# VICTORIA JUNIOR COLLEGE CHEMISTRY DEPARTMENT

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# INTRODUCTION TO ORGANIC CHEMISTRY

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# LECTURE OUTLINE

- **1** What is Organic Chemistry?
- 2 Formulae of Organic Compounds
- 3 Common Terminology
- 4 Hybridisation
- 5 Shapes of Organic Molecules
- 6 Types of Organic Reactions
- 7 Reaction Mechanisms
  - 7.1 Types of Reagents
  - 7.2 Names of Reaction Mechanisms
  - 7.3 Bond Fission (breaking of covalent bonds)
- 8 Factors Affecting Reactivity of Organic Compounds

# ASSESSMENT OBJECTIVES

Candidates should be able to:

- (a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:
  - (i) hydrocarbons (alkanes, alkenes and arenes)
  - (ii) halogen derivatives (halogenoalkanes and halogenoarenes)
  - (iii) hydroxyl compounds (alcohols and phenols)
  - (iv) carbonyl compounds (aldehydes and ketones)
  - (v) carboxylic acids and derivatives (acyl chlorides and esters)
  - (vi) nitrogen compounds (amines, amides, amino acids and nitriles)
- (b) interpret, and use the following terminology associated with organic reactions:
  - (i) functional group
  - (ii) degree of substitution: primary, secondary, tertiary, quaternary
  - (iii) homolytic and heterolytic fission
  - (iv) carbocation
  - (v) free radical, initiation, propagation, termination
  - (vi) electrophile (Lewis acid), nucleophile (Lewis base)
  - (vii) addition, substitution, elimination, condensation, hydrolysis
  - (viii) oxidation and reduction
  - [in equations for organic redox reactions, the symbols [O] and [H] are acceptable]
- (c) interpret, and use the following terminology associated with organic reactivities:
  - (i) delocalisation
  - (ii) electronic effect (electron-donating and electron-withdrawing effect)
  - (iii) steric effect (steric hindrance)
- (d) describe sp<sup>3</sup> hybridisation, as in ethane molecule, sp<sup>2</sup> hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule
- (e) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to  $\sigma$  and  $\pi$  carbon-carbon bonds
- (f) predict the shapes of, and bond angles in, molecules analogous to those specified in (e)
- (g) apply (b) and (c) to the understanding of mechanisms in terms of organic structure and bonding
- (h) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

# INTRODUCTION TO ORGANIC CHEMISTRY

### 1 What is Organic Chemistry?

- It is the study of the chemistry of carbon compounds other than its oxides, metallic carbonates and related compounds.
- More than 6 million organic compounds have been identified. This ability of carbon to form so many stable compounds is because
  - (i) strong bonds can be formed between two carbon atoms, e.g. C–C bond is much stronger compared to single bonds formed between atoms of other elements. This allows carbon to form long chains (catenation) and rings, resulting in a wide variety of possible molecules.

	bond energy / kJ mol <sup>-1</sup>
C–C	350
N–N	160
0–0	150

- (ii) carbon is tetravalent, which allows branching of carbon chains into side chains and formation of double or triple bonds, further increasing the number of carbon compounds which can be formed.
- (iii) carbon forms strong covalent bonds with other elements, e.g. H, N, O, S and the halogens.

### 2 Formulae of Organic Compounds

- Empirical formula shows the simplest ratio of the atoms of the different elements present in the compound. E.g.  $C_2H_4O$
- **Molecular formula** shows the **actual number** of atoms of each element present in one molecule of the compound. E.g. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>
- **Constitutional formula (structural formula)** shows how the constituent atoms of a molecule are **joined together**. E.g. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H and (CH<sub>3</sub>)<sub>2</sub>CHCO<sub>2</sub>H have different structural formulae but the same molecular formula of C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>.
- **Displayed formula or full structural formula** is the detailed structure of a molecule showing the arrangement of the atoms and **all the bonds** between them.

E.g.

$$\begin{array}{ccccc} H & H & O \\ - & - & - & H \\ H - C - C - C - O - H \\ H - C - C - C - C - O - H \\ H - H \\ H - C - H \\ H - H \\ H \\ H \end{array}$$

- Skeletal formula shows the carbon skeleton of the molecule without showing the carbon atoms and the C–H bonds and atoms in the molecule. Only the carbon–carbon bonds, bonds to functional groups and functional groups are shown.
  - E.g.



• Stereochemical formula shows the spatial arrangement of the bonds, atoms and groups in a molecule as a perspective 3-dimensional formula.

E.g.



# Making Thinking Visible

Question: Answer:	What are the possible types of carbon-carbon bonds? C–C, C=C, C $\equiv$ C, C $\equiv$ C (benzene)
Question:	What does a normal straight line, a solid wedge and a dashed wedge represent in the stereochemical formula?
Answer:	Normal straight line: bond lies on the plane of the paper Solid wedge: bond pointing out of the plane of the paper Dashed wedge: bond pointing into the plane of the paper

# 3 Common Terminology

Hydrocarbons are compounds containing carbon and hydrogen only. The simplest hydrocarbons, containing only single bonds are the alkanes with general formula C<sub>n</sub>H<sub>2n+2</sub>.

