

4.1 Basic concepts and hydrocarbons

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 CH₂
Saturated	All carbon to carbon bonds are single bonds
Unsaturated	Contain carbon to carbon multiple bonds (C=C or C≡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

- 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**

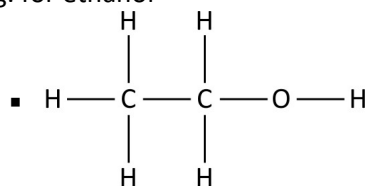
- Stem prefix

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-

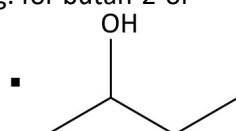
- Types of formulae

- 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: CH₃CH₂CH₂CH₃ or CH₃(CH₂)₂CH₃

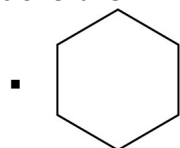
- Displayed formula
 - The relative positioning of atoms and the bonds between them
 - e.g. for ethanol



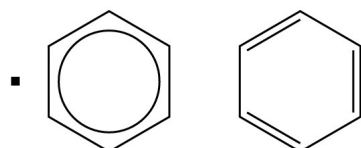
- Skeletal formula
 - The simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups
 - e.g. for butan-2-ol



- Cyclohexane



- Benzene



- Types of covalent bond fission

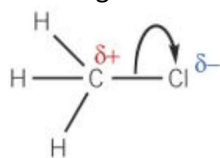
- Homolytic fission
 - **Each bonding atom receiving one electron** from the bonded pair forming 2 radicals
- Heterolytic fission
 - **One bonding atom receiving both electrons** from the bonded pair
 - The atom that takes both electrons becomes a negative ion
 - The atom that does not take the electrons becomes a positive ion
 - e.g. $\text{H}_3\text{C}-\text{Cl} \rightarrow \text{H}_3\text{C}^+ + \text{Cl}^-$

- Radical

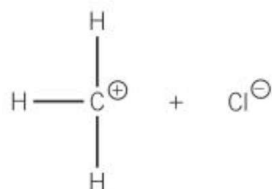
- A species with **an unpaired electron**
- Represented with a dot (•)
- e.g. $\text{H}_3\text{C}-\text{CH}_3 \rightarrow \text{H}_3\text{C}\cdot + \cdot\text{CH}_3$

- Curly arrows

- Showing the **movement of an electron pair**
- Showing either heterolytic fission or formation of a covalent bond



heterolytic fission



- Types of reaction

- Addition reaction
 - Two 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

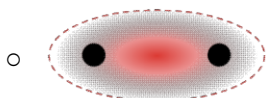
4.1.2 Alkanes

- 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

- Bonding in alkanes

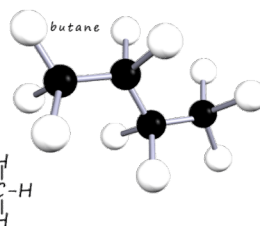
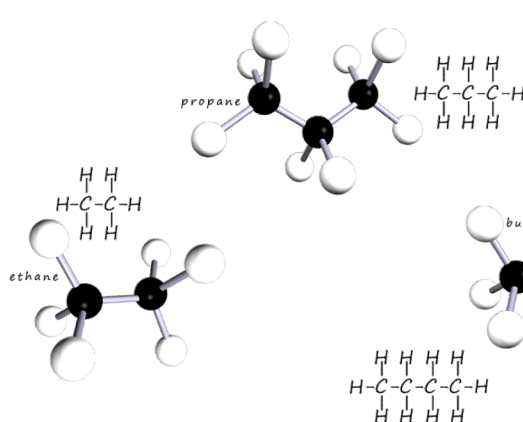
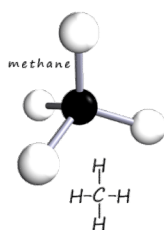
- Saturated hydrocarbons
- Only carbon and hydrogen atoms joined together by single covalent bonds
- Bond type = σ -bond (sigma bond)
 - σ -bond = **heads on** overlap of orbitals directly between the bonding atoms
 - One orbital from each bonding atom, each containing one electron
 - Positioned on a 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 electron 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
- Reactivity of alkanes
 - Low reactivity
 - C-C and C-H σ -bonds are strong
 - 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: $C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$
 - 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: $R-CH_3 + X_2 \rightarrow R-CH_2X + HX$
 - 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. $Cl_2 \xrightarrow{u.v.} 2Cl\bullet$
 - 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
 - A halogen radical reacts with a C-H bond in the methane → forming an alkyl radical + a hydrogen halide molecule
 - $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$
 - Second propagation step
 - Each alkyl radical reacts with another halogen molecule → forming haloalkane + new halogen radical
 - $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
 - 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)
- 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 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)

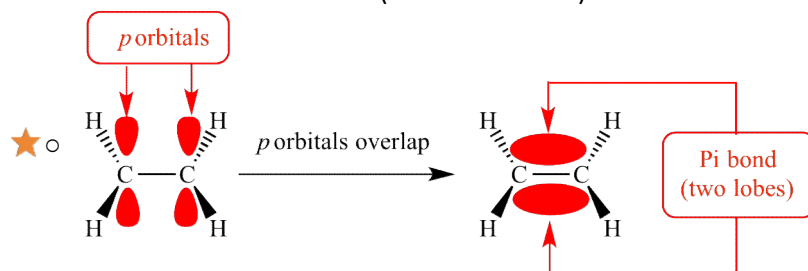
4.1.3 Alkenes

- 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 $\delta+$ charge
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)

