

Anglo-Chinese School (Independent)

Year 6 (2021) IBDP HL Chemistry



# **TOPIC 10 ORGANIC CHEMISTRY**

# (IBDP syllabus Topic 10)

10.1 Fundamentals of Organic Chemistry

- Essential Idea: Organic chemistry focuses on the chemistry of compounds containing carbon.

10.2 Functional Group Chemistry

- Essential Idea: Structure, bonding and chemical reactions involving functional group interconversions are key strands in organic chemistry.

# 20.1 Types of Organic Reactions

- Essential Idea: Key organic reaction types include nucleophilic substitution, electrophilic addition, electrophilic substitution and redox reactions. Reaction mechanisms vary and help in understanding the different types of reaction taking place.

# 20.2 Synthetic Routes

- Essential Idea: Organic synthesis is the systematic preparation of a compound from a widely available starting material or the synthesis of a compound via a synthetic route that often can involve a series of different steps.

# 20.3 Stereoisomerism

- Essential Idea: Stereoisomerism involves isomers which have different arrangements of atoms in space but do not differ in connectivity or bond multiplicity (ie whether single, double or triple) between the isomers themselves.

### 10.1 Fundamentals of organic chemistry

### Solution Nature of science:

Serendipity and scientific discoveries—PTFE and superglue. (1.4)

Ethical implications—drugs, additives and pesticides can have harmful effects on both people and the environment. (4.5)

#### Understandings:

- A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit.
- Structural formulas can be represented in full and condensed format.
- Structural isomers are compounds with the same molecular formula but different arrangements of atoms.
- Functional groups are the reactive parts of molecules.
- Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.



• Benzene is an aromatic, unsaturated hydrocarbon.

#### Applications and skills:

- Explanation of the trends in boiling points of members of a homologous series.
- Distinction between empirical, molecular and structural formulas.
- Identification of different classes: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, nitriles and arenes.
- Identification of typical functional groups in molecules eg phenyl, hydroxyl, carbonyl, carboxyl, carboxamide, aldehyde, ester, ether, amine, nitrile, alkyl, alkenyl and alkynyl.
- Construction of 3-D models (real or virtual) of organic molecules.
- Application of IUPAC rules in the nomenclature of straight-chain and branched chain isomers.
- Identification of primary, secondary and tertiary carbon atoms in halogenoalkanes and alcohols and primary, secondary and tertiary nitrogen atoms in amines.
- Discussion of the structure of benzene using physical and chemical evidence.

#### Guidance:

- Skeletal formulas should be discussed in the course.
- The general formulas (eg CnH<sub>2n+2</sub>) of alkanes, alkenes, alkynes, ketones, alcohols, aldehydes and carboxylic acids should be known.
- The distinction between class names and functional group names needs to be made. Eg for OH, hydroxyl is the functional group whereas alcohol is the class name.
- The following nomenclature should be covered:
  - o non-cyclic alkanes and halogenoalkanes up to halohexanes.
  - o alkenes up to hexene and alkynes up to hexyne.
  - compounds up to six carbon atoms (in the basic chain for nomenclature purposes) containing only one of the classes of functional groups: alcohols, ethers, aldehydes, halogenoalkanes, ketones, esters and carboxylic acids.

# 10.2 Functional group chemistry

### Solution Nature of science:

Use of data—much of the progress that has been made to date in the developments and applications of scientific research can be mapped back to key organic chemical reactions involving functional group interconversions. (3.1)

### Understandings:

Alkanes:

• Alkanes have low reactivity and undergo free-radical substitution reactions.

Alkenes:

- Alkenes are more reactive than alkanes and undergo addition reactions.
- Bromine water can be used to distinguish between alkenes and alkanes.

Alcohols:

• Alcohols undergo nucleophilic substitution reactions with acids (also called esterification or condensation) and some undergo oxidation reactions.

Halogenoalkanes:

• Halogenoalkanes are more reactive than alkanes. They can undergo (nucleophilic) substitution reactions. A nucleophile is an electron-rich species containing a lone pair that it donates to an electron-deficient carbon.

Polymers:

• Addition polymers consist of a wide range of monomers and form the basis of the plastics industry.

Benzene:

 Benzene does not readily undergo addition reactions but does undergo electrophilic substitution reactions.

### Applications and skills:

Alkanes:

- Writing equations for the complete and incomplete combustion of hydrocarbons.
- Explanation of the reaction of methane and ethane with halogens in terms of a free-radical substitution mechanism involving photochemical homolytic fission.

Alkenes:

- Writing equations for the reactions of alkenes with hydrogen and halogens and of symmetrical alkenes with hydrogen halides and water.
- Outline of the addition polymerization of alkenes.
- Relationship between the structure of the monomer to the polymer and repeating unit.

Alcohols:

- Writing equations for the complete combustion of alcohols.
- Writing equations for the oxidation reactions of primary and secondary alcohols (using acidified potassium dichromate(VI) or potassium manganate(VII) as oxidizing agents). Explanation of distillation and reflux in the isolation of the aldehyde and carboxylic acid products.
- Writing the equation for the condensation reaction of an alcohol with a carboxylic acid, in the presence of a catalyst (eg concentrated sulfuric acid) to form an ester.

Halogenoalkanes:

• Writing the equation for the substitution reactions of halogenoalkanes with aqueous sodium hydroxide.

### Guidance:

- Reference should be made to initiation, propagation and termination steps in free-radical substitution reactions. Free radicals should be represented by a single dot.
- The mechanisms of  $S_N1$  and  $S_N2$  and electrophilic substitution reactions are not required.

### 20.1 Types of organic reactions

### ØNature of science:

Looking for trends and discrepancies—by understanding different types of organic reactions and their mechanisms, it is possible to synthesize new compounds with novel properties which can then be used in several applications. Organic reaction types fall into a number of different categories. (3.1)

Collaboration and ethical implications—scientists have collaborated to work on investigating the synthesis of new pathways and have considered the ethical and environmental implications of adopting green chemistry. (4.1, 4.5)

### Understandings:

Nucleophilic Substitution Reactions:

- S<sub>N</sub>1 represents a nucleophilic unimolecular substitution reaction and S<sub>N</sub>2 represents a nucleophilic bimolecular substitution reaction. S<sub>N</sub>1 involves a carbocation intermediate. S<sub>N</sub>2 involves a concerted reaction with a transition state.
- For tertiary halogenoalkanes the predominant mechanism is  $S_N1$  and for primary halogenoalkanes it is  $S_N2$ . Both mechanisms occur for secondary halogenoalkanes.
- The rate determining step (slow step) in an SN1 reaction depends only on the concentration of the halogenoalkane, rate = k[halogenoalkane]. For  $S_N2$ , rate = k[halogenoalkane][nucleophile].  $S_N2$  is stereospecific with an inversion of configuration at the carbon.
- S<sub>N</sub>2 reactions are best conducted using aprotic, non-polar solvents and S<sub>N</sub>1 reactions are best conducted using protic, polar solvents.

Electrophilic Addition Reactions:

- An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.
- Markovnikov's rule can be applied to predict the major product in electrophilic addition reactions
  of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major
  product can be explained in terms of the relative stability of possible carbocations in the reaction
  mechanism.

Electrophilic Substitution Reactions:

 Benzene is the simplest aromatic hydrocarbon compound (or arene) and has a delocalized structure of π bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.

### Applications and skills:

Nucleophilic Substitution Reactions:

- Reference should be made to heterolytic fission for S<sub>N</sub>1 reactions.
- Explanation of why hydroxide is a better nucleophile than water.
- Deduction of the mechanism of the nucleophilic substitution reactions of halogenoalkanes with aqueous sodium hydroxide in terms of S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms. Explanation of how the rate depends on the identity of the halogen (ie the leaving group), whether the halogenoalkane is primary, secondary or tertiary and the choice of solvent.
- Outline of the difference between protic and aprotic solvents.

Electrophilic Addition Reactions:

• Deduction of the mechanism of the electrophilic addition reactions of alkenes with halogens/interhalogens and hydrogen halides.

Electrophilic Substitution Reactions:

• Deduction of the mechanism of the nitration (electrophilic substitution) reaction of benzene (using a mixture of concentrated nitric acid and sulfuric acid).

Reduction Reactions:

- Writing reduction reactions of carbonyl containing compounds: aldehydes and ketones to primary and secondary alcohols and carboxylic acids to aldehydes, using suitable reducing agents.
- Conversion of nitrobenzene to phenylamine via a two-stage reaction.

### Guidance:

- Reference should be made to heterolytic fission for S<sub>N</sub>1 reactions.
- The difference between homolytic and heterolytic fission should be understood.
- The difference between curly arrows and fish-hooks in reaction mechanisms should be emphasized.
- Use of partial charges (δ+ and δ-) and wedge-dash three-dimensional representations (using tapered bonds as shown below) should be encouraged where appropriate in explaining reaction mechanisms.



• Typical conditions and reagents of all reactions should be known (eg catalysts, reducing agents, reflux etc.). However, more precise details such as specific temperatures need not be included.

# 20.2 Synthetic routes

#### ØNature of science:

Scientific method—in synthetic design, the thinking process of the organic chemist is one which invokes retro-synthesis and the ability to think in a reverse-like manner. (1.3)

### Understandings:

- The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes.
- Retro-synthesis of organic compounds.

### Applications and skills:

• Deduction of multi-step synthetic routes given starting reagents and the product(s).

### Guidance:

- Conversions with more than four stages will not be assessed in synthetic routes.
- Reaction types can cover any of the reactions covered in topic 10 and sub-topic 20.1.

### 20.3 Stereoisomerism

### Solution Nature of science:

Transdisciplinary—the three-dimensional shape of an organic molecule is the foundation pillar of its structure and often its properties. Much of the human body is chiral. (4.1)

### Understandings:

- Stereoisomers are subdivided into two classes—conformational isomers, which interconvert by rotation about a  $\sigma$  bond and configurational isomers that interconvert only by breaking and reforming a bond.
- Cis–trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups) relative to a reference plane. According to IUPAC, E/Z isomers refer to alkenes of the form R1R2C=CR3R4 (R1 ≠ R2, R3 ≠ R4) where neither R1 nor R2 need be different from R3 or R4.
- A chiral carbon is a carbon joined to four different atoms or groups.
- An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposeable mirror images of each other. Diastereomers are not mirror images of each other.
- A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

### Applications and skills:

- Construction of 3-D models (real or virtual) of a wide range of stereoisomers.
- Explanation of stereoisomerism in non-cyclic alkenes and C3 and C4 cycloalkanes.
- Comparison between the physical and chemical properties of enantiomers.
- Description and explanation of optical isomers in simple organic molecules.
- Distinction between optical isomers using a polarimeter.

### Guidance:

- The term geometric isomers as recommended by IUPAC is now obsolete and cis-trans isomers and E/Z isomers should be encouraged in the teaching programme.
- In the E/Z system, the group of highest Cahn–Ingold–Prelog priority attached to one of the terminal doubly bonded atoms of the alkene (ie R1 or R2) is compared with the group of highest precedence attached to the other (ie R3 or R4). The stereoisomer is Z if the groups lie on the same side of a reference plane passing through the double bond and perpendicular to the plane
- containing the bonds linking the groups to the double-bonded atoms; the other stereoisomer is designated as E.
- Wedge-dash type representations involving tapered bonds should be used for representations of optical isomers.

# 10.1 Fundamentals of Organic Chemistry

The name organic chemistry came from the word organism. Prior to 1828, all organic compounds had been obtained from organisms or their remains. The belief then was that the synthesis of organic compounds from inorganic compounds in the laboratory was impossible. All efforts had failed, and scientists became convinced that some "vital force" that living organisms had was necessary to make an organic compound. The synthesis of urea from inorganic substances in 1828 led to the disappearance of this vital force theory. The great number of carbon compounds is possible because of the ability of carbon to form strong covalent bonds to each other (catenation) while also holding the atoms of other non-metals strongly. The simplest organic compounds made up of carbon and hydrogen atoms only are known as hydrocarbons. Even these run into thousands!

### **10.1.1 Homologous Series and Their Physical Properties**

A homologous series is a series of compounds of the same family, with the **same general formula**, which **differ from each other by a common structural unit**.

The carbon atom's ability to catenate creates series of organic compounds that have similar structural features and chemical properties but differ from its adjacent members by  $(-CH_2-)$  group These compounds are referred to as a homologous series.

In the example below, each alkane differs from the next in the series by a –CH<sub>2</sub>– unit.

Methane	Ethane	Propane	Butane
H H H H H	н <b>н н</b> н <b>с н</b>	H H H         HC	H H H H H C C C C H H H H
CH <sub>4</sub>	CH₃CH₃	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>

Each member of homologous series is called a **homologue** and all members in the series can be represented by a **common general formula**. For example, the general formula for the alkane homologous series is  $C_nH_{2n+2}$ , where n is equal or greater than 1.