E.g.	
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molecular formula	structural formula	name
CH <sub>4</sub>	CH <sub>4</sub>	methane
C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	ethane
C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	propane
C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	butane
C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	pentane

Alkyl group is a group of carbon and hydrogen having the general formula C<sub>n</sub>H<sub>2n+1</sub>. It is usually denoted by the letter R. The name follows that of corresponding alkane but with the suffix -yl instead of -ane.

E.g.

alkyl group	name
CH <sub>3</sub> –	methyl
CH₃CH <sub>2</sub> –	ethyl
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -	propyl

alkyl group	name
$CH_3(CH_2)_2CH_2-$	butyl
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> -	pentyl

Candidates should be able to:

(b) interpret, and use the following terminology associated with organic reactions:

- (i) functional group
- **Functional group** consists of an element (e.g. –Br) or combination of elements (e.g. –OH, –CO<sub>2</sub>H) **responsible for the chemical reactions** of an organic compound.
- Homologous series is a family of compounds containing the same functional group but differing by a common increment of a -CH<sub>2</sub>- group between one member and the next.

All compounds in any one homologous series

- (i) undergo **similar chemical reactions** (due to presence of the same functional group).
- (ii) can be prepared by similar methods.
- (iii) have a relative molecular mass 14 units greater than the preceding compound in the series (due to the presence of an additional –CH<sub>2</sub>– group).
- (iv) exhibit a **regular gradation of physical properties** (due to the increasing size of hydrocarbon chain).

Candidates should be able to:

- (a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:
  - (i) hydrocarbons (alkanes, alkenes and arenes)
  - (ii) halogen derivatives (halogenoalkanes and halogenoarenes)
  - (iii) hydroxyl compounds (alcohols and phenols)
  - (iv) carbonyl compounds (aldehydes and ketones)
  - (v) carboxylic acids and derivatives (acyl chlorides and esters)
  - (vi) nitrogen compounds (amines, amides, amino acids and nitriles)

class / name of functional group * not regarded as functional group		general formula	structure of functional group
	*alkanes	RH or $C_nH_{2n+2}$	_
	alkenes	$C_nH_{2n}$	)c=c
hydrocarbons	alkynes (not in syllabus)	$C_nH_{2n-2}$	-C≡C-
hydrocarbons	*arenes (contain benzene ring, )	_	(Note: The benzene ring is regarded as forming part of the hydrocarbon chain and is hence usually <b>not</b> classified as a functional group.)
	halogenoalkanes	RX (X= C <i>l</i> , Br, I)	-X
derivatives	halogenoarenes	(X = Cl, Br, I)	-X

class / name of functional group		general formula	structure of functional group
	alcohols	ROH	–OH
hydroxyl compounds and	phenols	О-он	–OH
	ethers (not in syllabus)	ROR'	-0-
carbonvl	aldehydes	*RCHO	о — С—Н
compounds	ketones	RCOR'	0 
	carboxylic acids	*RCO₂H	О —С–О–Н
carboxylic acids and derivatives	acyl chlorides	*RCOC <i>l</i>	$-\overset{O}{C}-Cl$
	esters	**RCO₂R', R'OCOR**	0 
	amines	$RNH_2$ , $R_2NH$ , $R_3N$	H H N-H,N-, N-H,N-,
nitrogen compounds	amides	*RCONH <sub>2</sub> , *RCONHR', *RCONR'R"	O H C-N-H, O H O C-N-,C-N-
	amino acids	RCH(NH <sub>2</sub> )(CO <sub>2</sub> H)	H O 
	nitriles	RCN	–C≡N

### Note:

\*: R can stand for a hydrogen atom as well as any alkyl group

\*\* for esters: R (attached to carbon) can be hydrogen atom or alkyl group but R'(attached to oxygen) must be an alkyl group

- Saturated compounds contain only single bonds in their molecules, e.g. alkanes, • halogenoalkanes. C:H ratio of such compounds is C<sub>n</sub>H<sub>2n+2</sub>.
- Unsaturated compounds contain multiple bonds in their molecules, e.g. c=c in • alkenes,  $\overset{O}{\overset{II}{\phantom{C}}}$  in aldehydes and ketones and –C=N in nitriles.

Presence of one pi bond decreases number of H atoms by two. E.g. C<sub>n</sub>H<sub>2n</sub> contains • one double bond,  $C_nH_{2n-2}$  contains two double bonds or one triple bond.

Candidates should be able to:

(b) interpret, and use the following terminology associated with organic reactions:

(ii) degree of substitution: primary, secondary, tertiary, quaternary

# • Degree of substitution

- (i) A primary carbon is attached to one other carbon atom.
- (ii) A secondary carbon is attached to two other carbon atoms.
- (iii) A tertiary carbon is attached to three other carbon atoms.
- (iv) A quaternary carbon is attached to four other carbon atoms.



