Alkanes Combustion

REACTANTS: Alkane and O₂ (oxygen)

CONDITIONS: Excess of Oxygen (for complete combustion)

PRODUCT(S): Carbon Dioxide and Water

REACTION TYPE: Combustion

REACTION:

 $C_5H_{12} + 80_2 \longrightarrow 5CO_2 + 6H_2O$

(example of pentane)

Alkane Oxygen Carbon Dioxide Water

- When excess oxygen is present complete combustion occurs so carbon dioxide and water are the only products.
- Incomplete combustion of alkanes occurs when oxygen becomes a limiting reagent, leading to the formation of carbon monoxide (CO) and solid carbon particulates (soot).



Alkanes Free Radical Substitution

REACTANTS: Alkanes and Halogen **CONDITIONS:** U.V (ultraviolet) light

PRODUCT: Halogenoalkane

REACTION TYPE: Free Radical Substitution

REACTION: (example of methane)

CH₄ + Cl₂

CH₃Cl + HCl

CH₃Cl + HCl

Alkane

Chlorine

Chloroalkane

Hydrogen Halide

- Chain reaction, occurring in three steps initiation, propagation and termination. See mechanism.
- U.V light is required to homolytically split halogen molecule, forming two radical species.
- Further substitution can occur, forming di, tri and tetra halogenoalkanes.



Halogenoalkanes Substitution (OH⁻)

REACTANTS: Halogenoalkane and Sodium Hydroxide, *NaOH* (for OH⁻ ions)

CONDITIONS: Heat under reflux, Aqueous ('aq' - water present)

PRODUCT(S): Alcohol and Halide Ion (sodium halide salt if sodium hydroxide used)

REACTION TYPE: Nucleophilic Substitution, *Hydrolysis*



- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Rate of hydrolysis can compared using aqueous silver nitrate (AgNO₃) within the reaction mixture and timing how long it takes to form precipitate (CI = **white** ppt, Br = **cream** ppt and I = **yellow** ppt).
- Reaction must be carried out in **aqueous conditions**, otherwise an elimination can occur.



Halogenoalkanes Substitution (CN⁻)

REACTANTS: Halogenoalkane and Sodium *or Potassium* Cyanide (NaCN *or KCN*) **CONDITIONS:** Heat under reflux, Ethanolic (ethanol as the solvent, **no water present**)

PRODUCT(S): Nitrile and Halide Ion (*forms salt with Na*⁺ *or K*⁺)

REACTION TYPE: Nucleophilic Substitution

REACTION: (example of pentane)

H—C—C—Br

reflux

H—C—C—CN

H—H

Halogenoalkane

Nitrile

- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest, giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Reaction must be carried out in ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form rather than the nitrile.
- Reaction is heated under reflux to ensure no volatile substances are lost.



Decomposition (Free Radical) Ozone

REACTANTS: Chlorine Radical and Ozone (O₃)

CONDITIONS: Upper Atmosphere, (u.v light to form chlorine radical)

PRODUCT(S): Oxygen

REACTION TYPE: Decomposition (Free Radical)

REACTION: (example of ozone)

$$\begin{array}{cccc}
\text{Cl} & + & 0_3 & \longrightarrow & \text{ClO} & + & 0_2 \\
\text{ClO} & + & 0_3 & \longrightarrow & \text{Cl} & + & 20_2
\end{array}$$

- Chlorine radical is formed by homolytic fission of chlorine molecule in upper atmopshere by u.v light.
- This is a chain reaction as the chlorine radical is reformed and can go on to decompose more ozone molecules.
- Ozone (O₃) prevents u.v radiation from reaching the surface of planet Earth. The use of CFC's (chlorofluourinated carbons) in the 20th century lead to a depletion of ozone in the upper atmosphere;
 CFCs were banned as a result.

Alkenes Addition (HBr)

REACTANTS: Alkene and Hydrogen Bromide (HBr)

CONDITIONS: Hydrogen Bromide Gas or (concentrated) Hydrobromic Acid

PRODUCT(S): Bromoalkane

REACTION TYPE: Electrophilic Addition

REACTION: (example of ethene)

$$C = C \xrightarrow{H} \xrightarrow{HBr} H \xrightarrow{\Pi} \overset{\Pi}{\downarrow} H$$

$$H \xrightarrow{Br} H$$

Bromoalkane

NOTES:

• For unsymetrical alkenes, there will be two possible products from the electrophilic addition.

