 - a. Anaerobic respiration in yeast is used to ferment sugar into alcohol and CO_2 .
 - b. A series of enzymes called zymase catalyses the reaction.
 - c. It is a batch process – if the ethanol gets too concentrated it denatures the enzymes.

- d. Stronger alcohols are produced by distilling or by adding more ethanol (fortified wines).
- Alcohols can also be industrially produced by the direct hydration of ethene, and this tends to be preferred as gives a higher yield and is continuous, although it is more expensive to run.
 - The boiling points of alcohols are affected by:
 - Chain length – the longer the chain length, the higher the boiling point as the intermolecular forces are greater.
 - Order of alcohol – primary alcohols have higher boiling points than tertiary alcohols as the molecules can get closer together.
 - Hydrogen bonding – this is experienced by hydroxyl groups, and increases the boiling point. The more hydroxyl groups, the higher the boiling point will be.
 - The solubility of alcohols is affected by increasing the carbon chain length – this lowers the solubility, as there will be more interactions between the alcohol molecules than between alcohol and water molecules.
 - Alcohols can be oxidised in the presence of an oxidising agent (shown as [O]). This can be either acidified potassium dichromate (VI) solution (potassium dichromate (VI) with sulphuric acid) or acidified potassium manganate (VII) solution:
 - Primary alcohols – these will oxidise to form an aldehyde. In this reaction one hydrogen is removed from the hydroxyl group, and one from the carbon to which the hydroxyl group is attached. The aldehyde can be further oxidised to a carboxylic acid by refluxing the mixture at a higher temperature.
 - Secondary alcohols – these will oxidise to form a ketone. These cannot be oxidised any further.
 - Tertiary alcohols – these will not oxidise, as there is no other hydrogen attached to the carbon to which the hydroxyl group is attached.
 - Alcohols can be tested for with an oxidising agent, as the oxidising agent will be reduced during oxidation of the alcohol. If a colour change occurs then either a primary or secondary alcohol is present:
 - Acidified potassium dichromate changes from orange ($\text{Cr}_2\text{O}_7^{2-}$ ions) to green (Cr^{3+} ions) when reduced.
 - Acidified potassium manganate changes from purple (MnO_4^- ions) to colourless (Mn^{2+} ions) when reduced.
 - To test for a primary or secondary alcohol, either Tollen's reagent or Fehling's solution can be used. Both react to oxidise aldehydes to carboxylic acids but do not react with ketones, so 1^0 and 2^0 alcohols can be distinguished.
 - Tollen's reagent will cause silver atoms to coat the test tube in the presence of an aldehyde:
 - This is a mixture of ammonia and silver nitrate, containing $[\text{Ag}(\text{NH}_3)_2]^+$ complex ions.
 - Silver (I) ions are reduced to Ag when the aldehyde is oxidised.
 - Fehling's solution will produce a brick red precipitate in the presence of an aldehyde:
 - This contains copper (II) ions in a complex.
 - Blue copper (II) ions are reduced to brick red copper (I) ions, producing Cu_2O precipitate.
 - Aldehydes and ketones can be reduced to form 1^0 and 2^0 alcohols respectively, in the presence of a reducing agent (shown as $2[\text{H}]$). This can be either sodium tetrahydridoborate (NaBH_4) dissolved in aqueous alcohol, or lithium tetrahydridoaluminate (LiAlH_4) dissolved in epoxyethane.
 - The dehydration of an alcohol to form an alkene works at a temperature of 180°C and a catalyst of either concentrated sulphuric acid or concentrated phosphoric acid:



- An H^+ ion from the acid is attracted to the δ^- charge on the oxygen of the hydroxyl group and the OH group is protonated.
- A molecule of H_2O is lost from the protonated alcohol to form a carbocation.
- The carbocation loses a proton (H^+ ion) to form an alkene.