### Making Thinking Visible

Question: What is the shape about the carbon atom in these functional groups: RCHO, RCOR', RCO<sub>2</sub>H, RCOC*l* and RCO<sub>2</sub>R'?

Answer: Trigonal planar

Question: What is the shape about the oxygen atom in these functional groups: ROR', ROH and

ΟН

Answer: Bent

Question: What is the shape about the nitrogen atom in these functional groups: RNH<sub>2</sub>, R<sub>2</sub>NH and R<sub>3</sub>N? Answer: Trigonal pyramidal

### Exercise

Write the full structural (or displayed) formulae of the following compounds. Circle the functional groups present in each of the structural formulae drawn and name the class of compounds in which the functional groups belong. [Practice drawing the skeletal formulae of these compounds.]

(a) CH<sub>3</sub>CH=CHCH<sub>2</sub>CHO

(b)  $HO_2CCH_2CO(CH_2)_2NH_2$ 

(c) CH<sub>2</sub>C*l*CH<sub>2</sub>OCOCH<sub>2</sub>OH

(d)  $CH_3CO_2C_2H_5$ 

Homework: You are ready to attempt Qn 1 of tutorial

# 4 Hybridisation

• Electronic configuration of C: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>2</sup>

Carbon atom in the ground state:



Carbon atom in the excited or bonding state is capable of forming four bonds.

However, if carbon were to use its 2s and 2p orbitals for bond formation, many structural features of carbon compounds cannot be accounted for. For example, in CH<sub>4</sub>, the bond angle would be 90° instead of the actual value of 109.5° and the four C–H bonds would not be identical which contradicts reality. [Diagram omits 2s and 2p<sub>z</sub> orbitals of carbon for simplicity.]

Hence, the theory of **hybridisation** (i.e. **mixing of orbitals**) was proposed to address these discrepancies.

• **sp<sup>3</sup> hybridisation** (4 regions of electron densities)





Four orbitals of carbon (2s,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ) are 'mixed' to form **four equivalent sp<sup>3</sup> hybrid orbitals** which are **tetrahedral and at 109.5**° **to one another**. The carbon atom forms 4 sigma bonds (all single bonds) with other atoms. Each sp<sup>3</sup> hybrid orbital contains ¼ s and  $\frac{3}{4}$  p character.

• **sp<sup>2</sup> hybridisation** (3 regions of electron densities)





Three orbitals of carbon (2s,  $2p_x$ ,  $2p_y$ ) are 'mixed' to form three equivalent  $sp^2$  hybrid orbitals which are trigonal planar and at 120° to one another. One  $2p_z$  orbital of carbon remains unchanged. The carbon atom forms 3 sigma and 1 pi bonds (1 double bond present) with other atoms. Each  $sp^2$  hybrid orbital contains  $\frac{1}{3}s$  and  $\frac{2}{3}p$  character.

• **sp hybridisation** (2 regions of electron densities)





Two orbitals of carbon (2s,  $2p_x$ ) are 'mixed' to form **two equivalent sp hybrid orbitals** which are **linear and at 180° to each other**. Two 2p orbitals of carbon remain unchanged. The carbon atom forms 2 sigma and 2 pi bonds (triple bond or 2 double bonds present) with other atoms. Each sp hybrid orbital contains  $\frac{1}{2}$  s and  $\frac{1}{2}$  p character.

• Each sp, sp<sup>2</sup> or sp<sup>3</sup> hybrid orbital has **one lobe larger than the other**.

In bond formation, the **larger lobe is used**, which allows for more effective overlapping, resulting in stronger bonds than if the unhybridised 2s or 2p orbitals had been used.



• Carbon uses the **hybrid orbitals** to form **sigma** bonds while it uses the **unhybridised 2p orbitals** to form **pi** bonds.

- The more s character a hybrid orbital has, the closer the electrons are to the nucleus.
  - sp<sup>3</sup>: 25% s character, 75% p character
  - sp<sup>2</sup>: 33% s character, 67% p character
  - sp: 50% s character, 50% p character

The more s character the bond has, the stronger the bond will be. For example, there is greater s-character in the  $sp^2$  hybrid orbital than in the  $sp^3$  hybrid orbital and the electrons in the  $sp^2$  hybrid orbital are **closer to the nucleus**. Hence, C–C bond with  $sp^2-sp^2$  overlap is **shorter** than that with  $sp^3-sp^2$  overlap.

type of bond	representative bond length / pm
sp <sup>3</sup> –sp <sup>3</sup>	154
sp <sup>3</sup> –sp <sup>2</sup>	150
sp³–sp	146
sp <sup>2</sup> –sp <sup>2</sup>	147
sp²–sp	143
sp–sp	137

# Making Thinking Visible

Question: Rank the following bonds in increasing bond energy:

Answer: Bond energy: sp<sup>3</sup>–sp<sup>3</sup> < sp<sup>3</sup>–sp<sup>2</sup> < sp<sup>3</sup>–sp, i.e. the greater the s character in the hybrid orbital, the stronger is the bond, the shorter is the bond length and the more endothermic is the bond energy.