Alkene

• Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (major product) and which product will be made less readily (minor product). See mechanism.



Alkenes Addition (Br₂)

REACTANTS: Alkene and Bromine (Br₉)

CONDITIONS: Bromine Liquid (pure Br₂) or Bromine Water (Br₂(aq))

PRODUCT(S): Dibromoalkane

REACTION TYPE: Electrophilic Addition, *Bromination*

REACTION: (example of ethene)

$$H = C = C + H \xrightarrow{Br_2} H = C - C - H$$

$$Br Br$$

Alkene

Dibromoalkane

- Double bond in alkene polarises the bromine molecule to form an electrophile (Br^{δ+}) that starts the reaction.
- Reaction can be used to test for the presence of an alkene. A sample is mixed with bromine water, if the bromine water turns colourless (from orange brown) an alkene is present in the sample.



Alkenes Hydration (to alcohol)

REACTANTS: Alkene and Steam (H₂O_(a))

CONDITIONS: Heat and Acid Catalyst (Phosphoric Acid, HaPO)

PRODUCT(S): Alcohol

REACTION TYPE: Electrophilic Addition, (acid catalysed) Hydration

REACTION: (example of ethene)

$$H = C = C \qquad H \qquad H_{20/H^{+}} \qquad H = C - C - H$$
Alkene Alcohol

- Acid catalyst is required to form hydroxonium ion (H₃O⁺) ion that is able to act as an electrophile to start the reaction.
- For unsymetrical alkenes, there will be two possible products from the electrophilic addition.
- Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (major product) and which product will be made less readily (minor product). See mechanism.



Alkenes Hydrogenation (to alkane)

REACTANTS: Alkene and Hydrogen, H₂

CONDITIONS: Approximately 150°C and Nickel (solid) Catalyst

PRODUCT(S): Alkane

REACTION TYPE: Addition, *Hydrogenation*

REACTION: (example of ethene)

$$H = C = C \xrightarrow{H} \xrightarrow{H_2(g) / \text{Ni(s)}} H = C - C - H$$
Alkene
Alkane

NOTES:

Hydrogen is 'added' across the double bond - addition reaction and the hydrocarbon becomes saturated (from unsaturated (alkene)).



Alcohols Oxidation

REACTANTS: Alcohol (primary or secondary) and Acidified Dichromate ions (Cr₂O₇²⁻ / H⁺)

CONDITIONS: Heat*, Acid Catalyst (sulfuric acid (HaSOa))

PRODUCT(S): Aldehyde, Ketone or Carboxylic Acid (see below)

REACTION TYPE: Oxidation

REACTIONS: (example of primary and secondary alcohol)

- *Primary alcohols form aldehydes and carboxylic acids when heated with an oxidising agent. To isolate aldehyde, distill aldehyde from reaction mixture as soon as it is formed. To obtain carboxylic acid, heat under reflux to ensure full oxidation of aldehydes already formed.
- Secondary alcohols form ketones and are unable to be further oxidised. Tertiary alcohols are unable
 to be oxidised at all.
- Oxidising agents can be repesented as [O].



Alcohols Halogenation (KBr)

REACTANTS: Alcohol and 50% (concentrated) H₂SO₄ and Potassium Bromide, KBr **CONDITIONS:** (concentrated) H₂SO₄, Warm Temperature (for distillation of product)

PRODUCT(S): Bromoalkane **REACTION TYPE:** Halogenation

REACTIONS: (example of ethanol)

- KBr and H₂SO₄ react together to form HBr that reacts with the alcohol to form the bromoalkane.
- Bromoalkane is isolated from the reaction mixture by distillation.



Alcohols Elimination (to alkenes)

REACTANTS: Alcohol

CONDITIONS: Heat, Acid Catalyst (concentrated H₂SO₄ or concentrated H₃PO₄)

PRODUCT(S): Alkene

REACTION TYPE: Elimination, dehydration

REACTION: (example of ethene)

- Acid catalyst provides H⁺ ion to start reaction and is reformed at the end when a H⁺ ion is released by reacting molecule.
- Water molecule is removed, **dehydration reaction**.



