

Organic Chemistry II - Reactions I

To succeed with this topic you need to

- Be able to name and draw organic molecules (Factsheet 15)
- have revisited Factsheet 5 ('Bonding') and Factsheet 06 ('Structure of elements and compounds') so you understand the bonding and shapes of organic molecules.

After working through this Factsheet you will

- Know the reactions of the families alkanes, alkenes and halogenoalkanes.
- Know the conditions and reagents for the reactions
- Understand how the bonding in the compounds influences their reactions
- Know some of the terms used in reaction mechanisms.

Reaction Mechanisms

When compounds or elements react then bonds are broken and bonds are formed in the chemical reaction.

The reaction mechanism is the method used to show the bond making and breaking processes by explaining what happens to the electrons involved in bonding.

N.B. A2 Units require a much more detailed use of reaction mechanisms.

Definition of Terms		
Term	Definition	Example
Free Radical	A species with a single unpaired electron	$\text{Cl}_2 \rightarrow \text{Cl}^\cdot + \text{Cl}^\cdot$ the \cdot on the Cl represents the unpaired electron
Nucleophile (literally 'liking the nucleus/ positive charge')	A donator of a lone pair of electrons (which so forms a new covalent bond)	
Electrophile (literally 'liking electrons/ negative charge')	An acceptor of a lone pair of electrons (so forming a new covalent bond)	The C^\ominus in the example above
Homolytic Fission	When a bond breaks and one electron goes to each atom (forming free radicals)	$\text{A} \cdot + \cdot \text{B}$ \downarrow $\text{A}^\cdot + \cdot \text{B}$
Heterolytic Fission	When a bond breaks and both electrons go to one atom (forming ions)	$\text{A} \cdot + \cdot \text{B}$ \downarrow $\text{A}^\ominus + \text{B}^\oplus$

Exam Hint - Unfamiliar compounds are used in questions but the secret is to learn how the family of compounds reacts. You identify the family the unfamiliar compound belongs to, remember how the family reacts and then apply this to the compound. Again, being able to name organic compounds is essential.

Reactions in organic chemistry



Substitution – When an atom or 'group' in a molecule is replaced by another atom or 'group'

Addition – When two molecules react to form a single product.

Elimination – When a simple molecule e.g. HCl, HBr, H₂O, is removed from a molecule and not replaced.

Hydrolysis - When water reacts with a molecule and the molecule is split into two parts.

Alkanes

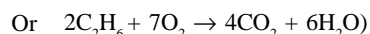
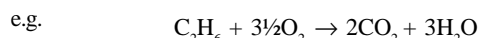
First let us revise what we covered in Factsheet number 15 about alkanes.

- Alkanes are hydrocarbons (made of carbon and hydrogen only).
- In an **homologous series** (differ from one another by only $-\text{CH}_2$).
- Alkanes have a **general formula** of $\text{C}_n\text{H}_{2n+2}$.
- Alkanes are saturated compounds (Contain only single carbon bonds i.e. C-C).

Reactions

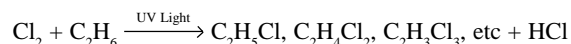
Alkanes are relatively unreactive because of the strength of the C-C and C-H bonds they contain. The two reactions **all** alkanes undergo are :

1. Burning in **excess oxygen** to form **carbon dioxide** and **water**



Reaction type : combustion

2. React with Cl_2 or Br_2 in the presence of UV light/sunlight to form a complex mix of halogenoalkanes and hydrocarbons.



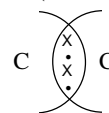
Reaction type: substitution

Mechanism: free radical

Alkenes

Unsaturated hydrocarbons (i.e. C=C) with a general formula of C_nH_{2n} .

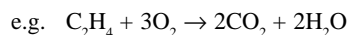
The C=C bond is



The double bond contains a π -bond and a σ -bond. The σ -bond is strong (the bond pair is in the plane between the two carbon nuclei) But the π -bond is weaker (the bond pair of electrons lies outside the plane of the nuclei). The π -bond will break so other atoms / groups **add** on to the C-C link.

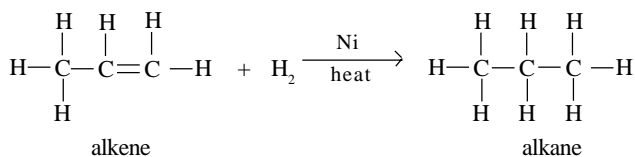
Reactions

1. Burning in **excess oxygen** to form **carbon dioxide** and **water**.



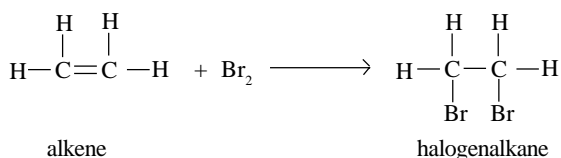
Reaction type: combustion

2. Alkenes and hydrogen react when mixed over **heated nickel catalyst**



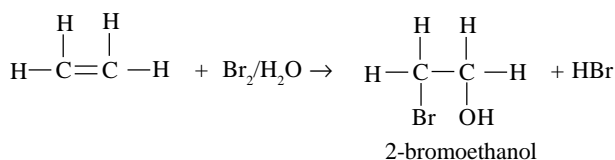
Reaction type: Addition
Condition: Heat + Ni
Mechanism: Electrophile