### Exercise

Histidine is an amino acid. What are the hybrid orbitals at C1, C2 and N3?

C1: .....

C**2**: .....

N**3**: .....



# 5 Shapes of Organic Molecules

Candidates should be able to:

- (d) describe sp<sup>3</sup> hybridisation, as in ethane molecule, sp<sup>2</sup> hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule
- (e) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to  $\sigma$  and  $\pi$  carbon-carbon bonds
- (f) predict the shapes of, and bond angles in, molecules analogous to those specified in (e)
- Methane, CH<sub>4</sub>

Displayed formula:

Carbon atom in  $CH_4$  forms four sigma bonds.



- Solution Number of hybrid orbitals: 4
- System Type of hybridisation: sp<sup>3</sup>
- Shape: tetrahedral around carbon atom, bond angle =  $109.5^{\circ}$
- Sigma bond formation: each C–H bond is formed by the head-on overlap of **sp**<sup>3</sup> hybrid orbital of C with 1s orbital of H
- Ethane, C<sub>2</sub>H<sub>6</sub>

Displayed formula:

Each carbon atom in  $C_2H_6$  forms four sigma bonds.



- Solution Number of hybrid orbitals: 4
- ⅍ Type of hybridisation: sp<sup>3</sup>
- Shape: tetrahedral around each carbon atom, bond angle = 109.5°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of sp<sup>3</sup> hybrid orbital of C with 1s orbital of H and the C–C bond is formed by the head-on overlap of sp<sup>3</sup> hybrid orbital of each C
- Ethene, C<sub>2</sub>H<sub>4</sub>

Displayed formula:

Each carbon atom in  $C_2H_4$  forms three sigma and one pi bonds.

- ♥ Number of hybrid orbitals: 3
- ♦ Number of p orbitals: 1
- ⅍ Type of hybridisation: sp<sup>2</sup>
- Shape: trigonal planar around each carbon atom, bond angle = 120°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of sp<sup>2</sup> hybrid orbital of C with 1s orbital of H and the C–C bond is formed by the head-on overlap of sp<sup>2</sup> hybrid orbital of each C
- Pi bond formation: carbon-carbon pi bond is formed by the side-on overlap of 2p<sub>z</sub> orbital of each C laterally. The resulting pi electron cloud is distributed above and below the plane of atoms.



sigma and pi bonds superimposed together

Benzene, C<sub>6</sub>H<sub>6</sub>

Kekule structure:



Note: Kekule structure does <u>NOT</u> represent the actual structure of benzene.

Each carbon atom in  $C_6H_6$  forms three sigma and one pi bonds.

- ✤ Number of hybrid orbitals: 3
- Number of p orbitals: 1
- ✤ Type of hybridisation: sp<sup>2</sup>
- Shape: trigonal planar around each carbon atom, bond angle = 120° Hence, benzene has a planar structure in which the six carbon atoms are bonded in a regular hexagonal ring.
- Sigma bond formation: each C–H bond is formed by the head-on overlap of sp<sup>2</sup> hybrid orbital of C with 1s orbital of H and the C–C bond is formed by the head-on overlap of sp<sup>2</sup> hybrid orbital of each C
- Pi bond formation: carbon–carbon pi bond is formed by the side-on overlap of 2p<sub>z</sub> orbital of each C with the adjacent 2p<sub>z</sub> orbitals on either side of it This results in two continuous doughnut-shaped electron clouds, one above and the other below the plane of the atoms.



pi bond formation

doughnut-shaped distribution of pi electrons

# Note:

- (i) The pi electrons move over a larger region of space in the actual structure of benzene, as compared to the Kekule structure. The **pi electrons** are said to be **delocalised around the whole ring** and this phenomenon is known as **resonance**.
- (ii) Each C–C bond in benzene is a **partial double bond** and is **identical** to one another.
- (iii) Structure of benzene is more accurately presented as () where the circle represents the delocalisation of six pi electrons.

• Ethyne, C<sub>2</sub>H<sub>2</sub>

Displayed formula:  $H-C\equiv C-H$ 

Each carbon atom in  $C_2H_2$  forms two sigma and two pi bonds.

- ♥ Number of hybrid orbitals: 2
- ♦ Number of p orbitals: 2
- ✤ Type of hybridisation: sp
- $\checkmark$  Shape: linear around each carbon atom, bond angle = 180°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of sp hybrid orbital of C with 1s orbital of H and the C–C bond is formed by the head-on overlap of sp hybrid orbital of each C
- Pi bond formation: one carbon–carbon pi bond is formed by the side-on overlap of 2py orbital of each C laterally and the other carbon–carbon pi bond is formed by the side-on overlap of 2pz orbital of each C laterally

Pi electron cloud forms a cylindrical sheath around the axis joining the carbon atoms.

sigma bond formation



overlap of 2p<sub>y</sub> orbitals pi bond formation (the two pi bonds can be formed by any two of the three p orbitals)



pi electron cloud forms a cylindrical sheath

# **Making Thinking Visible**

Question: State the number of regions of electron densities and the electron pair geometry about the carbon atom for the following hybridisation: sp<sup>3</sup>, sp<sup>2</sup> and sp.