•Aldehydes Reduction (NaBH₄)

REACTANTS: Aldehyde and NaBH₄ (reducing agent)

PRODUCT(S): Primary Alcohol **REACTION TYPE:** Reduction

REACTION:

- Aldehydes form primary alcohols when reduced.
- NaBH₄ is a reducing agent able to provide hydride (:H⁻) ions that are needed for the reduction of carbonyls.
- The hydrogens added in reduction reactions are often shown as [H].



•Ketones Reduction (NaBH₄)

REACTANTS: Ketone and NaBH₄ (reducing agent)

PRODUCT(S): Secondary Alcohol **REACTION TYPE:** Reduction

REACTION:

$$R-C \xrightarrow{0} R^{1} \xrightarrow{NaBH_{4}} R-C-H$$

$$R^{1}$$
Ketone (Secondary)

Alcohol

- Ketones form secondary alcohols when reduced.
- NaBH₄ is a reducing agent able to provide hydride (:H-) ions that are needed for the reduction of carbonyls.
- The hydrogens added in reduction reactions are often shown as [H].



Hydroxynitriles Formation (from carbonyls)

REACTANTS: Carbonyl (aldehyde or ketone) and KCN (in acid)

PRODUCT(S): Hydroxynitrile

REACTION TYPE: Nucleophilic Addition

REACTION:

$$R-C \nearrow \begin{matrix} 0 \\ R^1 \end{matrix} \xrightarrow{KCN(aq) / H_2SO_4(aq)} R-C-C \equiv N$$

Carbonyl Group

Hydroxynitrile

- HCN is sometimes written as the reactant, but HCN is very reactive and dangerous. By using KCN in dilute acid, the same product can be formed as with HCN.
- If a chiral carbon centre is formed in the product, the final product mixture will be **racemic**, containing both enantiomers in a 50:50 ratio. This is because carbonyl groups are planar and there is equal chance of the :CN⁻ nucleophile attacking the carbonyl group from above or below the plane producing two possible enantiomers in equal amounts.



Carboxylic Acids Acid-Base Reactions

Carboxylic acids are able to act as weak acids and react with bases as any weak acid does

$$2 \times \underset{R}{\overset{\circ}{\text{C}}} \underset{OH}{\overset{\circ}{\text{OH}}} + Zn \longrightarrow \underset{R}{\overset{\circ}{\text{C}}} \underset{O}{\overset{\circ}{\text{O}}} Zn^{2+} + H_2$$

$$Carboxylic \ Acid \qquad Metal \qquad Zinc \ Carboxylate \qquad Hydrogen \qquad (salt)$$

$$R \xrightarrow{\overset{\circ}{\text{C}}} \underset{OH}{\overset{\circ}{\text{O}}} + NaOH \longrightarrow \underset{(salt)}{\overset{\circ}{\text{C}}} \underset{(salt)}{\overset{\circ}{\text{C}}} \underset{(salt)}{\overset{\circ}{\text{C}}} + H^{\bullet} \underset{(salt)}{\overset{\circ}{\text{C}}}$$

NOTES:

 Salts formed by carboxylic acids are (usually) highly soluble in water and can be a useful source of conjugate bases for making buffer systems.



Esters Esterification (carboxylic acid and alcohol)

REACTANTS: Carboxylic Acid and Alcohol

CONDITIONS: Heat under reflux and (concentrated) Sulfuric Acid (H₂SO₄) catalyst

PRODUCT(S): Ester

REACTION TYPE: Condensation, Esterification

REACTION: $R-C \stackrel{\bigcirc{}0}{OH} + R^1-OH$ $\stackrel{H_2SO_4(aq)}{\longrightarrow}$ $R-C \stackrel{\bigcirc{}0}{\bigcirc} -R^1 + H_2O$ Carboxylic Acid Alcohol Ester Water

NOTES:

Reaction is reversible (see hydrolysis of esters), so a (concentrated) acid catalyst is needed to force
the position of equilibrium to the formation of ester.