Members of a homologous series have **similar chemical properties** and are prepared by the same methods. However, they possess **different physical properties**, e.g. melting, boiling points and density.

	Alkane	Boiling Point / °C
Methane	CH <sub>4</sub>	-164
Ethane	CH <sub>3</sub> CH <sub>3</sub>	-89
Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-42
Butane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-0.5
Pentane	$CH_3CH_2CH_2CH_3$	36
Hexane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	69
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_3$	98
Octane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	125

As the **chain length (numbers of carbons) increases, the melting and boiling points of the homologues gradually increases**. This is because the size of electron cloud increases (more polarisable), the strength of instantaneous induced dipole–induced dipole interactions increases and more energy is required to separate the molecules.

**Branched isomers of organic compounds have lower boiling points than straight chain isomers** of organic compounds. Straight chain molecules have an elongated electron cloud whilst branched molecules have a more compact spherical electron cloud. An elongated electron cloud allows more contact with a neighbouring molecule over a greater surface area than a spherical one. As a result, straight chain molecules are able to form stronger intermolecular forces (instantaneous induced dipole – induced dipole interactions / London dispersion forces) between the molecules.

# **10.1.2 Representation of Organic Molecules**



Type of Formula		Description	Example			
ر י 		Description	Butane	Butanoic Acid		
General		Represents any member of a homologous series.	$C_nH_{2n+2}$	$C_nH_{2n+2}COOH$		
Empirical		Represents the simplest ratio of different types of atoms in a molecule.	C₂H₅	C₂H₄O		
Molecular		Represents the exact number of atoms of each element in the compound.	$C_4H_{10}$	C₃H7COOH		
	Displayed / Full Structural Formula	Represents all the atoms and the bonds between them. A line represents one covalent bond, i.e. a double bond is represented by 2 lines.	H H H H H C C C C H H H H H H H H H			
Structural	Condensed	Represents an unambiguous structure without bonds, where atoms are arranged in groups. It shows how groups of atoms are sequentially arranged	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH		
	Stereochemical	Represents spatial 3– dimensional structure of a molecule Solid lines ( ) represent bonds on the same plane as the paper Dashed line ( ) represent bonds receding into the paper				
	Skeletal	Representsasimplifiedorganicformula by removinghydrogen atoms fromalkyl chains, leavingjustthecarbonskeletonandotherfunctional groups thatmay be present.Note:1. Each covalent bond is represent	sented by a line	ОН		
		<ol> <li>A carbon atom is at the inters</li> <li>Since carbon can form 4 bon</li> </ol>	section of 2 lines ids, the number of hydrogen ato	ms on each carbon atom is 4		

# Exercise 1

Complete the following table with the appropriate formulae.

Compound	Empirical Formula	Molecular Formula	Condensed Formula	Displayed / Full Structural Formula	Skeletal Formula
Propanol	C₃H₀O	C₃H7OH	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	H H H H	ОН
Ethane					NA
But-1-ene					
Propanoic acid					
Methyl ethanoate					

### 10.1.3 Nomenclature

The purpose of the IUPAC system of nomenclature is to establish an international standard of naming compounds to facilitate communication. The goal of the system is to give each structure a unique and unambiguous name, and to correlate each name with a unique and unambiguous structure. IUPAC nomenclature is based on naming a molecule's longest chain of carbons that includes the functional group. All deviations, either multiple bonds or substituent atoms other than carbon and hydrogen, are indicated by prefixes or suffixes according to a specific set of priorities.

The name of an organic molecule is made up of 3 parts: the **Prefix**, the **Stem** and the **Suffix**.



The stem part of the name refers to the longest possible continuous carbon chain that includes the functional group\*, if there are any. Functional groups of highest priority is indicated by suffix; the others are indicated by prefix (see table in rule 2).

Steps to naming:

**Rule 1:** Identify the longest continuous carbon chain – this gives the **stem** of the name as follows.

Number of carbon atoms in longest continuous chain	Stem in IUPAC name	Example
1	Meth-	CH4, Methane
2	Eth-	CH <sub>3</sub> CH <sub>3</sub> , Ethane
3	Prop-	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> , Propane
4	But–	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , Butane
5	Pent-	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , Pentane
6	Hex-	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> , Hexane

Rule 2: Identify the functional group.

The functional group usually determines the specific ending or **suffix** to the name. the suffixes used for some common functional groups are shown in the table below.

Class	Functional group	Name of functional group	Suffix in IUPAC name	General formula	Priority
Alkane			-ane	$C_nH_{2n+2}$	
Alkene		Alkenyl	ene	$C_nH_{2n}$	6
Alkyne	c <u>=</u> _c	Alkynyl	-yne	$C_nH_{2n-2}$	7
Alcohol	–OH	Hydroxyl	–anol	$C_nH_{2n+1}OH$	4
Ether	R–O–R'	Ether	–oxyalkane	R–O–R'	
Aldehyde	СН	Aldehyde	–anal	R–CHO	2
Ketone	R C==0	Carbonyl	-anone	R–CO–R'	3

IBDP Chemistry HL/ Organic Chemistry

Carboxylic acid	СОН	Carboxyl	–anoic acid	C <sub>n</sub> H <sub>2n+1</sub> CO OH	1
Ester	CR	Ester	-anoate	R-COO-R'	
Amide	О С Н	Carboxyamide	–anamide		
Amine	-NH <sub>2</sub>	Amine	-anamine	$C_nH_{2n+1}NH_2$	5
Nitrile	с <u></u> м	Nitrile	-anenitrile		
Arene	-C <sub>6</sub> H <sub>5</sub>	Phenyl	-benzene		

The position of a functional group is shown by a number between dashes inserted before the functional group ending. The number refers to the carbon atom to which the functional group is attached. The chain is numbered at the end that will give the smallest total number to the group.



Sometimes a functional group can only be in one place, and in these cases we do not need to give a number to show its position.







**Rule 3:** Identify the side chains or substituent groups

Side chains, or functional groups in addition to the one used as the suffix are known as **substituents** and are given as the first part or **prefix** of the name. some common examples are shown in the table.

Each substituent must be accompanied by a number, stating the position of the substituent on the carbon chain.

If there are more than 1 of the same type of substituent, the following are added to the prefix:

- 2 of the same substituents: di
- 3 of the same substituents: tri

Class	Functional group	Name of functional group	Prefix in IUPAC name	Example of compound
Alkane			Methyl (CH <sub>3</sub> ), Ethyl (CH <sub>3</sub> CH <sub>2</sub> ), Propyl (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ), etc. (C <sub>n</sub> H <sub>2n+1</sub> )	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> , 2–methylbutane CH(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> , 3–ethylpentane
Halogenoalkane	–F , –Cl , –Br , −I	Halogeno	Fluoro , chloro bromo , iodo	CH <sub>3</sub> CH <sub>2</sub> CI, Choloroethane CH <sub>3</sub> CHBrCH <sub>3</sub> , 2–bromopropane
Amine	-NH <sub>2</sub>	Amine	Amino	CH <sub>2</sub> (NH <sub>2</sub> )COOH, 2–aminoethanoic acid

### Rule 4:

- Numbers are separated by comma
- Numbers and letters are separated by dash
- Total number must be the least possible sum
- If there are more than one substituent, they will be arranged in alphabetical order

Examples to naming of organic molecules:



### **Naming Esters**

In naming esters, name the alcohol part first then the acid part, replacing "oic acid" with "oate". For example,  $CH_3CH_2COOH$  is propanoic acid, and  $CH_3CH_2COO$  is the propanoate group. The acid is named by counting up the total number of carbon atoms in the chain – including the one in the –COOH group.



**Ethyl propanoate** 

### Naming Carboxyamide (Amides)

In naming carboxyamide, use the alkane name for that chain but replace –e with –amide. More complex names are the carboxyamides that have one or two alkyl groups attached to the nitrogen atom in place of hydrogen atoms. In such cases, continue the naming process by naming the alkyl groups as attachments to the front of the name using N– to show their location.



### N,N–dimethlethanamide

### Naming Amines

In naming amine, use the alkane name for the longest amine chain but replace –e with –amine. More complex names are the amines that have one or two alkyl groups attached to the nitrogen atom in place of hydrogen atoms. In such cases, continue the naming process by naming the alkyl groups as attachments to the front of the name using N– to show their location.



### **Naming Nitriles**

In naming nitrile, select the longest carbon chain starting with the carbon in the nitrile group. Then use the alkane name for that chain and add in the word nitrile e.g. propanenitrile  $CH_3CH_2CN$ 

# Exercise 2

1. Name the following organic molecules



- 2. Draw the full structural, skeletal formula and write the condensed formula of the following organic molecules:
- (a) 3-methylpent-2-ene

(b) Butylpropanoate

(c) 3-hydroxy-2methylpropanoic acid

# 10.1.4 Types of Organic Compounds

Туре	Description	Example
Aliphatic	Straight chain	Molecular formula: C <sub>4</sub> H <sub>10</sub> (Butane)
(Open chain)	_	Condensed formula: CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
		Н Н Н Н         H——С——С——С——Н 
		Displayed formula: H H H H
		Skeletal formula:
	Branched chain	Molecular formula: $C_4H_{10}$ (2–methylpropane) Condensed formula: $CH_3CH(CH_3)CH_3$
		Н Н
		Displayed formula:
		Skeletal formula: / >

Туре	Description	Example
Cyclic	Alicyclic	Molecular & condensed formula: C <sub>5</sub> H <sub>10</sub> (Cyclopentane)
(Rings of	(1 ring)	Ц Ц Н
carbon atoms)	*excludes	
	benzene	н, С, н
		C C.
		$H \to H$
		H~ / / H
		Displayed formula:
		Skeletal formula:
	Polycyclic	Molecular & condensed formula: C10H18
	(2 or more	(Decahydronapthalene)
	rings linked	Г Г Г Г Г Г Г Г Г Г Г Г Г Г Г Г Г Г Г
	together)	⊣
		$H_{2}$ $C$ $C$ $H_{1}$
		│
		Displayed formula: H H H H
		$ \land \land $
		ſ Ŷ Ì
		Skeletal formula:
Heterocyclic	Ring	Molecular & condensed formula: C <sub>5</sub> H <sub>5</sub> N (Pyridine)
	containing	N
	than carbon	
	atoms	
	atoms	
Aromatic	Compounds	Molecular & condensed formula: CoHo, CooHo
Alomatic	containing one	
	or more	
	benzene rings	
		Benzene Napthalene

# 10.1.5 Summary of Functional Groups in Organic Chemistry

Functional Group	Alkar	ies	Alkenes		Arenes	
Types	Aliphatic	Cyclic	Aliphatic	Cyclic	Benzene	Substituted Benzene
Example	н н     нсн     н н					CH3
General Formula	C <sub>n</sub> H <sub>2n+2</sub>	C <sub>n</sub> H <sub>2n</sub>	C <sub>n</sub> H <sub>2n</sub>	$C_nH_{2n-2}$	C <sub>6</sub> H <sub>6</sub>	NA
Boiling / Melting Point	<ul> <li>Simple molecular structure / non-polar molecule</li> <li>As the size of molecule becomes bigger</li> <li>Size of electron cloud increases (more polarisable)</li> <li>Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases</li> <li>More energy is required to separate the molecules.</li> <li>As a result, the melting / boiling point increases as the carbon chain increases. There will be a change of physical state from gas to liquid.</li> <li>Branched isomers have lower melting / boiling point than straight chain isomers</li> <li>Extent of surface area of contact: branched &lt; straight chain isomers</li> <li>Extent of distortion of the electron cloud: branched &lt; straight chain isomers</li> <li>Extent of weak intermolecular instantaneous dipole-induced dipole attractions: branched &lt; straight chain isomers</li> </ul>		<ul> <li>Simple molecular structure</li> <li>Boiling point: cis-isomers &gt; trans-isomers</li> <li>Cis-isomers are polar as they have net dipole moments</li> <li>Strength of intermolecular permanent dipole-permanent dipole interactions &gt; instantaneous induced dipole-induced dipole interactions</li> <li>Melting point: trans-isomers &gt; cis-isomers</li> <li>Trans-isomers pack better into a regular lattice</li> <li>More extensive surface area of contact between molecules</li> <li>Strength of intermolecular instantaneous induced dipole interactions is more extensive</li> </ul>		<ul> <li>Simple molecular structure / non-polar molecule</li> <li>Comparable with cyclohexene and cyclohexane</li> <li>Higher boiling and melting point than hexane and hexene</li> </ul>	<ul> <li>Dependent on electron cloud size (due to attached R group)</li> </ul>
Solubility (Polar solvents)	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
Solubility (Non–polar solvents)	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Density (w.r.t. water)	Less dense	Less dense (More dense than aliphatic alkanes)	Less dense	Less dense	Less dense	Less dense

