VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

INTRODUCTION TO ORGANIC CHEMISTRY

LECTURE OUTLINE

Scan here for to ask question related to the lecture

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^3 hybridisation, as in ethane molecule, sp^2 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 σ and π 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^{-1}
C–C	350
N–N	160
O–O	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

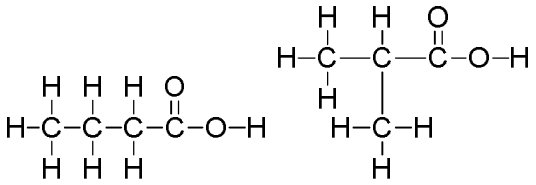
- **Empirical formula** shows the **simplest ratio** of the atoms of the different elements present in the compound. E.g. C_2H_4O

- **Molecular formula** shows the **actual number** of atoms of each element present in one molecule of the compound. E.g. $C_4H_8O_2$

- **Constitutional formula (structural formula)** shows how the constituent atoms of a molecule are **joined together**. E.g. $CH_3CH_2CH_2CO_2H$ and $(CH_3)_2CHCO_2H$ have different structural formulae but the same molecular formula of $C_4H_8O_2$.

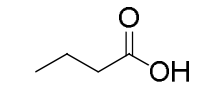
- **Displayed formula or full structural formula** is the detailed structure of a molecule showing the arrangement of the atoms and **all the bonds** between them.

  E.g.

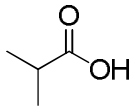


- **Skeletal formula** shows the carbon skeleton of the molecule without showing the carbon atoms and the C–H bonds and atoms in the molecule. Only the carbon–carbon bonds, bonds to functional groups and functional groups are shown.

  E.g.



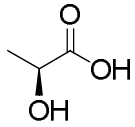
$CH_3CH_2CH_2CO_2H$



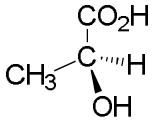
$(CH_3)_2CHCO_2H$

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

  E.g.



OR



Making Thinking Visible

Question: What are the possible types of carbon-carbon bonds?
Answer: C–C, C=C, C≡C, C═══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 $\mathbf{C_nH_{2n+2}}$.

  E.g.

molecular formula	structural formula	name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3(CH_2)_2CH_3$	butane
C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentane

- **Alkyl group** is a group of carbon and hydrogen having the general formula $\mathbf{C_nH_{2n+1}}$. 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_3–	methyl
CH_3CH_2–	ethyl
$CH_3CH_2CH_2$–	propyl

alkyl group	name
$CH_3(CH_2)_2CH_2$–	butyl
$CH_3(CH_2)_3CH_2$–	pentyl

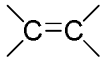
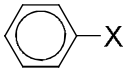
Candidates should be able to:
(b) interpret, and use the following terminology associated with organic reactions:
(i) functional group

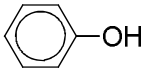
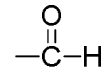
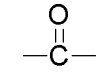
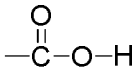
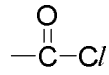
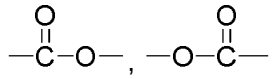
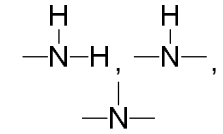
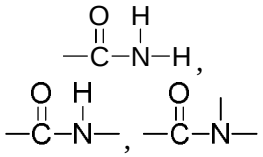
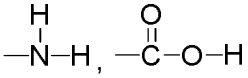
- **Functional group** consists of an element (e.g. –Br) or combination of elements (e.g. –OH, $–CO_2H$) **responsible for the chemical reactions** of an organic compound.

- **Homologous series** is a family of compounds containing the **same functional group** but differing by a common **increment of a $–CH_2–$ 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 $–CH_2–$ group).
  (iv) exhibit a **regular gradation of physical properties** (due to the increasing size of hydrocarbon chain).

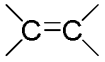
Candidates should be able to:
(a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:
(i) hydrocarbons (alkanes, alkenes and arenes)
(ii) halogen derivatives (halogenoalkanes and halogenoarenes)
(iii) hydroxyl compounds (alcohols and phenols)
(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**
hydrocarbons	***alkanes**	RH or C_nH_{2n+2}	–
	alkenes	C_nH_{2n}	
	alkynes (not in syllabus)	$C_nH_{2n–2}$	–C≡C–
	***arenes** (contain benzene ring, )	–	– (Note: The benzene ring is regarded as forming part of the hydrocarbon chain and is hence usually **not** classified as a functional group.)
halogen derivatives	halogenoalkanes	RX (X= C*l*, Br, I)	–X
	halogenoarenes	 (X= C*l*, Br, I)	–X

class / name of functional group		general formula	structure of functional group
hydroxyl compounds and derivatives	alcohols	ROH	–OH
	phenols		–OH
	ethers (not in syllabus)	ROR'	–O–
carbonyl compounds	aldehydes	*RCHO	
	ketones	RCOR'	
carboxylic acids and derivatives	carboxylic acids	*RCO_2H	
	acyl chlorides	*RCOC*l*	
	esters	**RCO_2R', R'OCOR**	
nitrogen compounds	amines	RNH_2, R_2NH, R_3N	
	amides	*$RCONH_2$, *RCONHR', *RCONR'R''	
	amino acids	$RCH(NH_2)(CO_2H)$	
	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_nH_{2n+2}.