Esters Hydrolysis

REACTANTS: Ester

CONDITIONS: Warm, Aqueous (with dilute acid or alkali)

PRODUCT(S): Carboxylic Acid (or carboxylate salt) and Alcohol

REACTION TYPE: Hydrolysis

REACTION(S):

$$R-C \xrightarrow{0} O -R^{1} \xrightarrow{OH_{(aq)}^{-}} R-C \xrightarrow{0} O + R^{1}-OH$$

Ester Carboxylate Ion Alcohol

- If alkaline (OH) conditions are used, a carboxylate ion is formed and can be isolated by adding a dilute
 acid.
- Fats and oils are tri-esters and can be broken down into three fatty acid molecules (carboxylic acids) and one alcohol molecule (glycerol) by hydrolysis.
- Biodisel can be made by the reaction of oil (tri-ester) with methanol in the presence of an acid catalyst, forming methyl esters that can be used as a diesel fuel.



Acyl Chlorides Formation (using SOCI₂)

REACTANTS: Carboxylic Acid and Sulfur Dichloride Oxide (SOCI₂)

PRODUCT(S): neat SOCI, (pure liquid SOCI,)

REACTION:
$$R-C \stackrel{O}{\searrow} OH \xrightarrow{SOCl_2} R-C \stackrel{O}{\searrow} Cl + SO_2 + HC$$

Carboxylic Acid

Acyl Chloride

NOTES:

Sulfur dioxide and hydrogen chloride gas are released as products.



Acyl Chlorides Addition-Elimination (H₂0)

REACTANTS: Acyl Chloride and H₂O **PRODUCT(S):** Carboxylic Acid and HCl

REACTION TYPE: Nucleophilic Addition-Elimination, Hydrolysis of acyl chloride

REACTION: $R = C \setminus Cl$ Acyl Chloride $R = C \setminus Cl$ $R = C \setminus Cl$ Carboxylic Acid

NOTES:

 Acyl chlorides are highly reactive and the reaction is vigorous, with heat given off (exothermic) and fumes of HCl released.



Acyl Chlorides Addition-Elimination (alcohol)

REACTANTS: Acyl Chloride and Alcohol

PRODUCT(S): Ester and HCI

REACTION TYPE: Nucleophilic Addition-Elimination, Esterification

REACTION: $R = C \setminus Cl$ $R = C \setminus Cl$ Acyl Chloride $R = C \setminus Cl$ $R = C \setminus Cl$ $R = C \setminus Cl$ Ester

NOTES:

Ester formed (esterification) has a sweet, fruity smell.



Acyl Chlorides Addition-Elimination (NH₃)

REACTANTS: Acyl Chloride and Ammonia

PRODUCT(S): Amide and HCl

REACTION TYPE: Nucleophilic Addition-Elimination

REACTION:

$$\begin{array}{c}
O \\
R
\end{array}$$

$$\begin{array}{c}
A \\
O \\
NH_{2}
\end{array}$$

$$\begin{array}{c}
O \\
NH_{4}
\end{array}$$

$$\begin{array}{c}
A \\
O \\
NH_{2}
\end{array}$$

$$\begin{array}{c}
A \\
O \\
NH_{4}
\end{array}$$

- Ammonia produces a primary amide and ammonium chloride salt when reacted with acyl chlorides.
- Primary amines produce a secondary amide and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.



Acyl Chlorides Addition-Elimination (amine)

REACTANTS: Acyl Chloride and Amine (primary)

PRODUCT(S): (Secondary) Amide and Alkyl Ammonium Chloride

REACTION TYPE: Nucleophilic Addition-Elimination

REACTION: $R^{1}NH_{2}$ $R^{1}NH_{2}$ $R^{1}NH_{2}$ $R^{1}NH_{2}$ $R^{1}NH_{2}$ $R^{2}NHR^{1}$ Acyl Chloride

Acyl Chloride

Acyl Chloride

- Primary amines produce a secondary amide and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.

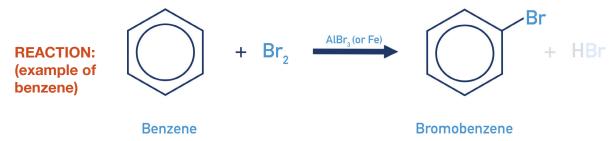


Benzene Bromination (adding Br₂)

REACTANTS: Benzene and Bromine (Br₂) **CONDITIONS:** Halogen Carrier (AlBr₃ or Fe)

PRODUCT(S): Bromobenzene

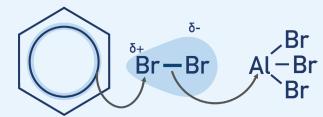
REACTION TYPE: Electrophilic Substitution, *Bromination*



NOTES:

 The delocalised electron system in benzene is unable to polarise the bromine molecule enough to form an electrophile.