Functional Group	Halogen De	erivatives	Hydroxyl Co	mpounds	Carbonyl Compounds	
Types	Halogenoalkanes	Halogenoarenes	Alcohol	Phenol	Aldehyde	Ketone
Example	$H \xrightarrow{H} H$ $H \xrightarrow{C} C \xrightarrow{C} X$ $H \xrightarrow{H} H$ $H$ $H$ $H$ $H$ $H$ $H$ $H$ $H$ $H$	where X = Cl, Br or I	н н     н—с—с—он     н н	ОН	R C===0 H	R C===0 R'
General Formula	CnH <sub>2n+1</sub> X	C <sub>6</sub> H₅ <b>X</b>	C <sub>n</sub> H <sub>2n+1</sub> <b>OH</b>	C <sub>6</sub> H₅ <b>OH</b>	C <sub>n</sub> H <sub>2n</sub> O	C <sub>n</sub> H <sub>2n</sub> O
Boiling / Melting Point	<ul> <li>C<sub>n</sub>H<sub>2n+1</sub>X</li> <li>C<sub>6</sub>H<sub>5</sub>X</li> <li>Simple molecular structure / polar molecule</li> <li>As the size of molecule becomes bigger (due to larger R group or size of X)</li> <li>Size of electron cloud increases (more polarisable)</li> <li>Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases</li> <li>More energy is required to separate the molecules.</li> <li>Higher boiling / melting point than corresponding alkanes</li> <li>Strength of intermolecular permanent dipole-permanent dipole interactions &gt; instantaneous induced dipole-induced dipole interactions</li> </ul>		CnH2n+1OH       C6H5OH         • Simple molecular structure / polar molecule       • As the size of molecule becomes bigger (due to larger R group or size of X)         • Size of electron cloud increases (more polarisable)       • Strength of intermolecular instantaneous induced dipole–induced dipole interactions increases         • More energy is required to separate the molecules.         • Higher boiling / melting point than corresponding alkanes / alkenes / halogenoalkanes         • Strength of intermolecular hydrogen bonding > instantaneous induced dipole–induced dipole dipole–induced dipole interactions / permanent dipole–permanent dipole		<ul> <li>Simple molecular stru         <ul> <li>As the size of molecular ger R)</li> <li>Size of electron polarisable)</li> <li>Strength of interrinduced dipole–induincreases</li> <li>More energy is remolecules.</li> <li>Higher boiling / melting alkanes / alkenes</li> <li>Strength of intermole permanent dipole induced dipole–induced dipole–induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole induced dipole for the strength of intermole permanent dipole for the strength of the stren</li></ul></li></ul>	cture / polar molecule le becomes bigger (due to cloud increases (more nolecular instantaneous ced dipole interactions quired to separate the g point than corresponding ecular permanent dipole— eractions > instantaneous ed dipole interactions g point than corresponding ecular permanent dipole— nteractions < hydrogen
Solubility (Polar solvents)	Insoluble	Insoluble	Lower alcohols are soluble due to ability to form H– bonding with water. Solubility decreases as number of C increases due	Partially soluble in r.t.p due to H–bonding but has big hydrophobic ring.	Lower aldenydes are soluble in water, ability to form H– bonding with water. Solubility decreases as number of C	Lower ketones are soluble in water, ability to form H– bonding with water. Solubility decreases as number of C

			to hydrophobic nature of alkyl chain	Solubility is enhanced by heating or addition of alkali.	increases due to hydrophobic nature of alkyl chain	increases due to hydrophobic nature of alkyl chain
Solubility (Non–polar solvents)	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble
Density (w.r.t. water)	Similar	Similar	Similar	Similar	Similar	Similar

Functional Group	Carboxylic Acids and Derivatives		Nitrogen Compounds		
Types	Carboxylic Acids	Acid Derivatives	Amines	Amides	
Example	Н О      H—С—С—ОН   Н	н о      н с с с с с с с и н	H H     HCNH₂     H H	H O H        HCNH   H	
General Formula	C <sub>n</sub> H <sub>2n+1</sub> COOH	C <sub>n</sub> H <sub>2n+1</sub> COCI	C <sub>n</sub> H <sub>2n+1</sub> NH <sub>2</sub> (1º amine)	R <b>CONH</b> 2 (1º amide)	
Boiling / Melting Point	<ul> <li>Simple molecular structure / polar molecule</li> <li>As the size of molecule becomes bigger (due to larger R group)</li> <li>Size of electron cloud increases (more polarisable)</li> <li>Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases</li> <li>More energy is required to separate the molecules.</li> <li>Higher boiling / melting point than corresponding alcohols due to more extensive intermolecular hydrogen bonding</li> </ul>	<ul> <li>Simple molecular structure / polar molecule</li> <li>As the size of molecule becomes bigger (due to larger R group)</li> <li>Size of electron cloud increases (more polarisable)</li> <li>Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases</li> <li>More energy is required to separate the molecules.</li> <li>Lower boiling / melting point than corresponding acids</li> <li>Strength of intermolecular permanent dipole-permanent dipole interactions </li> </ul>	<ul> <li>Simple molecular structure / polar molecule</li> <li>As the size of molecule becomes bigger (due to larger R group)</li> <li>Size of electron cloud increases (more polarisable)</li> <li>Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases</li> <li>More energy is required to separate the molecules.</li> <li>For 1° and 2° amines / amides: <ul> <li>Higher boiling / melting point than corresponding alkanes / alkenes / halogenoalkanes</li> <li>Strength of intermolecular hydrogen bonding &gt; instantaneous induced dipole-induced dipole-induced</li></ul></li></ul>		
Solubility (Polar solvents)	Lower acids are soluble in water, ability to form H–bonding with water. Solubility decreases as number of C increases due to hydrophobic nature of alkyl chain	Lower acid derivatives are soluble in water, ability to form H–bonding with water. Solubility decreases as number of C increases due to hydrophobic nature of alkyl chain	Lower amines are soluble in water, ability to form H–bonding with water. Solubility decreases as number of C increases due to hydrophobic nature of alkyl chain	Lower amides are soluble in water, ability to form H–bonding with water. Solubility decreases as number of C increases due to hydrophobic nature of alkyl chain	
Solubility (Non–polar solvents)	Soluble	Soluble	Soluble	Soluble	
Density (w.r.t. water)	Similar	Similar	Similar	Similar	

Organic Compounds	Primary	Secondary	Tertiary	Quaternary
Halogenoalkane ( <b>X</b> = halogen)				
	Primary C atom	Secondary C atom	Tertiary C atom	
Alcohols	нон     R	HO	R   	
Amines	н   Rн 	RNR	R R R R	$\begin{bmatrix} \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \end{bmatrix}^{+}$
Amides	О Н      RС	O H      R	0 R      R	

# 10.1.6 Classification of Organic Compounds

# **10.1.7 Basic Theoretical Principles of Organic Chemistry**

In the study of Organic Chemistry, there are many organic reactions but the reactions typically can be classified easily under a few categories.

### 10.1.7.1 Reactive Sites

Functional groups in molecules contain reactive sites that are attached by incoming species. A reactive site is either a region higher or lower electron density.

- (a) Electron deficient sites include:
  - Atoms with a partial  $\delta\text{+}$  charge because it is covalently bonded to a more electronegative atom



- (b) Electron rich sites include:
  - Atoms with a partial  $\delta\!-$  charge because it is covalently bonded to a less electronegative atom
  - Lone pairs
  - Double / triple bonds between carbon atoms due to presence of  $\pi$  electrons





• Delocalised  $\pi$  electron cloud, e.g. benzene



# 10.1.7.2 Attacking Species

In a covalent bond between **A** and **B**, if **A** is more electronegative than **B**, the distribution of bonding electrons can be represented as  ${}^{\delta_-}A-B^{\delta_+}$ . The bond is said to be polar. The reagents which attack organic compounds seek out either the partial positive or partial negative end of the bond. There are three main classes of attacking species:

### (a) Free Radicals

Free radicals are species with an unpaired electron that combines with another radical to form a sigma ( $\sigma$ ) bond. It is usually formed from the homolytic fission of a covalent bond. It is highly reactive and is electrically neutral. However, because they are one electron short of an octet, they are still considered electron deficient, like electrophiles.

### (b) Electrophiles

Electrophiles are electron pair acceptors and attack a region where electron density is high, for example, a  $\pi$  bond in an alkene or the  $\pi$  electron cloud of a benzene ring. This includes NO<sub>2</sub><sup>+</sup>, Cl<sup>+</sup> and CH<sub>3</sub><sup>+</sup>. Electrophiles are electron deficient. They are a pair of electrons short of an octet and hence they seek out a pair of electrons in their attack.

### (c) Nucleophiles

Nucleophiles are electron pair donors that attacks the electron deficient end of a polar covalent bond or a carbocation intermediate at the positive carbon. They are usually negatively charged ions such as  $CN^-$ ,  $OH^-$  or  $X^-$  where X is a halogen. It can also come in the form of molecules with lone pairs of electrons such as  $NH_3$  and  $H_2O$ .

The negatively charged hydroxide OH<sup>-</sup>, is a stronger nucleophile than the water molecule which is its conjugate acid. A negatively charged ion has a far greater attraction for an electrophile than does a neutral molecule.

### Exercise 3

- 1. Classify the following reagents as either free radicals, electrophiles or nucleophiles
- (a) CH<sub>3</sub>●
- (b) NO<sub>2</sub>+
- (c) H<sup>-</sup>
- (d) Br•

# 10.1.7.3 Types of Reactions

The reactions of organic compounds fall into different classes of organic reactions.

# (a) Substitution

A reaction in which **one atom or group replaces another atom or group in a molecule**. There are at least 2 products formed.

Example:  $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ 

# (b) Addition

A reaction in which two molecules react to form a single product. It usually involves a functional group with at least an unsaturated bond in organic reactions.

Example:  $C_2H_4 + HBr \rightarrow C_2H_5Br$ 

# (c) Elimination

A reaction in which **atoms or small molecules are removed from a single molecule**, usually to form a double bond. It is the opposite of addition reaction.

Example:  $C_2H_5Br \rightarrow C_2H_4 + HBr$ 

### (d) Condensation / Addition-elimination

A reaction in which **two molecules react to form a larger molecule** (the addition reaction) **followed by the expulsion of a small molecule** like  $H_2O$  or  $NH_3$  from the larger molecule (the elimination reaction).

Example:  $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$ 

# (e) Hydrolysis

A reaction in which a molecule split into two by the action of water and is catalysed by either an acid or alkali. In many cases, the agent causing the hydrolysis can be the hydroxide ion, OH<sup>-</sup>, instead of water.

Example:  $CH_3COOC_2H_5 + H_2O \rightarrow C_2H_5OH + CH_3COOH$ 

### (f) Acid-base

A reaction in which a proton is transferred from stronger acid to a weaker acid / base which may include in the formation of salt and water,  $H_2O$ .

Example:  $CH_3COOH + NaOH \rightarrow H_2O + CH_3COO^-Na^+$ 

### (g) Oxidation

A reaction in which **either oxygen added to the molecule or hydrogen being removed from the molecule**. In balancing organic redox reactions, the symbol [O] is used to denote oxidation.

Example:  $CH_3CH_2OH + [O] \rightarrow H_2O + CH_3CHO$ 

# (h) Reduction

A reaction in which **either hydrogen added to the molecule or oxygen being removed from the molecule**. In balancing organic redox reactions, the symbol [H] is used to denote reduction.

Example:  $CH_3CN + 4[H] \rightarrow CH_3CH_2NH_2$ 

In the redox reactions, the symbols [O] and [H] are used because they are easy. Note that the redox reactions can also be represented as ion–electron half equations.

### Exercise 4

- Classify the following organic reactions based on

   the attacking species (which is dependent on identifying the reactive sites)
   the type of reaction (particularly for substitution and addition)
- (a)  $CH_3CH_2CH_2Br + CN^- \rightarrow CH_3CH_2CH_2CN + Br^-$
- (b)  $C_2H_4 + HF \rightarrow CH_3CH_2F$
- (c)  $CH_3CH_3 + CI_2 \rightarrow CH_3CH_2CI + HCI$
- $(d) \quad C_6H_6 + CI_2 \rightarrow C_6H_5CI + HCI$

# **10.1.8 Mechanisms of Organic Reactions**

Organic reaction mechanisms usually consist of a series of labelled equations showing representation of plausible electron movements that happen as the reactants are converted to products. Note that each step in the mechanism involves species of opposite charges interacting with each other. The exception would be reactions involving free radicals. In a mechanism the following should be included.

### **10.1.8.1 Arrow Notations in Mechanism**

Organic reactions are typically concerned with the breaking and formation of covalent bonds. Therefore, a consideration of the movement of bonding and non-bonding electrons is imperative to understanding mechanisms.