- Answer: sp<sup>3</sup>: **4 regions** of electron densities and **tetrahedral** in electron pair geometry
  - sp<sup>2</sup>: **3 regions** of electron densities and **trigonal planar** in electron pair geometry
  - sp: 2 regions of electron densities and linear in electron pair geometry

Homework: You are ready to attempt Qn 2 & 3 of tutorial

# 6 Types of Organic Reactions

Candidates should be able to:

- (b) interpret, and use the following terminology associated with organic reactions:
   (vii) addition, substitution, elimination, condensation, hydrolysis
  - (viii) oxidation and reduction [in equations for organic redox reactions, the symbols [O] and [H] are acceptable]
- Addition reaction: Two or more molecules combine to form a **single** product. Usually occurs in unsaturated compound where the multiple bond is broken to form a saturated compound.

E.g.  $CH_2=CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$ 

• **Substitution** reaction: An atom or group of atoms **replaces** another atom or group of atoms.

E.g.  $CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$ 

• Elimination reaction: Removal of atoms or groups of atoms from two adjacent atoms to form a pi bond.

E.g. 
$$H H H H H H$$
  
 $H - C - C - H - F C = C + H_2O$   
 $H O - H H H$ 

• **Condensation** reaction: Two or more molecules **combine** to form a larger molecule with **elimination of a small molecule** such as water or HC*l*. In a condensation reaction, two functional groups from different molecules react with each other to form a larger molecule, and a small molecule is released as a byproduct.



• **Hydrolysis** reaction: It involves **reaction with water** and is usually catalysed by acids or bases. (Water molecule is broken up.)

E.g.  $CH_3CO_2CH_2CH_3 + H_2O \rightleftharpoons^{H^+}CH_3CO_2H + CH_3CH_2OH$ 

• Oxidation reaction: It involves a gain of oxygen or loss of hydrogen in a compound.

E.g.  $CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$  $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$ 

• Reduction reaction: It involves a gain of hydrogen or loss of oxygen in a compound.

E.g.  $CH_3CH_2COCH_3 + 2[H] \rightarrow CH_3CH_2CH(OH)CH_3$ 

Making T	hinking Visible	
Question:	How do you condensation?	know when a reaction is substitution, addition, elimination or
Answer:	Substitution:	two reactants form two products by replacing one group with another
	Elimination:	one reactant form two products by removing groups from adjacent atoms
	Condensation:	two reactants form two products with one of them being a small molecule such as water or $HCl$ molecule

### Exercise

Bromopropane reacts with water as shown. What is the type of reaction?

 $CH_3CH_2CH_2Br + H_2O \rightarrow CH_3CH_2CH_2OH + HBr$ 

Type of reaction: .....

# 7 Reaction Mechanisms

# 7.1 Types of Reagents

Candidates should be able to:

- (b) interpret, and use the following terminology associated with organic reactions:
  - (vi) electrophile (Lewis acid), nucleophile (Lewis base)
- An organic reaction is usually conceptualised as follows.

organic reactant + reagent  $\rightarrow$  product(s)



Depending on their nature, the **carbon atom of the functional group** of organic molecules are attacked by different types of reagents. There are three main classes of reagents.

- Nucleophiles (Lewis bases)
  - sare electron-rich species with a lone pair of electrons which can be donated to form a new bond.
  - $\stackrel{t_{s}}{\Rightarrow}$  can be anions, e.g. OH<sup>-</sup>, CN<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or neutral molecules, e.g. NH<sub>3</sub>, H<sub>2</sub>O, RNH<sub>2</sub>, ROH.
- Electrophiles (Lewis acids)
  - are electron-poor species capable of accepting an electron pair to form a new bond.
  - $\checkmark$  can be cations, e.g. H<sup>+</sup>, Br<sup>+</sup>, Cl<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, R<sup>+</sup> or neutral molecules, e.g. H–Cl, H–Br, H–I, H<sub>2</sub>SO<sub>4</sub> (H and S atoms have  $\delta$ + charge, which render the reagent electrophilic).
- Free radicals
  - $\forall$  are species with an **unpaired** electron, e.g. •Cl, •CH<sub>3</sub> (methyl radical).
  - sare **highly reactive** species due to the presence of the unpaired electron.
- Organic molecules can undergo the following modes of attack.

nature of organic reactant	reagent (attacking species)
Organic reactant contains electron–poor centre, typically a <b>carbon bonded to an electronegative atom</b> . E.g.	
$ \begin{array}{c c} -\overset{\delta_{+}}{\overset{-}{\overset{-}}} & \overset{\delta_{-}}{\overset{-}{\overset{-}}} \\ & \overset{\delta_{+}}{\overset{-}{\overset{-}}} & \overset{\delta_{-}}{\overset{-}{\overset{-}}} \\ & \overset{-}{\overset{-}{\overset{-}}} & \overset{\delta_{-}}{\overset{-}{\overset{-}}} \end{array} $	nucleophile
Organic reactant contains electron-rich centre, typically a <b>carbon that forms pi bonds</b> . E.g. C=C, benzene	electrophile
All organic compounds which contain C–H bonds.	
<b>Note:</b> While all organic compounds can be attacked by free radicals, this type of reaction is only of importance for <b>alkanes</b> which are relatively unreactive and hence cannot be attacked by other species.	free radical

# Making Thinking Visible

Question: Since a free radical has an unpaired electron, it is electron poor. Can we consider a free radical as an electrophile?

