ChemFactsheet

April 2001 **Number 16**

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.**

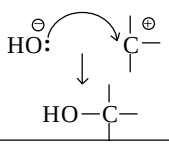
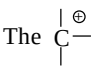
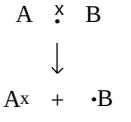
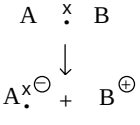
Reaction Mechanisms

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	$Cl_2 \rightarrow Cl^{\cdot} + Cl^{\cdot}$ 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  in the example above
Homolytic Fission	When a bond breaks and **one** electron goes to **each** atom (forming **free radicals**)	
Heterolytic Fisson	When a bond breaks and **both** electrons go to one atom (**forming ions**)	

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, H_2O, 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 $-CH_2$).
- Alkanes have a **general formula** of $\mathbf{C_nH_{2n+2}}$.
- 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**

   e.g. $C_2H_6 + 3½O_2 \rightarrow 2CO_2 + 3H_2O$

   Or $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O)$

   Reaction type : combustion

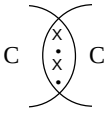
2. React with Cl_2 or Br_2 in the presence of UV light/sunlight to form a complex mix of halogenoalkanes and hydrocarbons.

   $$Cl_2 + C_2H_6 \xrightarrow{\text{UV Light}} C_2H_5Cl,\ C_2H_4Cl_2,\ C_2H_3Cl_3, \text{ etc} + HCl$$

   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.

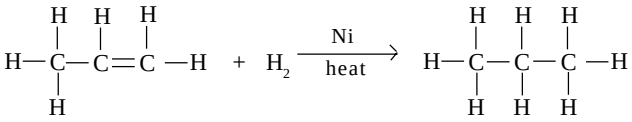
Reactions

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

   e.g. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

   Reaction type: combustion

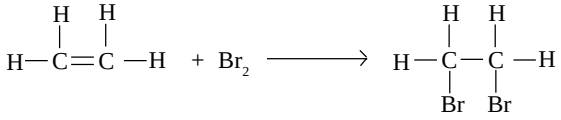
2. Alkenes and hydrogen react when mixed over **heated nickel catalyst**



alkene alkane

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

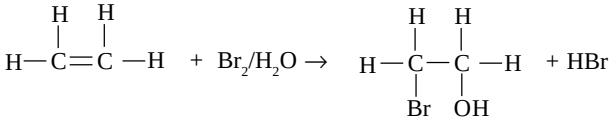
3. Alkenes react with **bromine / chlorine (halogens)**



alkene halogenalkane

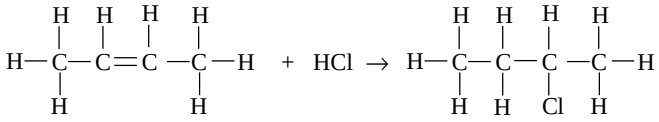
   Reaction type: Addition
   Mechanism: Electrophile

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 dectecting unsaturation. NB. if bromine water (solution of bromine and water) is used, the solution is also decolourised, but a different product is formed.



2-bromoethanol

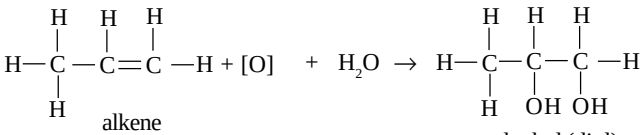
4. Alkenes add **hydrogen halides** (e.g. HCl, HBr, etc)



alkene halogenoalkane

   Reaction type: Addition
   Mechanism: Electrophile

5. Oxidation by alkaline **potassium manganate(VII) solution** ($KMnO_4(aq)$)



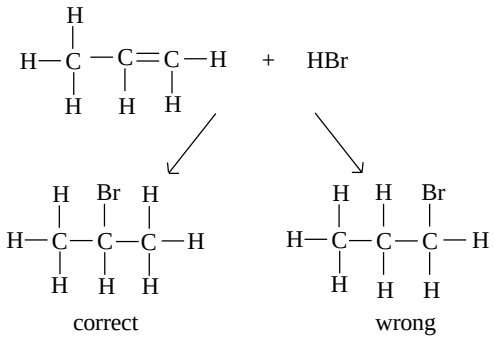
alkene alcohol (diol)

   Reaction type: Addition
   Condition: Alkaline
   Mechanism: Electrophile

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

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'.



correct wrong

Exam Hint *- This is very commonly tested in examinations*

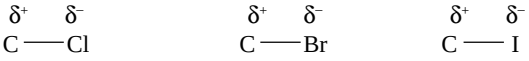
Halogenoalkanes (haloalkanes)

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 that bromine which in turn is more electronegative than iodine, so creating dipoles,

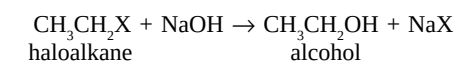


The C–Cl bond is stronger than C–Br, which means more energy is needed to break it so chloroalkanes will react slower than bromoalkanes,
i.e. rates of reactions, C–I > C–Br > C–Cl

Reactions

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

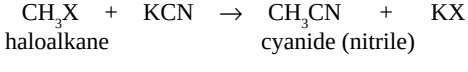
1. Reaction with **aqueous sodium (or potassium) hydroxide** to form an **alcohol**.