Types of Arrows	Illustrations	Remarks
A full-head on the	$\frown$	Heterolytic
arrow indicates the	A — B — ▶ A⁺ + : B⁻	fission
movement of an	Н	
electron pair		
A partial head	$\uparrow$	Homolytic
(fish-hook) on the	A—A — ≥ 2A·	fission
arrow indicates the	ļ	
movement of a		
single electron	н—_с́·́```сі —► н—_с́—_сі	

### (a) Homolytic fission

This type of fission usually takes place in **non–polar covalent bonds where the bond breaks evenly**. Each of the bonded atoms takes a single electron. Free radicals are thus formed which contain unpaired electrons.

Energy must be supplied, either as heat or electromagnetic radiation, to break the covalent bond. Homolytic fission often occurs in the gas phase. Radicals are usually short–lived reactive species.

### (b) Heterolytic fission

This type of fission usually takes place in **polar covalent bonds where the bond breaks unevenly**. When a polar bond breaks, one of the bonded atoms, usually the more electronegative atom, withdraws both of the bonding electrons to form an anion (negative ion). The rest of the molecule becomes a cation. (Curly arrows can be used to show the movement of an electron pair).

A molecular ion with a positive charge (and an electron deficient carbon atom) is known as a carbocation (sp<sup>2</sup> hybridised). A molecular ion with a negatively charged carbon atom is called a carbanion (sp<sup>3</sup> hybridised).

### **10.1.8.2 Reaction Intermediates**

These substances are formed in one of the steps of the reaction mechanism and consumed in subsequent steps. It represents an energy minimum in the reaction profile and can be characterised and isolated.

Some of these common organic intermediates that you will see in the chapter includes:



### 10.1.8.3 Rate-determining Step in Mechanisms

A mechanism should also denote the kinetics of the reaction. In most cases for organic mechanisms, the rate-determining step is usually the step that involves bond-breaking which are the endothermic reactions.

### 10.1.9 Isomerism

**Isomerism** refers to the existence of two or more compounds having the **same molecular formula but different structural formula or different spatial arrangements of atoms**. There are two main types of isomerism: **structural isomerism and stereoisomerism**.



### 10.1.9.1 Structural Isomerism

Compounds having the **same molecular formula but different structural formula** i.e. different arrangement of atoms

There are three types of structural isomerism:

- Chain isomerism
- Positional isomerism
- Functional group isomerism

### **Chain Isomerism**

Compounds having the same molecular formula but a **different arrangement of the carbon chain**. The carbon atoms may be arranged in either **straight or branched chain**. Chain isomers have **similar chemical properties but different physical properties**.

Example: Draw and name all the possible structural isomers of hexane, C<sub>6</sub>H<sub>14</sub>.

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Hexane

CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>3</sub> | CH<sub>3</sub>

3-methylpentane



CH<sub>3</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> |CH<sub>3</sub> 2-methylpentane CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub> |CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub>

### Positional Isomerism

Compounds having the same molecular formula but **different position of a functional group** on a carbon chain or ring. Positional isomers have similar chemical properties but different physical properties.

Example: Draw and name all the possible positional isomers of C<sub>3</sub>H<sub>7</sub>OH.



Example: Draw and name all the possible positional isomers of  $C_6H_4Cl_2$ .



### **Functional Group Isomerism**

Compounds having the same molecular formula but **different functional groups**. Functional group isomers have **different physical and chemical properties**.

н

С

н

O

С

Example: Draw and name all the possible functional group isomers of  $C_3H_6O_2$ .



н

C

н

O

**Methyl ethanoate** 

-H

Example: Draw and name all the possible functional group isomers of  $C_2H_6O$ .



### 10.1.9.2 Stereoisomerism

Compounds having the **same molecular and structural formula**, i.e. their position and type of functional group are identical, however they **differ in the way the atoms are arranged in spatial or 3-dimensional space**.

Stereoisomers are subdivided into two classes

- **Configurational** isomers that interconvert only by breaking and reforming a bond
- **Conformational** isomers that interconvert by rotation about a sigma ( $\sigma$ ) bond.

There are two types of configurational isomerism:

- Cis–trans isomerism (or E/Z isomerism)
- Optical isomerism (or Enantiomerism)

### 10.1.9.2.1 Cis-trans Isomerism

For this isomerism to occur, there must be

- 1. restricted rotation about a bond either by the presence of
  - A double bond (C=C, N=N or C=N); or
  - A ring structure
- 2. Two different groups attached to the atoms involved in the bond where there is restricted rotation (e.g. C=C in the case of an alkene)

In general, a molecule with n double bonds that can exhibit cis-trans isomerism has a maximum of  $2^n$  stereoisomers.

Example of cis-trans isomerism in alkenes

In alkenes, the C=C bond cannot undergo free rotation unless one of the weaker  $\pi$  bonds in the C=C bond is broken. As a result, isomers can be formed when there are two non–identical groups attached to the carbon atoms at each end of the carbon–carbon double bond.

**Cis**-isomer: same or similar substituents on the **same side** of the double bond (or ring, for cyclic compounds)



**Trans**–isomer: same or similar substituents on the **opposite side** of the double bond (or ring, for cyclic compounds)



The smallest alkene that can show cis-trans isomerism is but-2-ene.





An example of a ring compound that can show cis-trans isomerism is 1,2-dimethylcyclopropane.



*Cis* 1,2–dimethylcyclopropane



Trans 1,2-dimethylcyclopropane



### 10.1.9.2.2 E/Z Isomerism

However, there are many cases in alkenes where the cis–trans designation breaks down. This happens when the carbon atoms of the carbon–carbon double bond are bonded to more than two different substituents, as such:



As all the groups attached to the double bond are different, there are no 'same groups' to position relative to the reference plane. For these cases, a more comprehensive naming system has been developed, known as E/Z isomers.

E/Z isomerism is based on the Cahn–Ingold–Prelog **rules of priority**, which are applied in turn to the groups at each end of the double bond

The rules may be summarised as follows:

- 1. Look at the atom bonded to the carbon of the double bond. The atom with the higher atomic number has the higher priority
- 2. If the atoms are the same, apply the same rule to the next bonded atom. This implies that longer hydrocarbon chains have higher priority

Next we compare the positions of the highest priority groups on the two carbons of the double bond

- 1. If the two highest priority group are on the **same side** of the double bond, then the isomer is **'Z'**
- 2. If the two highest priority group are on the **opposite side** of the double bond, then the isomer is **'E'**

For example, in the molecule 1-bromo-2-methylbut-1-ene,



The following deductions may be made:

Priority:

- For left hand carbon: Br > H
- For right hand carbon: CH<sub>2</sub>CH<sub>3</sub> > CH<sub>3</sub>





# 10.1.9.2.3 Physical Properties of Cis-trans Isomers

Cis-trans isomers generally have different physical properties. Both have simple molecular structures.

Melting point:

- Cis-isomer < trans-isomer
- Cis-isomer has lower symmetry as it fits into a crystalline lattice more poorly
- Extent of surface area of contact:

cis–isomer < trans–isomer

- Extent of distortion of the electron cloud:
  - cis-isomer < trans-isomer
- Extent of weak intermolecular instantaneous dipole–induced dipole attractions:
  - cis-isomer < trans-isomer
- Energy required to overcome intermolecular instantaneous dipole-induced dipole attractions:

cis-isomer < trans-isomer

Boiling point:



**cis-isomer** net dipole moment polar



trans-isomer no net dipole moment non-polar

- Cis-isomer > trans-isomer
- Cis-isomer is polar while trans-isomer is non-polar
- Energy required to overcome weaker intermolecular instantaneous dipole-induced dipole attractions of trans-isomer < stronger intermolecular permanent dipole permanent dipole attractions of cis-isomer
# Exercise 5

1. Trans-butenedioic acid has a higher boiling point than cis-butenedioic acid. Which of the following statement(s) account for the differences in the boiling point between this pair of isomers?



**Cis-butenedioic acid** 

Trans-butenedoic acid

- I. The forces holding cis–butenedioic acid molecules together are weaker.
- II. Intramolecular hydrogen bonding is present only in cis-butenedioic acid.
- III. More extensive intermolecular hydrogen bonding is present in trans-butenedoic acid.

2. Which of the following pair(s) of compounds consist of cis-trans isomers?



## 10.1.9.2.4 Optical Isomerism (Enantiomerism)

This type of configurational isomer arises because of the **ability of these compounds to rotate the plane of the polarised light in solution**.



Plane polarised light differs from normal light in that electromagnetic waves vibrate in a single plane rather than in multitude of planes. Passing light through a polariser such as a polarised filter produces polarised light. If a beam of plane–polarised light is passed through a solution of one enantiomer, when light emerges, the plane of polarisation is rotated either clockwise or anti–clockwise. This is measured using a polarimeter.



A compound which rotates the plane of polarised light is said to be optically active and is the reason why they are called optical isomers. The **2 optically active isomers are known** as enantiomers.

The enantiomers which rotates the plane of polarised light in the clockwise direction, the compound is given the prefix, (+) or dextrorotatory. On the other hand, if the rotation of polarised light in the anti-clockwise direction, the compound is given the prefix, (-) or laevorotatory.

An optically active molecule must possess:

- 1. At least **one chiral carbon** : a chiral carbon is a sp<sup>3</sup> hybridised atom with 4 different substituents attached to it. It is denoted by a (\*) symbol.
- 2. **No plane of symmetry** : plane of symmetry is defined to be a plane that cuts through the middle of an object so that one half of the object is a mirror image of the other half.
- 3. **Non–superimposable mirror images** : in the figure below, the mirror images are non–superimposable (similar to the left and right hand).





Scan me to view a video on non– superimposable mirror images

# Drawing optical isomers (enantiomers)

- Draw mirror plane (dotted line)
- Show tetrahedral shape around the chiral C atom
- Draw 2 solid bonds, 1 fully shaded wedge and 1 dashed wedge
- Show correct bonding (e.g. C bonded to C of –CH<sub>3</sub>, C bonded to O of –OH)



In general, a molecule with m chiral centres has a maximum of  $2^m$  stereoisomers.

# 10.1.9.2.5 Racemic Mixtures

A racemic mixture is a **mixture containing equimolar amounts (i.e. 50% each) of each enantiomer**.

The mixture is **optically inactive as there is no NET rotation of plane polarised light** (due to exact cancellation of all possible rotation of plane–polarised light).

#### 10.1.9.2.6 Diastereomers

A diastereomer are molecules that have different configurations at one or more, but not all, chiral centres.

They are not mirror images of each other.



#### 10.1.9.2.7 Meso Compound

A meso compound is a stereoisomer that contains chiral centres but is optically inactive due to the presence of a plane of symmetry.

The optical rotary effect of the top half of the molecule exactly counteracts the opposite effect of the bottom half, making the molecule appear optically inactive.



The two compounds shown above are a pair of optical isomers (enantiomers) as they are non-superimposable mirror images. Hence, they are optically active.



The two compounds shown above are a pair of meso compounds as they are superimposable mirror images. Hence, they are optically inactive.

## 10.1.9.2.8 Physical and Chemical Properties of Optical Isomers (Enantiomers)

The physical properties of enantiomers that include density, refractive index, colour, melting and boiling points are also identical except their effects on plane–polarised light and interaction with other enantiomers. Enantiomers rotate the plane of polarised light in opposite directions (but to an equal degree).

As enantiomers contain the same groups attached to the same atoms, with the same angles between each group (unlike cis/trans isomers), they have exactly the same chemical properties. They undergo similar chemical reactions, reacting with reagents at identical rates as long as the reagents are not themselves chiral.

#### Enrichment: Enantiomer and significance of optical isomers in biological systems

Different stereoisomers exhibit different biological properties, e.g. in drug action.

Most drugs are chiral. Usually only one mirror image form of the drug provides the desired effect. The other mirror image form can be less active and even toxic.

Reason: To exert its biological action, a chiral drug molecule must fit into a chiral receptor at some target site in the body. Only one of the mirror images can fit properly into the receptor to exert the biological action. The other mirror image is thus inactive or may interact with other unintended receptors, giving rising to undesired side effects.

An example is the drug, thalidomide, used in the 1950s and 1960s to alleviate the symptoms of morning sickness in pregnant women. Around 15,000 children were affected by thalidomide, of whom about 12,000 in 46 countries were born with birth defects such as missing limbs, with only 8,000 of them surviving past the first year of life. Many of these survivors are still alive, nearly all with disabilities caused by the drug.



R (+)–thalidomide (sedative to curb morning sickness) S (–)–thalidomide (teratogenic, i.e. causes birth defects)

Evidence showed that the drug that was administered contained 2 enantiomers. The (+)-enantiomer had the intended effect of curing morning sickness while the (-)-enantiomer caused birth defects. The enantiomers are converted into each other in vivo. That is, if a human is given (+)-thalidomide or (-)-thalidomide, both isomers can be found in the serum. Hence, administering only one enantiomer will not prevent the adverse effect of the (-)-thalidomide.