Answer: No, an electrophile has a partial positive charge or full positive charge.

# 7.2 Types of Reaction Mechanisms

Candidates should be able to:

(g) apply (b) and (c) to the understanding of mechanisms in terms of organic structure and bonding

- The overall stoichiometric equation for an organic reaction does **not** tell us how the reaction takes place. There may be a **series of steps** in between the mixing of the reactants and the formation of the products. This series of steps is called the **reaction mechanism**. (Recall the mechanism that you have learnt in Kinetics.)
- In particular, the **mechanism for substitution and addition** reactions are classified according to the **type of attacking species** that initiates the reaction. The name of an organic mechanism typically comprises two components.

Mechanism name	=	(1) = nature of attacking species +		(2) substitution or addition
Examples		electrophilic nucleophilic free radical		addition substitution substitution

- The approach to identify the reaction mechanism involved
  - examining the **first** step to determine the nature of attacking species on the organic reactant.
  - scomparing the starting organic reactant and the final organic product to determine if the reaction is substitution or addition (ignore intermediate steps).
- Mechanism: .....



Mechanism: .....



### Exercise

State the name of the mechanism for the following reaction.



Mechanism: .....

### 7.3 Bond Fission (breaking of covalent bonds)

Candidates should be able to:

- (b) interpret, and use the following terminology associated with organic reactions:
  - (iii) homolytic and heterolytic fission
    - (iv) carbocation
  - (v) free radical, initiation, propagation, termination
- (h) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

#### Homolytic fission

- Solution Two shared electrons in the covalent bond are split **equally** between the two atoms. Products formed are **free radicals**.
- Solution Movement of electrons is depicted by **half** arrow ( ) which denotes the movement of a **single** electron from the tail to the head of the arrow.

E.g. 
$$C_{l} \xrightarrow{\frown} C_{l} \xrightarrow{\downarrow} 2C_{l} \xrightarrow{\downarrow} 2C_{l} \xrightarrow{\downarrow} H \xrightarrow{\downarrow} C_{l} \xrightarrow{\downarrow} H \xrightarrow{\downarrow} H \xrightarrow{\downarrow} C_{l} \xrightarrow{\downarrow} H \xrightarrow{\downarrow} H \xrightarrow{\downarrow} C_{l} \xrightarrow{\downarrow} H \xrightarrow{\downarrow} H \xrightarrow{\downarrow} H \xrightarrow{\downarrow} H$$

- Solution the topic, Alkanes.
- Heterolytic fission
  - Solution Two shared electrons in the bond are split **unequally** between the two atoms. One of the atoms keeps both electrons, and hence acquires a negative charge. The other atom is deficient in one electron and hence acquires a positive charge.
  - Solution Movement of electrons is depicted by **full** arrow ( ) which denotes the shift of a **pair** of electrons from the tail to the head of the arrow.

E.g.



In ion (I), the positive charge is on the carbon atom. Such ions are known as carbocations or carbonium ions.

E.g.



In ion (II), the negative charge is on the carbon atom. Such ions are known as carbanions.

# • Movement of electrons in reaction mechanisms

- ✤ For mechanisms involving electrophiles and nucleophiles, the flow of electrons is from electron-rich to electron-poor sites.
- E.g. Electrophile, Cl<sup>+</sup>, in electrophilic substitution of benzene



E.g. Nucleophile, OH<sup>-</sup>, in nucleophilic substitution of halogenoalkane



transition state

# Making Thinking Visible

Question: Can Cl-Cl undergo heterolytic cleavage? Answer: Yes. When  $Cl_2$  reacts with an alkene, it undergoes heterolytic cleavage.

Question: Can HC*l* undergo homolytic cleavage? Answer: Yes.

Question: How would I know if a bond can undergo homolytic or heterolytic cleavage? Answer: If the right amount of energy is supplied for heterolytic cleavage, then the bond will not undergo homolytic cleavage and vice versa.