3. Alkenes react with **bromine / chlorine (halogens)**

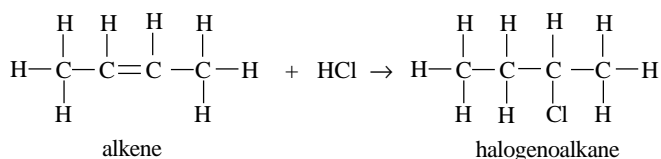


Reaction type: Addition
Mechanism: Electrophile

Key A solution of bromine in hexane (or trichloromethene) without heating, decolourises when added to a compound containing a C=C or triple bonds. This is an important test used for detecting unsaturation. NB. if bromine water (solution of bromine and water) is used, the solution is also decolourised, but a different product is formed.

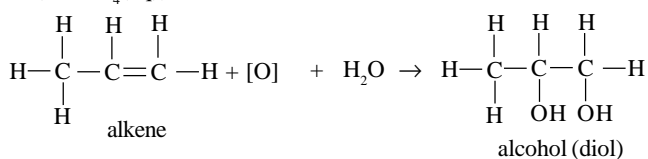


4. Alkenes add **hydrogen halides** (e.g. HCl, HBr, etc)



Reaction type: Addition
Mechanism: Electrophile

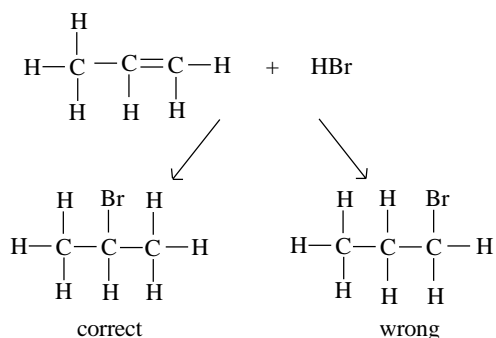
5. Oxidation by alkaline **potassium manganate(VII) solution** (KMnO₄(aq))



Reaction type: Addition
Condition: Alkaline
Mechanism: Electrophile

Markovnikov's Rule

'When a hydrogen halide is added to a double bond, the hydrogen always goes to the C atom with the most H atoms on it already'.



Exam Hint - This is very commonly tested in examinations

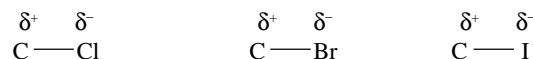
Halogenoalkanes (haloalkanes)

The general formula is C_nH_{2n+1}X, where X = Cl, Br or I. This means the **functional group** is a **halogen atom**.

All halogenoalkanes react in the **same way** with the **same reagents**, but the different halogens do affect the **rates of reaction**. The difference in the rate is explained by the **bond energies** shown below:

C-Cl	338 kJ mol ⁻¹
C-Br	276 kJ mol ⁻¹
C-I	238 kJ mol ⁻¹

Cl is a more **electronegative** atom than bromine which in turn is more electronegative than iodine, so creating dipoles,

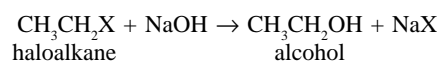


The C-Cl bond is stronger than C-Br, which means more energy is needed to break it so chloroalkanes will react slower than bromoalkanes, i.e. rates of reactions, C-I > C-Br > C-Cl

Reactions

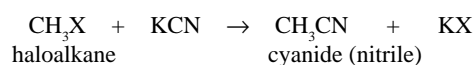
In the following examples 'X' is used for the halogen because Cl, Br and I will all react in the same way.

1. Reaction with **aqueous sodium (or potassium) hydroxide** to form an **alcohol**.



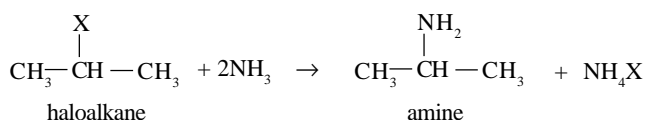
Reaction type: Substitution
Conditions: Aqueous + boil under reflux
Mechanism: Nucleophilic

2. Reaction with **potassium cyanide** to form a **nitrile (or cyanide)**.

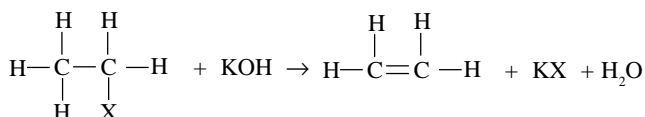


Reaction type: Substitution
Conditions: KCN in water/ethanol + boil under reflux
Mechanism: Nucleophilic

Key The decolourisation of an alkaline potassium manganate(VII) solution is another test for C=C bonds/unsaturation.