haloalkane alcohol

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

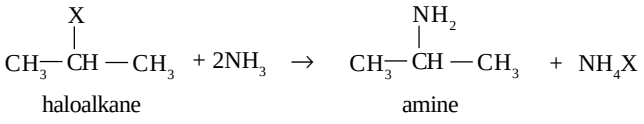
2. Reaction with **potassium cyanide** to form a **nitrile** (**or cyanide**).



haloalkane cyanide (nitrile)

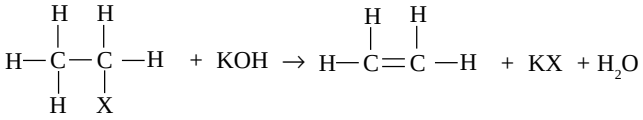
   Reaction type: Substitution
   Conditions: KCN in water/ethanol + boil under reflux
   Mechanism: Nucleophilic

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, $Br_2(aq)$	Colour of bromine solution goes from brown to colourless
Chloroalkane C-Cl	1. Warm with NaOH(aq)	White precipitate - soluble in dil.$NH_3(aq)$
Bromoalkane C-Br	2. Add dilute HNO_3 until just acidic	Cream precipitate - soluble in conc. $NH_3(aq)$
Iodoalkane C-I	3. Add $AgNO_3(aq)$	Yellow precipitate - insoluble in conc. $NH_3(aq)$

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

Practice Questions

1. Propane will react with bromine under the correct conditions.
   (a) What are the conditions used?
   (b) Give the formula of <u>four</u> compounds likely to be formed by the reactions.
   (c) What type of reaction is this?

2. Write the balanced chemical equations for the reaction of the following compounds with oxygen.
   (a) Propane (b) Octane (c) Butane

3. Which family do the following hydrocarbons belong to?
   (a) C_5H_{12}, (b) $C_{10}H_{20}$ (c) C_4H_8 (d) $C_{11}H_{24}$

4. But–1–ene reacts with each of the following:
   (i) HI (ii) Br_2 (iii) $KMnO_4$ (iv) H_2
   For each reaction give the
   (a) Balanced chemical equation
   (b) reactions and conditions

5. 2–bromopropene will react with each of the following:
   (i) KCN
   (ii) KOH (aq)
   (iii) NH_3
   For each reaction give the
   (a) balanced chemical equation
   (b) reagents and conditions

6. Give the name and structural formula of the organic product in each reaction.
   (a) $CH_3CHICH_3 \xrightarrow{NaOH(aq)}$ A
   (b) $CH_3—CH_2Br \xrightarrow[KOH]{ethanolic}$ B
   (c) $CH_3—CH=CH_2 \xrightarrow{HBr}$ C
   (d) $CH_2=CH_2 \xrightarrow{H_2}$ D

Answers

1. (a) UV Light / Sunlight
   (b) HBr, C_3H_7Br, $C_3H_6Br_2$, $C_3H_5Br_3$, etc
   (c) Substitution

2. (a) $C_3H_6 + 4½O_2 \rightarrow 3CO_2 + 3H_2O$ (or 'doubled')
   (b) $C_8H_{18} + 12½O_2 \rightarrow 8CO_2 + 9H_2O$ (or 'doubled')
   (c) $C_4H_{10} + 6½O_2 \rightarrow 4CO_2 + 5H_2O$ (or 'doubled')

3. (a) alkane (b) alkene (c) alkene (d) alkane

4. (i) $CH_3CH_2CH=CH_2 + HI \rightarrow CH_3CH_2CHCH_3$
   Condition: goes at room teperature

   (ii) $CH_3CH_2CH=CH_2 + Br_2 \rightarrow CH_3CH_2CHICH_2$
   Condition: Br_2 in hexane at room temperature

   (iii) $CH_3CH_2CH=CH_2 + [O] + H_2O \rightarrow CH_3CH_2CHBr\text{-}CH_2Br$
   Condition: $KMnO_4$ in alkaline soultion

   (iv) $CH_3CH_2CH=CH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$
   Condition: Heat + Nickel catalyst

5. (i) $CH_3\text{-}\underset{Br}{CH}\text{-}CH_3 + KCN \rightarrow CH_3\text{-}\underset{CN}{CH}\text{-}CH_3 + KBr$
   Condition: boil KCN dissolved in mixture of water and ethanol

   (ii) $CH_3\text{-}\underset{Br}{CH}\text{-}CH_3 + NaOH \rightarrow CH_3\text{-}\underset{OH}{CH}\text{-}CH_3 + NaBr$
   Condition: boil under reflux with NaOH(aq)

   (iii) $CH_3\text{-}\underset{Br}{CH}\text{-}CH_3 + 2NH_3 \rightarrow CH_3\text{-}\underset{NH_2}{CH}\text{-}CH_3 + NH_4Br$
   Condition: heat concentrated solution of NH_3 in ethanol

6. A = $CH_3CHOHCH_3$ Propan-2-ol
   B = $CH_2=CH_2$ Ethene
   C = $CH_3CHBrCH_3$ 2-bromopropane
   D = CH_3CH_3 Ethane

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