Homework: You are ready to attempt Qn 4 to 6 of tutorial

# 8 Factors Affecting Reactivity of Organic Compounds

# Candidates should be able to:

(c) interpret, and use the following terminology associated with organic reactivities:

- (i) delocalisation
- (ii) electronic effect (electron-donating and electron-withdrawing effect)
- (iii) steric effect (steric hindrance)

# • Delocalisation of pi electrons (resonance effect)

In molecules with alternate double and single bonds, it is possible for three or more adjacent p orbitals to overlap with one another. This allows the pi electrons to move over a greater region in space, i.e. the pi electrons are delocalised, and results in extra stability as more resonance structures exist. E.g. benzene



- Electronic effect (electron-donating and electron-withdrawing inductive effect)
  - \$ In a polar bond formed between atoms of **different electronegativities**, the more electronegative atom pulls the pair of electrons in the covalent bond towards itself and acquires a  $\delta$  charge. This, in turn, will **induce** a shift of electrons in the **neighbouring bonds**.

- Solution of the arrow represents the movement of electrons and Cl is said to exert an **electron–withdrawing inductive effect**.
- In general, any atom or group which attracts electrons more strongly than hydrogen is said to have an electron-withdrawing or negative inductive effect (-I) while any atom or group which attracts electrons less strongly than hydrogen is said to have an electron-donating or positive inductive effect (+I).



by The stability of a charged system is increased by the dispersal of the charge.

	G: electron-donating group	G: electron-withdrawing group			
cation	$\begin{array}{c} \text{Charge is dispersed} \\ \Rightarrow \text{ cation is} \\ \text{ stabilised} \end{array} \qquad $	Charge is intensified $\Rightarrow$ cation isdestabilised			
anion	$G \rightarrow C \qquad \bigcirc 0^{-}$ Charge is intensified $\Rightarrow$ anion is <b>destabilised</b>	$G \leftarrow C \longrightarrow O^{-}$ Charge is dispersed $\Rightarrow$ anion is stabilised			

- Strength of inductive effect **increases with increasing number** of groups present and **decreases with increasing distance** between the group and the charge.
- E.g. Electron-donating inductive effect of alkyl group disperses positive charge of carbocation, thus stabilising it.

As **more alkyl groups** are attached to C with positive charge, strength of inductive effect increases and charge is dispersed to a greater extent. Hence, **carbocation becomes more stable**.



E.g. Electron-withdrawing inductive effect of -Cl disperses negative charge of carboxylate ion, thus stabilising it.

As **C***l* atom gets nearer to the negative charge, strength of inductive effect increases and charge is dispersed to a greater extent. Hence, **carboxylate ion becomes more stable**.





### Making Thinking Visible

Question: With reference to the above example, arrange  $CH_2ClCH_2CH_2CO_2H$ ,  $CH_3CHClCH_2CO_2H$  and  $CH_3CH_2CHClCO_2H$  in increasing  $K_a$  value.

Answer: Increasing  $K_a$  value: CH<sub>2</sub>C/CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H < CH<sub>3</sub>CHC/CH<sub>2</sub>CO<sub>2</sub>H < CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H The more stable the anion, the stronger is the acid, the greater the  $K_a$  value (or smaller the p $K_a$  value).

### • Steric effect (steric hindrance)

This refers to the **steric hindrance** which occurs when **large groups** on a molecule 'get in the way' and thus hinder the reaction.

E.g. 2,6-dimethylbenzoic acid is resistant to normal methods of esterification because of the steric hindrance of the adjacent methyl groups which hinders the reaction of –CO<sub>2</sub>H group.



Homework: You are ready to attempt Qn 7 & 8 of tutorial

# Making Thinking Visible

 Question:
 Is steric effect a form of inter-electronic repulsion?

 Answer:
 Yes.

 Question:
 Can you summarise the four important ways in which a charge (positive or negative) can be dispersed or intensified?

 Answer:
 Electron-donating inductive effect:
 disperse positive charge but intensify negative charge

 Electron-withdrawing inductive effect:
 intensify positive charge but disperse negative charge

### Exercise

For each of the following sets, consider inductive effects exerted by relevant groups and hence arrange the ions in order of increasing stability.

(i)  $CH_{3}O^{-}$   $CH_{3}CH_{2}O^{-}$   $CH_{3}CH_{2}O^{-}$ (ii)  $CH_{3}CH(NO_{2})CH_{2}O^{-}$   $CH_{3}CH_{2}CH(NO_{2})O^{-}$   $CH_{2}(NO_{2})CH_{2}CH_{2}O^{-}$ 

### Additional Exercises: Check your answers on SLS

1 Auremycin is a powerful antibiotic. The structural formula of a derivative of auremycin is shown below.



Name the functional groups numbered 1 to 3.

2 A chemist carried out a series of reactions on compound X to produce compound Y.



Which functional groups in compound **X** have taken part in the series of reactions to give the corresponding new functional groups in compound **Y**?

(For this question, there may be one or more correct options.)

- A aldehyde  $\rightarrow$  phenol
- **C** nitrile  $\rightarrow$  amine

- **B** alkene  $\rightarrow$  chlorobenzene
- ${\rm \textbf{D}} \hspace{0.5cm} \text{acyl chloride} \rightarrow \text{carboxylic acid} \\$

# Summary

# (a) Classes of compounds and functional groups

Refer to table of functional groups on pages 4 and 5 of lecture notes.