3. Reaction with **ammonia** to form **amines**.

Reaction type: Substitution
 Conditions: NH_3 in ethanol + heat
 Mechanism: Nucleophilic

4. Reaction with **ethanolic potassium hydroxide** to form **alkenes**.

Reaction type: Elimination
 Conditions: KOH in ethanol + boil under reflux

Tests for functional groups

Group/Family	Test	Result
Alkene C=C	Shake with bromine water, $\text{Br}_2(\text{aq})$	Colour of bromine solution goes from brown to colourless
Chloroalkane C-Cl	1. Warm with $\text{NaOH}(\text{aq})$	White precipitate - soluble in $\text{dil. NH}_3(\text{aq})$
Bromoalkane C-Br	2. Add dilute HNO_3 until just acidic	Cream precipitate - soluble in $\text{conc. NH}_3(\text{aq})$
Iodoalkane C-I	3. Add $\text{AgNO}_3(\text{aq})$	Yellow precipitate - insoluble in $\text{conc. NH}_3(\text{aq})$

Exam Hint - Candidates will be expected to know the tests for functional/family groups. Thorough knowledge of the reactions outlined in this Factsheet may be expected.

Practice Questions

- Propane will react with bromine under the correct conditions.
 - What are the conditions used?
 - Give the formula of four compounds likely to be formed by the reactions.
 - What type of reaction is this?
- Write the balanced chemical equations for the reaction of the following compounds with oxygen.
 - Propane
 - Octane
 - Butane
- Which family do the following hydrocarbons belong to?
 - C_5H_{12}
 - $\text{C}_{10}\text{H}_{20}$
 - C_4H_8
 - $\text{C}_{11}\text{H}_{24}$
- But-1-ene reacts with each of the following:
 - HI
 - Br_2
 - KMnO_4
 - H_2
 For each reaction give the
 - Balanced chemical equation
 - reactions and conditions

5. 2-bromopropene will react with each of the following:

- KCN
 - KOH (aq)
 - NH_3
- For each reaction give the
- balanced chemical equation
 - reagents and conditions

6. Give the name and structural formula of the organic product in each reaction.

- $\text{CH}_3\text{CHICH}_3 \xrightarrow{\text{NaOH}(\text{aq})}$ A
- $\text{CH}_3-\text{CH}_2\text{Br} \xrightarrow[\text{KOH}]{\text{ethanolic}}$ B
- $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr}}$ C
- $\text{CH}_2=\text{CH}_2 \xrightarrow{\text{H}_2}$ D

Answers

- UV Light / Sunlight
 - HBr, $\text{C}_3\text{H}_7\text{Br}$, $\text{C}_3\text{H}_6\text{Br}_2$, $\text{C}_3\text{H}_5\text{Br}_3$, etc
 - Substitution
- $\text{C}_3\text{H}_6 + 4\frac{1}{2}\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$ (or 'doubled')
 - $\text{C}_8\text{H}_{18} + 12\frac{1}{2}\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$ (or 'doubled')
 - $\text{C}_4\text{H}_{10} + 6\frac{1}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$ (or 'doubled')
- alkane
 - alkene
 - alkene
 - alkane
- $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{CHICH}_3$
Condition: goes at room temperature
 - $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHICH}_2$
Condition: Br_2 in hexane at room temperature
 - $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + [\text{O}] + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CHBr}-\text{CH}_2\text{Br}$
Condition: KMnO_4 in alkaline solution
 - $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
Condition: Heat + Nickel catalyst
- $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + \text{KCN} \rightarrow \begin{array}{c} \text{CN} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + \text{KBr}$
Condition: boil KCN dissolved in mixture of water and ethanol
 - $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + \text{NaOH} \rightarrow \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + \text{NaBr}$
Condition: boil under reflux with $\text{NaOH}(\text{aq})$
 - $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + 2\text{NH}_3 \rightarrow \begin{array}{c} \text{NH}_2 \\ | \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array} + \text{NH}_4\text{Br}$
Condition: heat concentrated solution of NH_3 in ethanol
- A = $\text{CH}_3\text{CHOHCH}_3$ Propan-2-ol
 - B = $\text{CH}_2=\text{CH}_2$ Ethene
 - C = $\text{CH}_3\text{CHBrCH}_3$ 2-bromopropane
 - D = CH_3CH_3 Ethane

Acknowledgements:

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