# **Exercise 6**

**1.** Name the type(s) of stereoisomerism exhibited by CH<sub>3</sub>CH=CHCHCICH<sub>2</sub>NH<sub>2</sub>. Illustrate the isomerism(s) using suitable diagrams.



**2.** Nepetalactone is the active ingredient found in catnip. It is a terpene with the following structure. How many chiral centres are there in nepetalactone?



**3.** The anti–asthma drug, Intal, contains disodium cromoglycate, which has the structure shown below. How many chiral centres are there in Intal?



# 10.2 Functional Group Chemistry

# 10.2.1 Alkanes

Alkanes are a family of **saturated hydrocarbon** with **general formula**,  $C_nH_{2n+2}$ . Alkanes make up the fuel that drives our vehicles as well as our power stations. They are found naturally as crude oil or natural gases and are separated into useful fractions by fractional distillation.

Alkanes are **generally unreactive**. They are inert towards most bases, acids, oxidising agents and reducing agents. The lack of reactivity is **due to the non-polarity of the C-H bond since C and H are very similar in electronegativity**. Hence, there is a lack of electron rich or electron deficient sites on the alkane molecule. The non-polar nature of the alkanes makes them unreactive to polar reagents and ions. The **C-C bond and C-H bond are also very strong bonds which are difficult to break under ordinary conditions**.

## 10.2.1.1 Nomenclature (See Section 10.1.3)

#### 10.2.1.2 Physical Properties of Alkanes

## Melting / boiling point

Melting / boiling point increases as the carbon chain increases. There will be a change of physical state from gas to liquid.

- Simple molecular structure / non-polar molecule
- As the size of molecule becomes bigger
- Size of electron cloud increases (more polarisable)
- Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases
- More energy is required to overcome the intermolecular forces of attraction.



Branched isomers have lower melting / boiling point than straight chain isomers

- Extent of surface area of contact:
  - branched < straight chain isomers
- Extent of distortion of the electron cloud:
  - branched < straight chain isomers
- Extent of weak intermolecular instantaneous dipole-induced dipole attractions: branched < straight chain isomers
- Energy required to overcome intermolecular instantaneous dipole–induced dipole attractions: branched < straight chain isomers

# Solubility

Soluble in non-polar solvents but insoluble in polar solvents and water.

- The weak instantaneous induced dipole-induced dipole attractions between alkane molecules is similar in strength / compatible to the weak instantaneous induced dipole-induced dipole attractions between non-polar solvent molecules.
- Strong hydrogen bonding between water molecules is not compatible to the weak instantaneous induced dipole-induced dipole interactions between non-polar alkane molecules.

# 10.2.1.3 Chemical Reactions

# 10.2.1.3.1 Combustion of Alkanes

For **complete combustion**: Occurs in **sufficient (excess) supply of oxygen**. Flame is nonsooty for the smaller alkanes. Only CO<sub>2</sub> and H<sub>2</sub>O are produced. E.g.: CH<sub>4</sub> (g) + 2O<sub>2</sub> (g)  $\rightarrow$  CO<sub>2</sub> (g) + 2H<sub>2</sub>O (I)

For incomplete combustion: Occurs in a limited supply of oxygen, alkanes burn to produce C or CO and  $H_2O$ .

$$\begin{split} & \text{E.g.: CH}_4 \ (g) + \frac{3}{2} \text{O}_2 \ (g) \rightarrow \text{CO} \ (g) + 2 \ \text{H}_2 \text{O} \ (\text{I}) \\ & \text{E.g.: CH}_4 \ (g) + \text{O}_2 \ (g) \rightarrow \text{C} \ (s) + 2 \text{H}_2 \text{O} \ (\text{I}) \end{split}$$

## 10.2.1.3.2 Reaction Mechanism: Free Radical Substitution

$C_{n}H_{2n+2}(g) + X_{2}(g)$	$\xrightarrow{\text{UV light}} C_n H_{2n+1} \mathbf{X} (g) + H \mathbf{X} (g)$	
Reagent and condition	$\mathbf{X}_{2}$ (g) , UV light (where $\mathbf{X} = CI$ , Br)	
Type of reaction	Free radical substitution	
Observation	Decolourisation of brown Br <sub>2</sub> gas (if Br <sub>2</sub> is used)	

Alkanes undergo free radical substitution reaction with chlorine and bromine in the presence of ultraviolet (UV) radiation.

$$CH_4 (g) + Cl_2 (g) \xrightarrow{UV \text{ light}} CH_3Cl (g) + HCl (g)$$

There are three steps in the mechanism of this reaction, namely initiation, propagation and termination.

Step 1: Initiation

Homolytic fission of CI–CI bond forming chlorine radicals. This step is induced by UV light or heat (250–400 °C).

$$CI \xrightarrow{CI} CI (g) \xrightarrow{UV light} \bullet CI (g) + \bullet CI (g)$$

Step 2: Propagation

The chlorine radical removes a hydrogen atom from the  $CH_4$  molecule, resulting in another reactive intermediate, a methyl radical,  $\bullet CH_3$ . The methyl radical then reacts with a  $CI_2$  molecule to produce  $CH_3CI$  and a new  $\bullet CI$ , and so on.  $CH_3CI$  can undergo further substitution in the presence of excess  $CI_2$  to form further substituted products like  $CH_2CI_2$ ,  $CH_3CI$  and  $CCI_4$ .

 $CH_4 (g) + \bullet CI (g) \rightarrow \bullet CH_3 (g) + HCI (g)$  $\bullet CH_3 (g) + CI_2 (g) \rightarrow CH_3CI (g) + \bullet CI (g)$ 

Step 3: Termination

The propagation steps may continue until all the hydrogen atoms are substituted. However, they do not go on forever. The reaction slowly diminishes as the concentrations of the reactants run out and also because of the occurrence of chain termination steps.

 $\begin{array}{l} \bullet CI (g) + \bullet CI (g) \rightarrow CI_2 (g) \\ \bullet CH_3 (g) + \bullet CI (g) \rightarrow CH_3CI (g) \\ \bullet CH_3 (g) + \bullet CH_3 (g) \rightarrow CH_3CH_3 (g) \end{array}$ 

#### 10.2.2 Alkenes

Alkenes are unsaturated hydrocarbons with a carbon–carbon double bond, C=C with the general formula,  $C_nH_{2n}$ , where n > 1. The first member of the series is ethene and it is an important raw material for the petrochemical industry. Alkenes are obtained mainly from the cracking of heavier alkanes.

In an alkene molecule, the two carbon atoms that joined by the double bond are  $sp^2$  hybridised with their unhybridised p-orbitals overlapping sideways to form the  $\pi$ -bond. The rest of the carbon atoms in the chain are  $sp^3$  hybridised.

The greater chemical reactivity of alkenes as compared to alkanes is due to the C=C double bond. The loosely held  $\pi$ -electrons provide an "electron–rich" region and is highly susceptible to "attack" by electrophiles (electron pair acceptors).

## 10.2.2.1 Nomenclature (See Section 10.1.3)

Similar to alkanes, the alkene parent chain is the longest continuous carbon chain that contains the C=C bond. The position of the C=C bond is given priority in numbering and is indicated by the smaller of the two number labelling the carbon atoms.

#### 10.2.2.2 Stereoisomerism – Cis-trans Isomerism (See Section 10.1.9.2.1)

#### Exercise 7

1. How many stereoisomers can the following molecules exhibit?



## **10.2.2.3 Physical Properties of Alkenes**

# Melting / boiling point

Melting point:



- Cis–isomer < trans–isomer
- Cis-isomer has lower symmetry as it fits into a crystalline lattice more poorly
- Extent of surface area of contact:

cis-isomer < trans-isomer

• Extent of distortion of the electron cloud:

cis–isomer < trans–isomer

• Extent of weak intermolecular instantaneous dipole-induced dipole attractions:

cis–isomer < trans–isomer

• Energy required to overcome intermolecular instantaneous dipole-induced dipole attractions:

cis-isomer < trans-isomer

Boiling point:



**cis–isomer** net dipole moment polar



trans-isomer no net dipole moment non-polar

- Cis–isomer > trans–isomer
- Cis-isomer is polar while trans-isomer is non-polar
- Energy required to overcome weaker intermolecular instantaneous dipole-induced dipole attractions of trans-isomer < stronger intermolecular permanent dipole-permanent dipole attractions of cis-isomer

# Solubility

Soluble in non-polar solvents but insoluble in polar solvents and water.

- The weak instantaneous induced dipole-induced dipole attractions between alkene molecules is similar in strength / compatible to the weak instantaneous induced dipole-induced dipole attractions between non-polar solvent molecules.
- Strong hydrogen bonding between water molecules is not compatible to the weak instantaneous induced dipole–induced dipole interactions between non–polar alkene molecules.

## **10.2.2.3 Chemical Reactions**

#### 10.2.2.3.1 Reduction of Alkenes (Hydrogenation)



Reagent	H <sub>2</sub> (g)		
Condition	Ni catalyst in the presence of high temperature (≈150 °C) and high pressure OR Pd catalyst at r.t.p. / Pt catalyst at r.t.p.		
Type of reaction	Reduction		
Observation	Decrease in pressure (if pressure gauge is connected)		

#### Applications of reduction of alkenes

Hydrogenation is an important industrial process used to convert liquid vegetable oils into margarine. Vegetable oils contain a high proportion of mono– or polyunsaturated fats. Hydrogenation of vegetable oils under controlled conditions will cause some of the C=C bonds to react and become a more "solid" form.



The downside of this process is the formation of the unhealthy trans-fat molecules during the hydrogenation process. Consumption of trans-fats has been linked to coronary heart disease.

## 10.2.2.3.2 Electrophilic Addition of Alkenes

The main chemistry of alkenes revolves around the C=C double bond. The C=C bond is an electron–rich region with the  $\pi$ –electrons susceptible to "attack" by electrophiles. Alkenes tend to undergo electrophilic addition reaction which involves the breaking of the  $\pi$ –bond and the two electrons in the  $\pi$ –bond are used to form  $\sigma$ –bonds with other atoms.



An electrophile being attracted to the  $\pi$ -electrons in the C=C bond. The electrophile will form a covalent bond with one of the two C atoms in the C=C bond and a positive charge would be acquired by the other carbon atom. The X-Y molecule undergoes heterolytic fission to form the Y<sup>-</sup> nucleophile.

Step 2 (fast step):



This positively charged and electron deficient intermediate is known as a carbocation. The carbocation will continue to react with  $Y^-$  nucleophile which donates a pair of electrons to form a single bond with the positive carbon.

# Electrophilic addition of halogen in organic solvent (Halogenation)



Reagent and condition	$\mathbf{X}_{2}$ (I) , CCI <sub>4</sub> solvent , r.t.p. , in the dark (where $\mathbf{X} = CI$ , Br, I)
Type of reaction	Electrophilic addition
Observation	For Br <sub>2</sub> : Decolourisation of orange–red bromine solution (also used as a chemical test for the presence of alkene functional group) For Cl <sub>2</sub> : Decolourisation of pale yellow solution

Although the halogen molecule is non–polar, the random movement of electrons or the influence of the environment as the molecule approaches the alkene, will result in the formation of an instantaneous dipole as shown below. This is a result of the electron repulsion between the  $\pi$ -electrons in the C=C bond and the halogen molecule



The positive (slightly electron deficient) end of the molecule,  $\delta$ +, will behave as the electrophile (electron pair acceptor) in the reaction. An important point to note is the type of solvent used will affect the product formed.

Step 1 (slow step):



### Electrophilic addition of halogen in water

Reagent and condition	$\mathbf{X}_2$ (aq) , r.t.p. in the dark (where $\mathbf{X} = CI$ , Br, I)	
Type of reaction	Electrophilic addition	
Observation	For Br <sub>2</sub> : Decolourisation of orange bromine solution (also used as a chemical test for the presence of alkene functional group) For Cl <sub>2</sub> : Decolourisation of pale yellow solution	

If aqueous bromine,  $Br_2$  (aq), is used, the  $H_2O$  nucleophile will be present in large quantities as it is present as the solvent.

In Step 2 of the electrophilic addition,  $H_2O$  nucleophile will compete with  $Br^-$  nucleophile to react with the carbocation.

н

Н

н

The following will be formed as the major product instead of 1,2–dibromoethane:



The mechanism for the formation of this major product is shown below.