- **Unsaturated compounds** contain **multiple bonds** in their molecules, e.g.  in alkenes,  in aldehydes and ketones and –C≡N in nitriles.

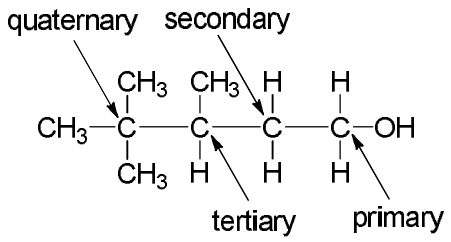
- **Presence of one pi bond decreases number of H atoms by two.** E.g. C_nH_{2n} contains one double bond, C_nH_{2n-2} contains two double bonds or one triple bond.

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**

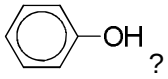
(i) A primary carbon is attached to one other carbon atom.
(ii) A secondary carbon is attached to two other carbon atoms.
(iii) A tertiary carbon is attached to three other carbon atoms.
(iv) A quaternary carbon is attached to four other carbon atoms.

E.g.



Making Thinking Visible

Question: What is the shape about the carbon atom in these functional groups: RCHO, RCOR', RCO_2H, RCOC*l* and RCO_2R'?
Answer: Trigonal planar

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

?
Answer: Bent

Question: What is the shape about the nitrogen atom in these functional groups: RNH_2, R_2NH and R_3N?
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) $CH_3CH{=}CHCH_2CHO$

(b) $HO_2CCH_2CO(CH_2)_2NH_2$

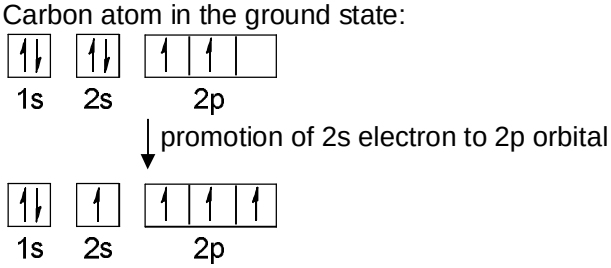
(c) $CH_2ClCH_2OCOCH_2OH$

(d) $CH_3CO_2C_2H_5$

4 Hybridisation

- Electronic configuration of C: $1s^2 2s^2 2p^2$

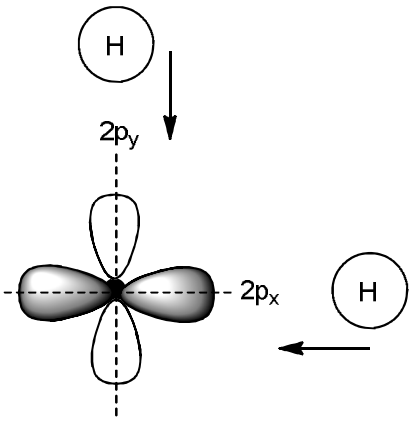
Carbon atom in the ground state:



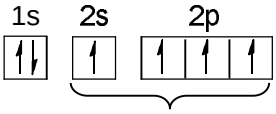
Carbon atom in the excited or bonding state is capable of forming four bonds.

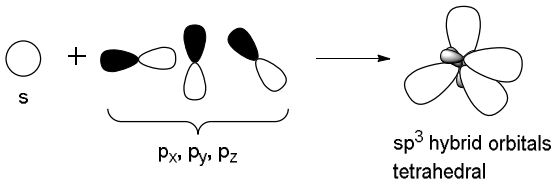
- However, if carbon were to use its 2s and 2p orbitals for bond formation, many structural features of carbon compounds cannot be accounted for. For example, in CH_4, the bond angle would be 90° instead of the actual value of 109.5° and the four C–H bonds would not be identical which contradicts reality. [Diagram omits 2s and $2p_z$ orbitals of carbon for simplicity.]