- 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)

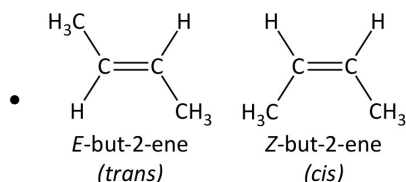


- **Trigonal planar** shape around each carbon atom in the C=C bond (120° bond angle)
 - 3 regions of electron density around each carbon atom
 - The 3 regions repel each other as far apart as possible

- 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

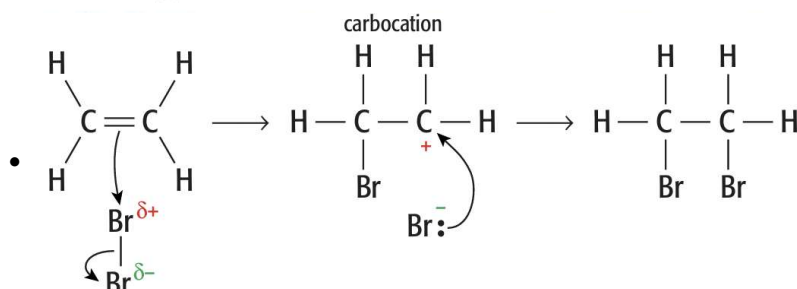
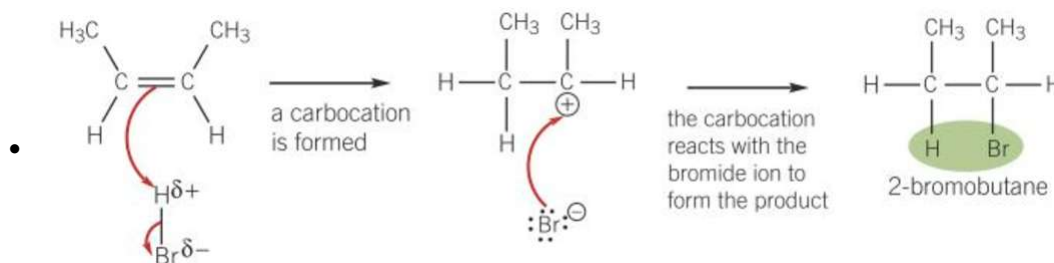
- Stereoisomer
 - Compounds with the **same structural formula** but with a **different arrangement in space**
- E/Z isomerism / geometrical isomerism
 - An type of stereoisomerism
 - Different groups attached to each carbon atom of a C=C double bond may be arranged differently in space because of the 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



- 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**
- 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 alkenes

Reaction	Condition	Detail
Hydrogenation	<ul style="list-style-type: none"> Nickel catalyst 423 K (150°C) High pressure 	<ul style="list-style-type: none"> Alkene + hydrogen \rightarrow alkane / $\text{R-CH=CH}_2 + \text{H}_2 \rightarrow \text{R-CH}_2\text{-CH}_3$ Type: hydrogenation / addition
Halogenation	<ul style="list-style-type: none"> RTP 	<ul style="list-style-type: none"> Alkene + halogen \rightarrow dihaloalkane e.g. $\text{R-CH=CH}_2 + \text{Br}_2 \rightarrow \text{R-CHBr-CH}_2\text{Br}$ Type: electrophilic addition (see below for mechanism) Reaction of alkenes with bromine can be used to test if the organic compound is unsaturated <ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> Room temperature 	<ul style="list-style-type: none"> Alkene + halogen halide \rightarrow haloalkane e.g. $\text{R-CH=CH}_2 + \text{HBr} \rightarrow \text{R-CHBr-CH}_3$ 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	<ul style="list-style-type: none"> Steam Phosphoric acid (H_3PO_4) catalyst 	<ul style="list-style-type: none"> Alkene + $\text{H}_2\text{O}_{(g)} \rightarrow$ alcohol Type: hydration $\text{R-CH=CH}_2 + \text{H}_2\text{O} \rightarrow \text{R-CH(OH)-CH}_3$ * 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 \rightarrow 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

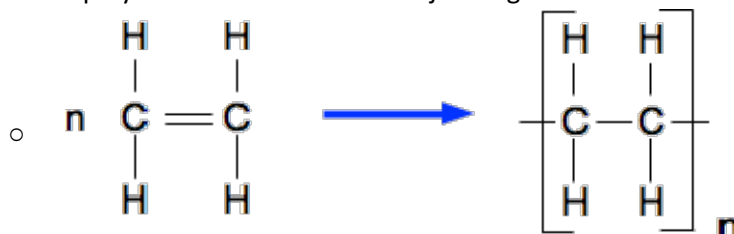
Type	Definition
Primary	1 alkyl group attached to the positively charged carbon atom
Secondary	2 alkyl groups attached to the positively charged carbon atom
Tertiary	3 alkyl groups attached to the positively charged carbon atom

Using Markownikoff's rule to predict formation of major organic product

- For **unsymmetrical alkanes**
- The hydrogen attaches itself to the carbon atom with the **larger number of hydrogen atoms**
- Stability: tertiary carbocation > secondary carbocation > primary carbocation
- Major product = halide / OH⁻ ion attached to the **most stable carbocation**

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
 - 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, CO₂ 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