# Step 1 (slow step): Same as mechanism shown in Pg 52







Scan me to view a video for test for alkenes vs alkanes using bromine water



# Electrophilic addition of hydrogen halide



Reagent and condition	HX (g) or HX in CCl <sub>4</sub> , r.t.p. (where $X = CI$ , Br, I)
Type of reaction	Electrophilic addition

Step 1 (slow step):



Step 2 (fast step):



# Electrophilic addition of inter-halogen compounds



Reagent and condition	BrCl (I) , CCl₄ solvent , r.t.p.
Type of reaction	Electrophilic addition

The electron density between the two atoms is skewed towards the more electronegative chlorine atom. Thus, the electrophile for this reaction is the bromine atom and is assigned the  $\delta$ + charge in the Br–Cl bond.

Step 1 (slow step):



Step 2 (fast step):



## Electrophilic addition of steam



## **Industrial conditions:**

Reagent and condition	$H_2O~(g)$ , 300 °C, 65 atm , concentrated $H_3PO_4$ as catalyst	
Type of reaction	Electrophilic addition	

#### Lab conditions:

Reagent and condition	Concentrated sulfuric acid , $H_2SO_4$ followed by boiling with $H_2O$ (I)	
Type of reaction	Electrophilic addition	

## **Exercise 8**

- 1. Name and draw the full structure of the main product when but-2-ene is bubbled into,
  - (a) Bromine in CCl<sub>4</sub> solvent

(b) Aqueous bromine

(c) Water

2. Liquid bromine in added to two hydrocarbons, **P** and **Q**. The following observations were made.

Hydrocarbon	Observation	
Р	The liquid bromine was decolourised almost instantly.	
Q	No visible reaction.	

- (a) Which hydrocarbon is likely to be an alkene?
- (b) What are the likely functional groups or homologous series of the other hydrocarbon?

#### 10.2.2.3.4 Markovnikov's Rule

When an asymmetrical reagent is added across the double bond of an asymmetrical alkene, two products are possible. For example,



When an asymmetrical alkene undergoes electrophilic addition reaction with an asymmetrical reagent, HX (or  $H_2O$ ), the H atom of HX (or  $H_2O$ ) shall be attached to the unsaturated C atom with more H atoms to form the major product.

#### Concept:

The major product is the one formed when the electrophile (E) attaches itself to the unsaturated C atom with the larger number of H atoms.

In all organic chemistry mechanisms, there is a driving force to move towards stability. Stability may be achieved by delocalisation of electrons or dispersion of charge (i.e. reduction of intensity of charge). This process is known as **positive inductive effect**.

The greater the no. of electron–donating alkyl (R) groups

 $\Rightarrow$  the greater the electron–donating effect

 $\Rightarrow$  the greater the extent of dispersal of the positive charge on the carbocation / greater reduction of the intensity of the positive charge on the carbocation

 $\Rightarrow$  the greater the stability of the carbocation forms.



# Exercise 9

**1.** By showing the mechanism, explain why CH<sub>3</sub>CHCICH<sub>2</sub>I is the major product formed in the reaction below:

 $\begin{array}{ccccc} \mathsf{CH}_3\mathsf{CH}{=}\mathsf{CH}_2 & + & \mathsf{ICI} & \rightarrow & \mathsf{CH}_3\mathsf{CHCICH}_2\mathsf{I} & + & \mathsf{CH}_3\mathsf{CHICH}_2\mathsf{CI} \\ & & \mathsf{major} & & \mathsf{minor} \end{array}$ 

- 2. Draw the structure of the possible products obtained when the following reactants are reacted under the conditions given. Identify the major product formed in cases where there is more than one possible product.
  - (a) But–1–ene with hydrogen chloride in an inert solvent.

(b) 2–methylpropene with BrCl in CCl<sub>4</sub>.

(c) 1-methylcyclohexene with hydrogen iodide.

## 10.2.2.3.5 Addition Polymerisation

Polymerisation is the chemical process where **smaller molecules (monomers) react to form chemical bonds to form macromolecules (polymers)**.

Typically a polymer molecule is made up of  $10^4 - 10^6$  monomers.

There are mainly two types of polymerisation process: addition polymerisation and condensation polymerisation.

Alkenes or substituted alkenes tend to undergo addition polymerisation.

For example,

Addition polymerisation of ethene to form poly(ethene):



Addition polymerisation of prop–1–ene to form poly(prop–1–ene):



Addition polymerisation is an important process where plastics are formed. Some common addition polymers are shown in the table below.

Polymer / Common Name	Monomer	General Formula	Uses
Poly(ethene) PE	Ethene H H C===C H H	$ \begin{array}{c c}     H & H \\     \hline     C & C \\     \hline     C & C \\     H & H \\     n \end{array} $	plastic bottles, toys, plastic bags, film wrap
Poly(chloroethene) Polyvinylchloride / PVC	Chloroethene H C <sup>I</sup> C===C H H	$ \begin{array}{c c} H & C^{I} \\ \hline \\ C & C \\ \hline \\ H & H \\ \end{array} \right) $	plastic pipes, artificial leather, wire insulation
Poly(tetrafluoroethene)	Tetrafluoroethene F F C===C F F	$ \begin{array}{c c} F & F \\ \hline C & C \\ \hline C & C \\ \hline F & F \\ \hline n \end{array} $	coating for non– stick pans
Poly(propene) PP	Ргорепе	$ \begin{array}{c c}     H & CH_3 \\     \hline     C & C \\     \hline     C & C \\     H & H \\     n \end{array} $	lab equipment, automobile parts
Poly(styrene) PS	Styrene H H C C H H		foamed packaging, disposable cups and plates

## 10.2.2.3.6 Preparation of Alkenes

Alkenes are prepared by the elimination reaction.

Elimination involves the **removal of atoms or groups of atoms from two adjacent carbon atoms to form a**  $\pi$ **-bond**.



#### Elimination of halogenoalkanes



# Saytzeff's Rule

Allows us to determine the major alkene formed from an elimination reaction.

If more than one alkene can be obtained as a result of an elimination reaction, then the major product is the alkene which is more highly substituted, i.e. alkene with greater number of R groups.



For example,

In the elimination of water from 2-methylbutan-2-ol



### 10.2.3 Arenes

## 10.2.3.1 Structure of Benzene

Other than alkenes and alkynes, there is another class of unsaturated hydrocarbons and these compounds are of great importance. They are collectively known as the aromatic compounds (or arenes) and they all contain at least one benzene ring in their structures.



Kekulé structure

Kekulé (1865) proposed a cyclohexatriene structure for benzene; the structure consists of a 6–carbon cyclic hydrocarbon molecule,  $C_6H_6$ , with alternating single and double bonds. Such a structure was found to be incorrect due to is observed chemical properties, hence benzene ring is more correctly represented as a hybrid of the two Kekulé structures I and II.



It is now usually represented by its resonance hybrid structure with a circle depicting the six delocalised  $\pi$ -electrons enclosed in the hexagonal carbon ring.



Figure (a):

Benzene is a planar molecule, all the carbon atoms are sp<sup>2</sup> hybridised and its C–C bonds are 120° apart.

#### Figure (b):

Each unhybridised p orbital overlaps with both neighbouring unhybridised p orbitals, resulting in the delocalisation of the 6  $\pi$ -electrons.

Figure (c):

This forms a continuous ring of  $\pi$ -electron density above and below the six-carbon ring structure.



The perfect hexagonal shape observed (by X–ray crystallography) in a benzene ring indicates the absence of alternating C–C single and double bonds in a benzene ring. Studies have shown that all the C–C bond lengths in a benzene ring are equivalent and each bond length is between that of a single and double bond.

Other than physical evidence, the delocalisation of the  $\pi$ -electrons has great implications on the chemistry of aromatic compounds. Most significantly, though unsaturated like the alkenes, a benzene ring does not show the same chemical properties as an alkene. It does not undergo electrophilic addition reactions and is relatively unreactive.

Thermodynamic studies have shown that the benzene ring is much more stable than cyclohexatriene. One such study is the enthalpy of hydrogenation as shown below:



Hence, the delocalisation of the  $\pi$ -electrons has great implications on the chemistry of aromatic compounds. Most significantly, though unsaturated like the alkenes, a benzene ring does not show the same chemical properties as an alkene. It **does not undergo electrophilic addition reactions but undergoes electrophilic substitution reactions** under appropriate conditions where the stability of the delocalised  $\pi$ -electrons system is preserved at the end of the reaction.

Summary on the structure of benzene using physical and chemical evidence:

Kekulé Structure	Actual Structure
The bond length of C–C single bond is 0.154 nm and that of C=C is 0.134 nm. Hence, the Kekule structure should have alternating longer and shorter carbon-carbon bond lengths.	All carbon–carbon bond lengths of benzene are of equal length, 0.140 nm.
The Kekulé structure, with its distinctive alkene functional group, should undergo electrophilic addition mechanism.	Benzene undergoes electrophilic substitution mechanism.
When one mole of cyclohexene undergoes reduction with one mole of $H_2$ (g), 120 kJ of heat energy is evolved.	Enthalpy change of hydrogenation of benzene = -202 kJ mol <sup>-1</sup> .
Enthalpy change of hydrogenation of cyclohexene $= -120 \text{ kJ mol}^{-1}$ .	This indicates that structure of benzene is more stable than the Kekulé structure.
Hence, enthalpy change of hydrogenation of cyclohexa–1,3,5–triene) = $3 \times (-120) = -360 \text{ kJ mol}^{-1}$ .	The difference between the expected $-360 \text{ kJ mol}^{-1}$ and actual $-202 \text{ kJ mol}^{-1}$ is due to resonance energy.

# 10.2.3.1 Nomenclature (See Section 10.1.3)

# 10.2.3.2 Physical Properties of Arenes

#### Appearance

Exists as a colourless liquid with a characteristic 'aromatic' odour. It is non-polar and carcinogenic in nature.

# Melting / boiling point

- Low melting / boiling point
- Simple molecular structure / non-polar molecule
- Weak intermolecular instantaneous induced dipole-induced dipole interactions
- Low amount of energy is required to overcome the intermolecular forces of attraction.

# Solubility

Soluble in non-polar solvents but insoluble in polar solvents and water.

- The weak instantaneous induced dipole-induced dipole attractions between arene molecules is similar in strength / compatible to the weak instantaneous induced dipole-induced dipole attractions between non-polar solvent molecules.
- Strong hydrogen bonding between water molecules is not compatible to the weak instantaneous induced dipole-induced dipole interactions between non-polar arene molecules.

## **10.2.3.3 Chemical Reactions**

Like alkenes, benzene is unsaturated in nature. But why is benzene less susceptible to electrophilic addition reactions?

- Benzene ring is resonance stabilised by the delocalisation of the  $\pi$ -electrons cloud. Addition reactions result in the destruction of the ring of delocalised  $\pi$ -electrons in benzene which is energetically not feasible.
- Hence benzene would undergo electrophilic substitution but not electrophilic addition to preserve the stable aromatic benzene ring structure ( $\pi$ -delocalised system).

In contrast to alkenes, why does benzene need a positively charged E<sup>+</sup> electrophile but alkene only needs a partially charged  $\delta$ + electrophile for reaction?

• Delocalisation (i.e. resonance stabilisation) of the  $\pi$ -electrons of benzene ring make the  $\pi$ -electrons less nucleophilic compared to the  $\pi$ -electrons localised in C=C, increasing the  $\pi$ -electrons density of C=C. Thus a stronger electrophile is needed for benzene ring.

## **General Mechanism:**

Step 1: Generation of a positively charged electrophile, E<sup>+</sup>.

Step 2 (slow step): The  $\pi$ -electron system of benzene attacking the electrophile to form a non-aromatic carbocation intermediate.



Step 3 (fast step): The abstraction of H<sup>+</sup> to restore the delocalised  $\pi$ -electron ring system.



# Electrophilic substitution of nitric acid (Nitration)



Reagent and condition	Concentrated $HNO_3$ , concentrated $H_2SO_4$ , 50 °C	
Type of reaction	Electrophilic substitution	

Step 1:

 $\mathsf{HNO}_3 + 2\mathsf{H}_2\mathsf{SO}_4 \Longrightarrow \mathsf{NO}_2^+ + \mathsf{H}_3\mathsf{O}^+ + 2\mathsf{HSO}_4^-$ 

Step 2 (slow step):



Step 3 (fast step):



# Reduction of nitrobenzene to form phenylamine



Type of reaction Reduction

# \*Electrophilic substitution of halogen (Halogenation) (Enrichment)



Reagent and condition	$Br_2$ , anhydrous $FeBr_3$ as catalyst , r.t.p.
Type of reaction	Electrophilic substitution

Step 1:

 $FeBr_3 + Br_2 \rightarrow Br^+ + FeBr_4^-$ 

Step 2 (slow step):



# Arrangement of bonds at C atom undergoing electrophilic substitution



benzene

carbocation intermediate

nitrobenzene

Species	Hybridisation around C	Arrangement
Benzene	sp²	Planar
Carbocation intermediate	sp³	Tetrahedral
Nitrobenzene	sp²	Planar

#### 10.2.4 Halogenoalkanes

Halogenoalkanes are also known as alkyl halides. All members of halogen derivatives contain carbon-halogen single bond (C-X), where one or more hydrogen atoms in an alkane have been replaced by halogen atoms.