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



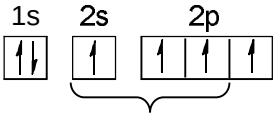
- **sp^3 hybridisation** (4 regions of electron densities)

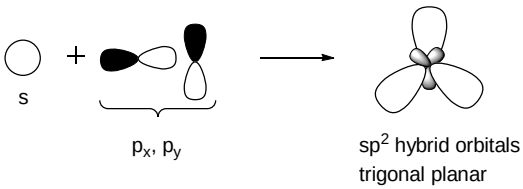




Four orbitals of carbon (2s, $2p_x$, $2p_y$, $2p_z$) are 'mixed' to form **four equivalent sp^3 hybrid orbitals** which are **tetrahedral and at 109.5° to one another**. The carbon atom forms 4 sigma bonds (all single bonds) with other atoms. Each sp^3 hybrid orbital contains ¼ s and ¾ p character.

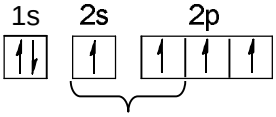
- **sp^2 hybridisation** (3 regions of electron densities)

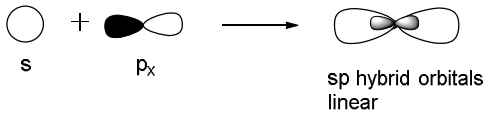




Three orbitals of carbon (2s, $2p_x$, $2p_y$) are 'mixed' to form **three equivalent sp^2 hybrid orbitals** which are **trigonal planar and at 120° to one another**. One $2p_z$ orbital of carbon remains unchanged. The carbon atom forms 3 sigma and 1 pi bonds (1 double bond present) with other atoms. Each sp^2 hybrid orbital contains ⅓ s and ⅔ 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). Each sp hybrid orbital contains ½ s and ½ p character.

- Each sp, sp^2 or sp^3 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^3: 25% s character, 75% p character
  sp^2: 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^3–sp^3	154
sp^3–sp^2	150
sp^3–sp	146
sp^2–sp^2	147
sp^2–sp	143
sp–sp	137

Making Thinking Visible

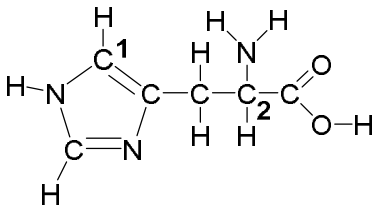
Question: Rank the following bonds in increasing bond energy:
sp^3–sp^3 sp^3–sp^2 sp^3–sp
Answer: Bond energy: sp^3–sp^3 < sp^3–sp^2 < sp^3–sp, i.e. the greater the s character in the hybrid orbital, the stronger is the bond, the shorter is the bond length and the more endothermic is the bond energy.

Exercise
Histidine is an amino acid.
What are the hybrid orbitals at C**1** and C**2**?

C**1**: ……

C**2**: ……

histidine

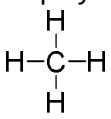


5 Shapes of Organic Molecules

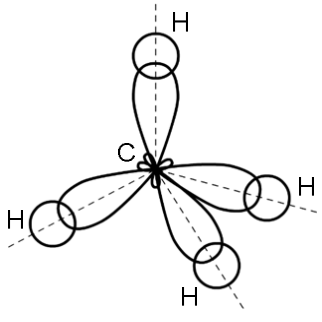
Candidates should be able to:
(d) describe sp^3 hybridisation, as in ethane molecule, sp^2 hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule
(e) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds
(f) predict the shapes of, and bond angles in, molecules analogous to those specified in (e)

- Methane, CH_4

  Displayed formula:



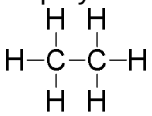
  Carbon atom in CH_4 forms four sigma bonds.
  ↳ Number of hybrid orbitals: 4

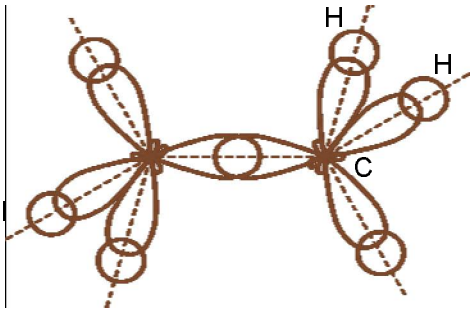


- Type of hybridisation: sp^3
- Shape: tetrahedral around carbon atom, bond angle = 109.5°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of **sp^3 hybrid orbital of C with 1s orbital of H**

- Ethane, C_2H_6

Displayed formula:



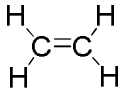


Each carbon atom in C_2H_6 forms four sigma bonds.