A halogen carrier (AIBr₂ or Fe) is used to form the bromine electrophile.



H⁺ ion removed from benzene ring combines with Br from halogen carrier intermediate, [AlBr₄]⁻ to form HBr and reform the halogen carrier (AlBr₂)



Benzene Acylation (with acyl chlorides)

REACTANTS: Benzene and Acyl Chloride **CONDITIONS:** Warm and AlCl₃ catalyst **PRODUCT(S):** (Aromatic) Ketone

REACTION TYPE: Electrophilic Substitution, *Acylation (Friedel Crafts)*

NOTES:

Acylium (RCO+) ion is formed by reacting an acyl chloride with a halogen carrier (AlCl₃).

H⁺ ion removed from benzene ring combines with [AlCl₄]⁻ to reform AlCl₃ catalyst and form HCl.
 HCl. + AlCl₃

Halogen Carrier

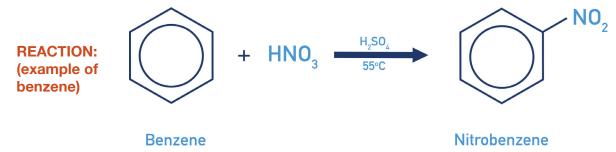
Benzene Nitration (adding NO₂)

REACTANTS: Benzene and (concentrated) Nitric Acid (HNO₂)

CONDITIONS: (Concentrated) Sulfuric Acid (HaSOa)

PRODUCT(S): Nitrobenzene

REACTION TYPE: Electrophilic Substitution, *Nitration*



NOTES:

Nitronium ion is formed by the reaction of concentrated nitric acid with concentrated sulfuric acid.

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

Nitronium Ion

H⁺ ion removed from benzene ring combines with hydrogen sulfate (HSO₄⁻) ion to reform catalyst H₂SO₄.



Benzene Alkylation (with halogenoalkanes)

REACTANTS: Benzene and Halogenoalkane **CONDITIONS:** Warm and AlCl₃ (or AlBr₃) catalyst

PRODUCT(S): Alkylbenzene

REACTION TYPE: Electrophilic Substitution, *Alkylation (Friedel-Crafts)*



NOTES:

• Alkyl (R+) ion is formed by reacting an acyl chloride with a halogen carrier (AlCl₂).

H⁺ ion removed from benzene ring combines with [AlCl₄] to reform AlCl₃ catalyst and form HCl.

Nitriles Reduction (to form primary amine)

REACTANTS: Nitrile and Reducing Agent - LiAlH₄, or Hydrogen gas (H₂(g)) **CONDITIONS:** Dry ether* (if using LiAlH₄), Nickel catalyst (if using H₂(g))

PRODUCT(S): Amine

REACTION TYPE: Reduction, *Hydrogenation*

REACTION:

R-C≡N

 $\begin{array}{c}
\text{LiAlH}_{4} \\
\text{or} \\
H_{2}(g) / \text{Ni}
\end{array}$

R-CH₂-NH₂

Nitrile

Amine

- If H₂(g) and a nickel catalyst is used, the reaction is an example of catalytic hydrogenation.
- *Dry ether must be used with LiAlH₄ (LiAlH₄ reacts violently with water). To obtain the amine as a final product, dilute acid must be added to the inital product from reduction.



Nitriles Acid Hydrolysis (to form carboxylic acids)

REACTANTS: Nitrile and (dilute) Hydrochloric Acid (HCl)

CONDITIONS: Heat under reflux

PRODUCT(S): Carboxylic Acid and Ammonium Chloride

REACTION TYPE: Hydrolysis

REACTION:

$$R-C\equiv N \xrightarrow{\text{(dilute)}} R-C \nearrow 0$$

Nitrile Carboxylic Acid

NOTES:

Full reaction:

$$RCN + 2H_2O + HCI \rightarrow RCOOH + [NH_4]^{\dagger}CI^{\dagger}$$

 Nitriles can also be hydrolysed in alkaline conditions (heated under reflux) using sodium hydroxide, forming the sodium carboxylate salt of the carboxylic acid.