General formula:  $C_nH_{2n+1}X$  (where X = F, CI, Br or I) for mono–substituted alkyl halides.

Halogenoalkanes (alkyl halides) are represented as RX where R is an alkyl group.

Example: CH<sub>3</sub>Cl

CH₃CI	chloromethane
CH <sub>3</sub> CH <sub>2</sub> Br	bromoethane

Halogenoalkanes are classified as primary (1°), secondary (2°) or tertiary (3°) halogenoalkanes, depending on the number of R groups attached to the carbon atom bonded to the halogen atom.

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Halogenoalkane ( <b>X</b> = halogen)	X R Primary C atom	X C R Secondary C atom	X C R Tertiary C atom

# 10.2.4.1 Nomenclature (See Section 10.1.3)

The naming of the halogenoalkanes is similar to that of alkanes with the addition of a prefix to indicate the position of the carbon atom to which the halogen is attached to. The numbering of the carbon should be the smallest possible. If there is more than one type of halogen, the order of naming will follow the alphabetical order.

For example,



## **10.2.4.2 Physical Properties of Halogenoalkanes**



Halogens are more electronegative than carbon. The carbon–halogen bond will be polarised with the partial positive charge residing on the carbon atom as shown below. The polarisation of the carbon–halogen  $\sigma$ –bond is most pronounced in the C–F bond and the least in the C–I bond. Halogenoalkanes are usually polar molecules as the dipole moments do not cancel out (except in some like CCl<sub>4</sub>).
# **Boiling point**

	F	CI	Br	Ι	Increasing
Methane	195	249	277	316	point (in K)
Ethane	235	285	312	345	
Propane	276	320	344	376	
Butane	306	351	374	403	ł
	I	Increasing boiling point (in K)			

- Simple molecular structure / polar molecule
- As the size of molecule becomes bigger
- Size of electron cloud increases (more polarisable)
- Strength of intermolecular instantaneous induced dipole-induced dipole interactions increases
- More energy is required to overcome the intermolecular forces of attraction.

Higher boiling point than non-polar alkanes / alkenes of similar Mr:

 Higher amount of energy is required to overcome the stronger permanent dipole– permanent dipole interactions between polar halogenoalkane molecules compared to the weak instantaneous induced dipole–induced dipole interactions between non–polar alkane / alkene molecules.

## Solubility

Soluble in non-polar solvents but insoluble in polar solvents and water.

- The weak instantaneous induced dipole-induced dipole attractions between halogenoalkane molecules is similar in strength / compatible to the weak instantaneous induced dipole-induced dipole attractions between non-polar solvent molecules.
- Strong hydrogen bonding between water molecules is not compatible to the weak instantaneous induced dipole-induced dipole interactions between halogenoalkane molecules.

## **10.2.4.3 Chemical Reactions**

#### 10.2.4.3.1 Nucleophilic Substitution of Halogenoalkanes

In halogenoalkane, the carbon ( $\delta$ +), which is bonded to the halogen ( $\delta$ -), is susceptible to attack by nucleophiles. Nucleophiles are species (an ion or a molecule) which are strongly attracted to region of positive charge. Nucleophiles are either negatively charged ions or neutral molecules with an available lone pair, imparting a strongly  $\delta$ - charge on a molecule. Examples of nucleophiles in the IB syllabus are the hydroxide ion (OH<sup>-</sup>). In a nucleophilic substitution reaction, the halogen will be substituted by the nucleophile.

 $RX + OH^- \rightarrow ROH + X^-$  (X = F, Cl, Br or I)

Nucleophilic substitution reactions occur by either  $S_N 1$  or  $S_N 2$  mechanism, depending on the types of halogenoalkanes involved in the reaction.

#### Unimolecular Nucleophilic Substitution (S<sub>N</sub>1) Reaction Mechanism (Two steps)

- This mechanism is **favoured when the carbocation formed is more stable**. (Stability of carbocation: tertiary (3°) > secondary (2°) > primary (1°) > methyl)
- Generally for tertiary halogenoalkanes
- Two steps:
  - **first step is the rate determining (slow) step**, involving the halogenoalkane only to form the carbocation intermediate
  - second step is the fast step, involving the carbocation intermediate and the nucleophile
- Overall first order kinetics
- Rate equation: Rate = k [RX]; units of rate constant, k = s<sup>-1</sup>

Step 1 (slow step): Polarised C–X bond undergoes heterolytic fission, forming an  $X^-$  ion and a highly reactive trigonal planar carbocation intermediate



- The nucleophile attacks the sp<sup>2</sup> hybridised trigonal planar carbocation intermediate from either top or bottom of the plane with equal probability.
- This will **lead to the formation of a racemic mixture** (if the carbon being attacked by the nucleophile is a chiral carbon in the product formed)

Energy profile diagram for  $S_N 1$  mechanism:



Progress of reaction

## Bimolecular Nucleophilic Substitution (S<sub>N</sub>2) Reaction Mechanism (One step)

- This mechanism is favoured when there is less steric hindrance on the organic reactant molecule for nucleophilic attack. It is easier for the nucleophile to attack the C atom if there are less bulky R groups around the C atom.
  (Steric hindrance on RX: tertiary (3°) > secondary (2°) > primary (1°) > methyl)
- Generally for **pimary** halogenoalkanes
- **One step**, involving the halogenoalkane and the nucleophile
- Overall second order kinetics
- Rate equation: Rate = k [RX] [Nu<sup>-</sup>]; units of rate constant, k = mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>

One step mechanism: Nucleophile attacks the partially electron deficient  $\delta$ + C atom of the polarised C–X bond to form a pentacoordinate transition state in a single step. This is the rate determining step.



Inversion of symmetry due to  $S_N 2$  mechanism:

• The nucleophile attacks the C atom from the side opposite of the halogen atom. If the C atom is chiral, then the product would have an inversion of configuration as compared to the reactant.



Energy profile diagram for  $S_N 2$  mechanism:



# Nucleophilic substitution of OH<sup>-</sup> (Formation of alcohol)

 $RX + NaOH \rightarrow ROH + NaX$  (X = F, Cl, Br or I)

Reagent and condition	NaOH (aq) , heat under reflux OR KOH (aq) , heat under reflux
Type of reaction	Nucleophilic substitution

## \*Nucleophilic substitution of OR<sup>-</sup> (Formation of ether)

 $RX + R'O^{-}Na^{+} \rightarrow R'OR + NaX \qquad (X = F, CI, Br \text{ or } I)$ 

Reagent and condition	Na (s) in excess alcohol (R'O-Na+) , heat under reflux
Type of reaction	Nucleophilic substitution

## \*Nucleophilic substitution of NH<sub>3</sub> (Formation of amine)

 $RX + NH_3 \rightarrow RNH_2 + HX$  (X = F, Cl, Br or I)

Reagent and condition	Excess concentrated ammonia in ethanol, heat in sealed tube
Type of reaction	Nucleophilic substitution

In excess halogenoalkane, a mixture of amines (NH<sub>2</sub>R, NHR<sub>2</sub>, and NR<sub>3</sub>) and quaternary ammonium salt NR<sub>4</sub><sup>+</sup>X<sup>-</sup>) will be formed as follows:

- $RX + RNH_2 \rightarrow R_2NH + HX$  (Nucleophile:  $RNH_2$ )
  - $R\textbf{X} + R_2\textbf{NH} \rightarrow R_3\textbf{N} + H\textbf{X} \qquad (Nucleophile: R_2\textbf{NH})$
- $R\mathbf{X} + R_3 \mathbf{N} \rightarrow NR_4^+ X^-$  (Nucleophile:  $R_3 \mathbf{N}$ )

•

## \*Nucleophilic substitution of CN<sup>-</sup> (Formation of nitrile)

 $RX + KCN \rightarrow RCN + KX$  (X = F, Cl, Br or I)

Reagent and condition	KCN in ethanol, heat under reflux
Type of reaction	Nucleophilic substitution

Application of nucleophilic substitution reactions with CN<sup>-</sup> as nucleophile

- To increase the no. of C atoms in a chain (1C for each substitution of X with CN), i.e. step-up reaction
- The resulting nitrile product, RCN can be hydrolysed to form carboxylic acids or reduced to form amines.

\*General Reaction Equations for Nitriles

Formation of carboxylic acids

 $\text{RCN} + 2\text{H}_2\text{O} + \text{H}^{\scriptscriptstyle +} \rightarrow \text{RCOOH} + \text{NH}_4^{\scriptscriptstyle +}$ 

Reagent and condition	HCI (aq) or $H_2SO_4$ (aq), heat under reflux
Type of reaction	Acidic Hydrolysis

Formation of carboxylate salts

 $\text{RCN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{RCOO}^- + \text{NH}_3$ 

Reagent and condition	NaOH (aq) or KOH (aq), heat under reflux
Type of reaction	Basic Hydrolysis

Formation of amines

$RCN + 4[H] \rightarrow RCH_2NH_2$ $RCN + 2H_2 \rightarrow RCH_2NH_2$		(for reagent 1) (for reagents 2 and 3)
Reagent and condition	1. 2.	LiAlH <sub>4</sub> in dry ether, r.t.p. or H <sub>2</sub> with Ni catalyst, heat or
Type of reaction	3. Red	H <sub>2</sub> with Pd or Pt catalyst, r.t.p.

## Elimination of halogenoalkanes



#### 10.2.4.3.2 Preparation of Halogenoalkanes

#### Free radical substitution of alkanes

$C_{n}H_{2n+2}(g) + X_{2}(g)$	$\xrightarrow{\text{UV light}} C_n H_{2n+1} \mathbf{X} (g) + H \mathbf{X} (g)$
Reagent and condition	$\mathbf{X}_{2}$ (g) , UV light (where $\mathbf{X} = CI$ , Br)
Type of reaction	Free radical substitution

#### Electrophilic addition of hydrogen halide on alkenes



Reagent and condition	HX (g) or HX in CCl <sub>4</sub> , r.t.p. (where $X = CI$ , Br, I)
Type of reaction	Electrophilic addition

#### Electrophilic addition of halogen in organic solvent on alkenes



Reagent and condition	$\mathbf{X}_2$ (I) , CCI <sub>4</sub> solvent , r.t.p. , in the dark (where $\mathbf{X} = CI$ , Br, I)
Type of reaction	Electrophilic addition

## \*Nucleophilic substitution of alcohols



## 10.2.4.4 Rate of Nucleophilic Substitution Reactions

The rate of nucleophilic substitution depends on:

- 1. Type of halogenoalkanes and the mechanism
- 2. Type of halogen / leaving group
- 3. Type of nucleophile
- 4. Type of solvent

#### 10.2.4.4.1 Type of Halogenoalkanes and the Mechanism (see section 10.2.4.3.1)

The type of mechanism for nucleophilic substitution is determined by the structure of the halogenoalkanes:

The inductive and steric effects of substituents can help to explain why primary halogenoalkane tend to undergo  $S_N 2$  while tertiary halogenoalkanes tend to undergo  $S_N 1$  reactions (see section 10.2.4.3.1). In both cases it is helpful to consider the intermediate or transition state formed.

Substitution reactions involving the ionic  $S_N1$  mechanism are generally faster than those proceeding via the  $S_N2$  mechanism. Thus the hydrolysis of a tertiary chloroalkane with water or hydroxide ions is faster than the hydrolysis of a primary chloroalkane under the same conditions.

In decreasing order of reactivity:



## 10.2.4.4.2 Type of Halogen / Leaving Group

C–X bond	C–F	C–CI	C–Br	C–I
Bond energy / kJ mol <sup>-1</sup>	492	324	285	228

The properties of a good leaving group, in this case the halogens (-CI, -Br, -I), depends on the size of the halogen.

Size of the halogen: CI < Br < ICarbon-halogen bond length: C-CI < C-Br < C-I, due to more diffused overlap of the valence orbitals Bond strength: C-CI > C-Br > C-IAmount of energy to break carbon-halogen bond: C-CI > C-Br > C-IRate of nucleophilic substitution: R-CI < R-Br < R-I

## 10.2.4.4.3 Type of Nucleophile

The reactivity of a nucleophile depends on its electron density. Anions tend to be more reactive than the corresponding neutral species. For example, the rate of substitution with hydroxide ions is faster than with water molecules.

Among species with the same charge, a less electronegative atom carrying a lone pair of electrons is a better nucleophile than a more electronegative one. Thus ammonia is a better nucleophile than water. This is because the less electronegative atom can donate its pair of electrons more easily as they are held less strongly.