# (b) Hybridisation of carbon

bond formed by carbon	type of hybridisation of C	shape and bond angle about C	examples
4 sigma bonds (all single bonds) (4 regions of electron densities)	sp³	tetrahedral, 109.5°	methane (CH <sub>4</sub> ) ethane (CH <sub>3</sub> –CH <sub>3</sub> )
3 sigma and 1 pi bonds (1 double bond present) (3 regions of electron densities)	sp²	trigonal planar, 120º	ethene (CH <sub>2</sub> =CH <sub>2</sub> ) benzene
2 sigma and 2 pi bonds (triple bond or 2 double bonds present) (2 regions of electron densities)	sp	linear, 180º	ethyne (HC≡CH) carbon dioxide (O=C=O)

### **Overlapping of orbitals**

C–C **sigma** bonds are formed from the head-on overlap of **hybrid orbitals** of the two C atoms while C–H sigma bonds are formed from the head-on overlap of hybrid orbital of C atom with 1s orbital of H atom.

Pi bonds are formed from the side-on overlap of p orbitals.

# **Drawing of orbitals**

sp<sup>3</sup> hybridisation (as illustrated by ethane):



sp<sup>2</sup> hybridisation (as illustrated by ethene):



sigma bond formation



pi bond formation



sigma and pi bonds superimposed together

sp hybridisation (as illustrated by ethyne):

H C C H

H

sigma bond formation

overlap of 2p<sub>y</sub> orbitals pi bond formation (the two pi bonds can be formed by any two of the three p orbitals)

overlap of 2p<sub>7</sub> orbitals

# (c) Reaction mechanisms

# Types of reagents (attacking species)

Electrophile (Lewis acid): An **electron-deficient** species that **accepts an electron pair**, e.g.  $Cl^+$ ,  $NO_2^+$ 

Nucleophile (Lewis base): An **electron-rich** species with a **lone pair of electrons**, e.g.  $OH^-$ ,  $Cl^-$ ,  $NH_3$ 

Free radical: A species that has an unpaired electron, e.g. Clo, oNO2

### Types of mechanisms

	(1)		(2)
Mechanism	= nature of attacking species	+	substitution or addition
name	(electrophilic, nucleophilic or		
	free radical)		

### Approach for recognising mechanisms

Examine <u>first</u> step to determine nature of species attacking organic reactant. **Note:** Electron–rich C=C or benzene C is usually attacked by electrophiles and C with  $\delta$ + charge is usually attacked by nucleophiles.

Compare **starting organic** reactant and **final organic** product to determine whether reaction is substitution or addition. (Ignore intermediate steps.)

Substitution: An atom or group of atoms **replaces** another atom or group of atoms.

Addition: Two or more molecules combine to form a **single product**, involves **breaking of pi bonds**.

# (d) Other types of organic reactions

• Elimination reaction: Removal of atoms or groups of atoms from two adjacent atoms to form a pi bond.

• **Condensation** reaction: Two or more molecules **combine** to form a larger molecule with **elimination of a small molecule** such as water or HC*l*. In a condensation reaction, two functional groups from different molecules react with each other to form a larger molecule, and a small molecule is released as a byproduct.

E.g.  $CH_3CH_2COOH + HOCH_2CH_3 \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$ 

**Hydrolysis** reaction: It involves **reaction with water** and is usually catalysed by acids or bases. (Water molecule is broken up.)

E.g.  $CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$ 

- Oxidation reaction: It involves a gain of oxygen or loss of hydrogen in a compound.
   E.g. CH<sub>3</sub>CH<sub>2</sub>OH + 2[O] → CH<sub>3</sub>CO<sub>2</sub>H + H<sub>2</sub>O
- Reduction reaction: It involves a gain of hydrogen or loss of oxygen in a compound.
   E.g. CH<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> + 2[H] → CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub>

### (e) Factors affecting reactivity of organic compounds

### (i) Delocalisation of pi electrons (resonance effect)

The six p orbitals of the benzene carbon atoms overlap sideways with one another, causing the **pi electrons** to be **delocalised** over the whole ring and conferring **stability** on the molecule.





(ii) Electronic effect (electron-donating and electron-withdrawing inductive effect) Electron-donating groups stabilise cations while electron-withdrawing groups stabilise anions.

Strength of inductive effect increases with increasing number of groups and decreases with increasing distance from atom with the charge.

Examples:

(1) Stability of carbocations:





Alkyl group exerts **electron-donating inductive effect**, hence **disperses positive charge** and **stabilises carbocations**. **Greater number** of alkyl groups attached to C with positive charge, hence **stronger** inductive effect exerted.

(2) Stability of carboxylate ions:



-Cl exerts electron-withdrawing inductive effect, hence disperses negative charge and stabilises anions. As -Cl gets further from oxygen with negative charge, inductive effect weakens.

### (iii) Steric effect (steric hindrance)

**Steric hindrance** occurs when **large groups** on a molecule 'get in the way' and thus hinder the reaction. Steric effect refers to the effect on a molecule, a reaction, etc. due to the size of atoms or groups.