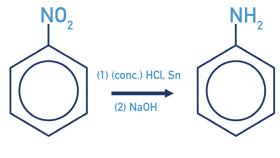


Nitroarenes Reduction (to form aromatic amines)

REACTANTS: Nitroarene and (concentrated) Hydrochloric Acid (HCI), followed by NaOH

CONDITIONS: Tin catalyst **PRODUCT(S)**: Aromatic Amine **REACTION TYPE**: Reduction

REACTION: (example of nitrobenzene)



Nitroarene

Phenylamine

NOTES:

When reacted with concentrated HCl, the nitroarene will form an ammonium ion -NH₃⁺. The aromatic amine can be obtained by adding dilute sodium hydroxide (to form -NH₂).



Phenol Bromination (Br₂)

REACTANTS: Phenol and Bromine water (Br₂(aq))

PRODUCT(S): 2,4,6-tribromopenol

REACTION TYPE: Electrophilic Substitution, *Bromination*

Phenol 2,4,6-tribromophenol

- Bromine water changes from orange-brown to colourless and a white precipitate forms.
- Unlike with benzene, no halogen carrier catalyst is needed for the bromination of phenol. This
 is due to the increased electron density in the delocalised electron ring (from the -OH group),
 making phenol more reactive than benzene.

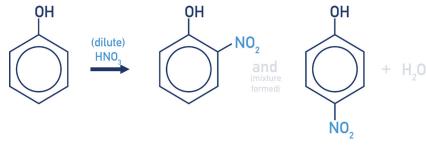


Phenol Nitration (using dilute nitric acid, HNO₃)

REACTANTS: Phenol and dilute Nitric Acid (HNO₃) **PRODUCT(S):** 2-nitrophenol and 4-nitrophenol (mixture)

REACTION TYPE: Electrophilic Substitution, *Nitration*

REACTION: (example of phenol)



Phenol

2-nitrophenol

4-nitrophenol

- Unlike with benzene, no sulfuric acid (H₂SO₄) catalyst is needed for the bromination of phenol.
 This is due to the increased electron density in the delocalised electron ring (from the -OH group) making phenol more reactive than benzene.
- If concentrated nitric acid is used, three NO₂ groups can be substituted, forming 2,4,6-trinitrophenol.



· Amines Acting as Bases (with acids)

REACTANTS: Amine and Acid

PRODUCT(S): Alkyl Ammonium Salt

REACTION TYPE: Acid-Base

REACTION:
$$R-N-H$$
 + HCl \longrightarrow $\begin{bmatrix} H \\ R-N-H \end{bmatrix}$ Cl Amine Acid Alkyl ammonium salt

NOTES:

Nitrogen atom in amine has lone pair of electrons that can act as a base and accept a H⁺ ion
in an acidic solution, forming an alkyl ammonium salt (with the negative ion from the acid).

• Butylamine with hydrochloric acid:

CH₃CH₂CH₂CH₂NH₃ + HCI → [CH₃CH₂CH₂CH₃NH₃]⁺Cl⁻ (butylammonium chloride)



Polymers Addition (from alkenes)

REACTANTS: Alkene

PRODUCT(S): Poly(alkene)

REACTION TYPE: Addition Polymerisation

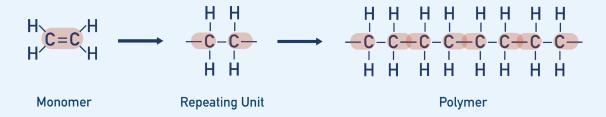
REACTION: (example of ethene)

$$n \times H = C = C + H \longrightarrow \begin{pmatrix} C & C \\ C & C \\ H & H \end{pmatrix}$$

Ethene

Polyethene

- The carbon-carbon double bond in the alkene breaks, allowing each carbon atom to form a new bond (with another carbon atom from another molecule).
- The alkenes that form a polymer are called **monomers**.
- The polymer is made up of **repeating units**.



Amino Acids Condensation Polymerisation (form proteins)

REACTANTS: Amino Acids

PRODUCT(S): Polyamide (polypeptide)

REACTION TYPE: Condensation Polymerisation

REACTION:

Amino Acid

Polyamide

- Polymer formed is a polyamide, often referred to as a polypeptide in biology.
- Polyamide chains formed by amino acids are used in nature to make up proteins.
- DNA is a 'code' used by organisms to give the correct amino acid sequence for a particular protein. A section of DNA that codes for a given protein is called a gene.