When all other variables are kept constant, the rate of nucleophilic substitution of a particular halogenoalkane with various nucleophiles is in the following sequence:

 $CN^- > OH^- > NH_3 > H_2O$ (fastest) (slowest)

## 10.2.4.4.3 Type of Solvent

There are two classes of organic solvent

- Protic solvents, which contain –OH or –NH<sub>2</sub> groups.
- Polar aprotic solvents like propanone, which contain strong dipoles but no –OH or –NH<sub>2</sub> groups.

#### Protic solvent

Protic solvents such as H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>COOH surrounds the incoming nucleophile and stabilize it by forming ion–dipole interactions in a process known as solvation.



Thus, the **reactivity of the nucleophile to donate a pair of electrons to an electrophile is reduced**.

#### Polar aprotic solvent



DMF DMSO HMPA DMA

Polar aprotic solvents such as acetonitrile (CH<sub>3</sub>CN), acetone (CH<sub>3</sub>COCH<sub>3</sub>), dimethylformamide (DMF) [(CH<sub>3</sub>)<sub>2</sub>NC=OH], dimethyl sulfoxide, DMSO [(CH<sub>3</sub>)<sub>2</sub>SO], hexamethylphosphoramide, HMPA {[(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PO} and dimethylacetamide (DMA) **solvate the cation counterion of the nucleophile but not the nucleophile**.



Thus, the reactivity of the nucleophile to donate a pair of electrons to an electrophile is increased.

## Effect of the solvent on rate of $S_N 1$ reactions

- For S<sub>N</sub>1 reactions, the solvent affects the rate only if it influences the stability of the carbocation intermediate. The Nu:<sup>-</sup> is not involved in the rate determining step hence solvent effects on the Nu:<sup>-</sup> do not affect the rate of S<sub>N</sub>1 reactions.
- Polar solvents, both protic and aprotic, will solvate and stabilize the carbocation, lowering the activation energy thus accelerating the rate of  $S_N1$  reactions.
- Solvent polarity is usually expressed by the 'dielectric constant', e, which is a measure of the ability of a solvent to act as an electric insulator.
- Polar solvents are good electric insulators because their dipoles surround and associate with charged species.

Aprotic solvents		Protic solvents	
Name	Dielectric constant	Name	Dielectric constant
Hexane	1.9	Acetic acid	6.2
Benzene	2.3	Acetone	20.7
Diethyl ether	4.3	Ethanol	24.3
Chloroform	4.8	Methanol	33.6
HMPA	30	Formic acid	58.0
DMF	38	Water	80.4
DMSO	48		

• Dielectric constants of some common solvents are given in the following table

## Effect of the solvent on rate of $S_N 2$ reactions

- Protic solvents such as H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>COOH surrounds the incoming nucleophile and stabilize it by forming hydrogen bonding in a process known as solvation. Thus, the reactivity of the nucleophile to donate a pair of electrons to an electrophile is significantly reduced.
- Polar aprotic solvent would solvate the cation counterion of the nucleophile instead of the nucleophile. Thus, the reactivity of the nucleophile to donate a pair of electrons to an electrophile is significantly increased.
- Since the choice of nucleophile is part of the rate-determining step, using polar aprotic solvent for an  $S_N2$  reaction would significantly increase the rate of reaction.

# Summary of $S_{\text{N}}1$ and $S_{\text{N}}2$ mechanisms:

Mechanism	S <sub>N</sub> 1	S <sub>N</sub> 2
Favoured by	Tertiary halogenoalkanes	Primary halogenoalkanes
Nature of mechanism	Two–step mechanism via carbocation intermediate	Concerted one-step mechanism with unstable pentacoordinate transition state
Relative rate	Higher	Lower
Favoured solvent	Polar, protic	Polar, aprotic
Energy profile diagram	transition state 1 carbocation intermediate reactants reactants extent of reaction	be transition state reactants reactants reactants reactants

#### 10.2.4.5 Chemical Tests

 $\mathsf{R}\textbf{X} + \mathsf{NaOH} \to \mathsf{R}\textbf{OH} + \mathsf{Na}\textbf{X}$ 

(Nucleophilic substitution)

 $Ag^{+}(aq) + X^{-}(aq) \rightarrow AgX$  (s) (X = F, Cl, Br or I) (Precipitation)

Reagent and	1. NaOH (aq) OR KOH (aq), heat under reflux followed by the
condition	addition of dilute HNO <sub>3</sub>
condition	2. Add AgNO <sub>3</sub> (aq)
Observations and	White precipitate of AgCI formed, RCI present
deductions	Cream precipitate of AgBr formed, RBr present
ueuuclions	Yellow precipitate of AgI formed, RI present





Scan me to view a video for chemical test for halogenoalkanes

# 10.2.5 Alcohols

Alcohols belong to a homologous series with the general formula  $C_nH_{2n+1}OH$ . The basic structure of an alcohol is shown below. The functional group of the alcohol is the hydroxyl group, –OH.

Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) alcohols, depending on the number of R groups attached to the carbon atom bonded to the oxygen atom.

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Alcohols	H H R Primary C atom	R C C OH R Secondary C atom	R C C OH R Tertiary C atom

## 10.2.5.1 Nomenclature (See Section 10.1.3)

#### **10.2.5.2 Physical Properties of Alcohols**

#### **Boiling point**

Alcohols have much higher boiling points compared to alkanes of similar Mr.

Organic compound	Mr	Boiling point / °C
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	72	36
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	72	35
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	74	117

Higher amount of energy is required to overcome the stronger hydrogen bonds between alcohol molecules compared to the weak instantaneous induced dipole–induced dipole interactions between non–polar alkane molecules (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) or permanent dipole–permanent dipole interactions between polar CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> molecules.



Alcohol	Mr	Boiling point / °C
(CH₃)₃COH	74	82
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	74	117

Branched isomers have lower melting / boiling point than straight chain isomers

• Extent of surface area of contact:

branched < straight chain isomers

• Extent of distortion of the electron cloud:

branched < straight chain isomers

• Extent of weak intermolecular instantaneous dipole-induced dipole attractions:

branched < straight chain isomers

• Energy required to overcome intermolecular instantaneous dipole–induced dipole attractions: branched < straight chain isomers

# Solubility



The oxygen atom on the hydroxyl group has two lone pairs which are capable of forming hydrogen bonds with water molecules.



However, the extent of solubility of alcohols in water is dependent on the chain length of the alkyl group. Alcohols up to three carbons long are completely miscible with water. Alcohols with four carbons or more are partially miscible or immiscible with water due to their lower polarity resulting from the hydrophobic nature of the alkyl chain.

## **10.2.5.3 Chemical Reactions**

## 10.2.5.3.1 Combustion of Alcohols

All alcohols combust completely in excess oxygen to form carbon dioxide and water. In some countries (e.g. Brazil), ethanol is combined with gasoline (petrol) to produce a fuel for cars called gasohol. Although this makes the country less reliant on the supply and cost of pure gasoline, it will not produce as much energy. This can be verified by comparing the standard enthalpies of combustion of ethanol and octane.

C<sub>2</sub>H<sub>5</sub>OH (I) + 3O<sub>2</sub> (g) → 2CO<sub>2</sub> (g) + 3H<sub>2</sub>O (I)  $\Delta H^{\theta} = -1371 \text{ kJ mol}^{-1}$ C<sub>8</sub>H<sub>18</sub> (I) + 12<sup>1</sup>/<sub>2</sub>O<sub>2</sub> (g) → 8CO<sub>2</sub> (g) + 9H<sub>2</sub>O (I) $\Delta H^{\theta} = -5512 \text{ kJ mol}^{-1}$ 

Since the values are given per mole this means that 46 g of ethanol produces 1371 kJ of energy and 114g of octane produce 5512 kJ of energy. Thus, one gram of ethanol produces 29.8 kJ of energy when it is completely combusted whereas the same mass of octane produces 48.4 kJ of energy.

 $C_{n}H_{2n+1}OH(I) + (\frac{3n}{2})O_{2}(g) \rightarrow nCO_{2}(g) + (n+1)H_{2}O(I)$ 

Reagent and condition	Excess oxygen
Type of reaction	Combustion

#### 10.2.5.3.2 Oxidation of Alcohols

Alcohols can be oxidised to form carbonyl compounds or carboxylic acids, depending on the class of alcohol and the oxidation conditions employed. Generally, primary and secondary alcohols can be easily oxidised but not tertiary alcohols.



Diagram showing the resulting colour after the oxidation of primary (propan–1–ol), secondary (propan–2–ol) and tertiary (2–methylpropan–2–ol) using acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.



heat under reflux



- Primary alcohols are readily oxidised to aldehydes under controlled conditions, the aldehydes can be further oxidised to form carboxylic acids. The distillation setup above prevents the further oxidation of aldehyde to the carboxylic acid as it can separate the different compounds based on boiling points. Aldehydes which has a lower boiling point than the alcohol is collected as a gas and passes into the condensing tube, which is surrounded by cold flowing water. The gas condenses back into a liquid, which is collected in the beaker at the bottom.
- Ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, a primary alcohol, can be oxidised to ethanoic acid, CH<sub>3</sub>COOH. Common oxidising agents used are acidified aqueous potassium dichromate(VI) or potassium manganate(VII) solution. The orange dichromate(VI) ion (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) is reduced to form the green chromium(III) ion (Cr<sup>3+</sup>), which is green in colour. Purple manganate(VII) ions (MnO<sub>4</sub><sup>-</sup>) will be reduced to form colourless Mn<sup>2+</sup> ions.

Reaction	$RCH_2OH + [O] \rightarrow RCHO + H_2O$
Reagent and condition	Acidified $K_2Cr_2O_7$ , heat with immediate distillation
Type of reaction	Oxidation
Reaction	$RCH_2OH + 2[O] \rightarrow RCOOH + H_2O$
Reagent and condition	Acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> OR KMnO <sub>4</sub> , heat under reflux

Type of reaction Oxidation



• Secondary alcohols are oxidised to ketones

Reaction	$RCH(OH)R' + [O] \to RCOR' + H_2O$
Reagent and condition	Acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> OR KMnO <sub>4</sub> , heat under reflux
Type of reaction	Oxidation



• Tertiary alcohols do not undergo oxidation.

## 10.2.5.3.3 Cleavage of O-H Bond in RO-H

• \*Acid–metal displacement with sodium



Reagent and condition	Reactive metals (e.g. Na and K) , r.t.p.
Type of reaction	Acid-metal displacement

• Condensation with carboxylic acid to form esters



Reagent and condition	Carboxylic acid , RCOOH and concentrated $H_2SO_4$ as catalyst , heat
Type of reaction	Condensation / acyl nucleophilic substitution

Alcohols undergo esterification or condensation reaction with carboxylic acids under reflux to form sweet–smelling esters. Esters are commonly used as flavourings in food industries.

The reaction is slow and reversible, taking hours to reach equilibrium. The reactant mixture is refluxed and concentrated sulfuric acid catalyst is added to speed up the reaction. The concentrated sulfuric acid also acts as a dehydrating agent, removing water from the equilibrium mixture to favour the forward reaction to increase the yield of ester

For example,



\*Condensation with acid chlorides to form esters



Reagent and condition	Anhydrous acid chloride , RCOCI , r.t.p.
Type of reaction	Condensation / acyl nucleophilic substitution

## 10.2.5.3.4 \*Cleavage of R-O Bond in R-OH

• Nucleophilic substitution to form halogenoalkanes



## 10.2.5.3.5 Elimination of H<sub>2</sub>O





#### 10.2.5.3.6 Preparation of Alcohols

#### Electrophilic addition of steam to alkenes



#### Industrial conditions:

Reagent	H <sub>2</sub> O (g)
Condition	300 °C, 65 atm , concentrated $H_3PO_4$ as catalyst
Type of reaction	Electrophilic addition

#### Lab conditions:

Reagent	H <sub>2</sub> O (I)
Condition	Concentrated sulfuric acid , $H_2SO_4$ followed by boiling with $H_2O$ (I)
Type of reaction	Electrophilic addition

# Nucleophilic substitution of OH<sup>-</sup> to halogenoalkanes

# $RX + NaOH \rightarrow ROH + NaX$ (X = F, CI, Br or I)

Reagent and condition	NaOH (aq) , heat under reflux OR KOH (aq) , heat under reflux
Type of reaction	Nucleophilic substitution

#### Reduction of aldehydes, ketones and carboxylic acids

Aldehydes and carboxylic acids can undergo reduction to form primary (1°) alcohols while ketones can undergo reduction to form secondary (2°) alcohols.





Reagent and condition	LiAlH <sub>4</sub> in dry ether followed by addition of dilute acid , r.t.p.
Type of reaction	Reduction

In order of decreasing reducing strength:  $LiAIH_4 > NaBH_4 > H_2$