- Number of hybrid orbitals: 4
- Type of hybridisation: sp^3
- 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^3 hybrid orbital of C with 1s orbital of H** and the C–C bond is formed by the head-on overlap of **sp^3 hybrid orbital of each C**

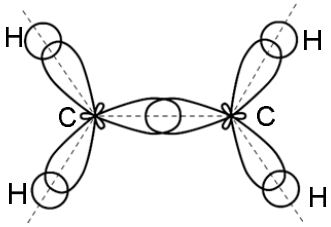
- Ethene, C_2H_4

Displayed formula:

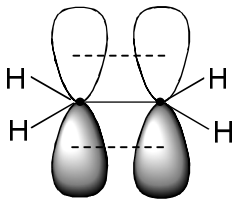


Each carbon atom in C_2H_4 forms three sigma and one pi bonds.

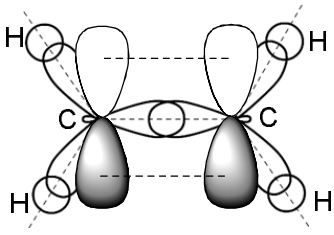
- Number of hybrid orbitals: 3
- Number of p orbitals: 1
- Type of hybridisation: sp^2
- Shape: trigonal planar around each carbon atom, bond angle = 120°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of **sp^2 hybrid orbital of C with 1s orbital of H** and the C–C bond is formed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



sigma bond formation



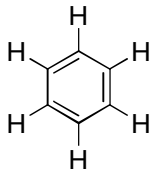
pi bond formation



sigma and pi bonds superimposed together

- Benzene, C_6H_6

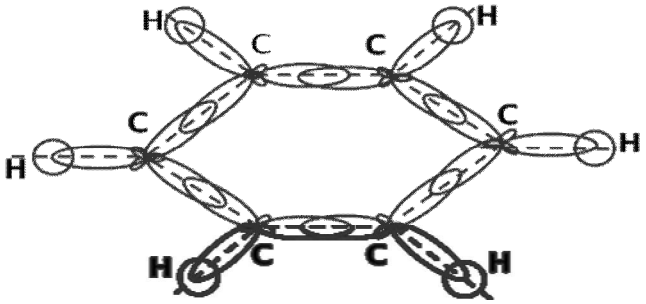
Kekule structure:



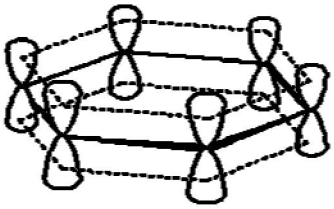
Note: Kekule structure does **NOT** represent the actual structure of benzene.

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

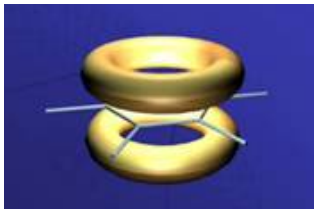
- Number of hybrid orbitals: 3
- Number of p orbitals: 1
- Type of hybridisation: sp^2
- Shape: trigonal planar around each carbon atom, bond angle = 120^o
  Hence, benzene has a **planar** structure in which the six carbon atoms are bonded in a **regular hexagonal ring**.
- Sigma bond formation: each C–H bond is formed by the head-on overlap of **sp^2 hybrid orbital of C with 1s orbital of H** and the C–C bond is formed by the head-on overlap of **sp^2 hybrid orbital of each C**
- Pi bond formation: carbon–carbon pi bond is formed by the side-on overlap of **$2p_z$ orbital** of each C with the adjacent **$2p_z$ 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**.



sigma bond formation



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.

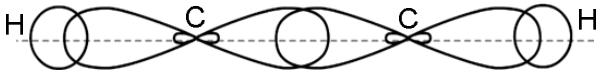
(iii) Structure of benzene is more accurately presented as  where the circle represents the delocalisation of six pi electrons.

- Ethyne, C_2H_2

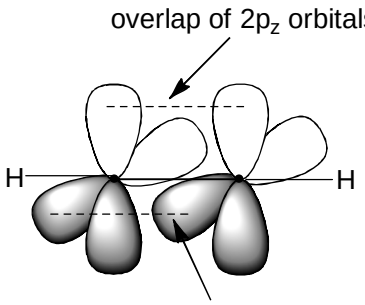
Displayed formula: H–C≡C–H

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

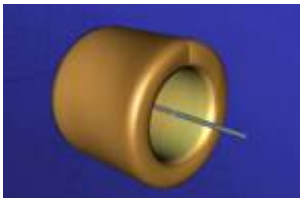
- Number of hybrid orbitals: 2
- Number of p orbitals: 2
- Type of hybridisation: sp
- Shape: linear around each carbon atom, bond angle = 180°
- Sigma bond formation: each C–H bond is formed by the head-on overlap of **sp hybrid orbital of C with 1s orbital of H** and the C–C bond is formed by the head-on overlap of **sp hybrid orbital of each C**
- Pi bond formation: one carbon–carbon pi bond is formed by the side-on overlap of **$2p_y$ orbital** of each C **laterally** and the other carbon–carbon pi bond is formed by the side-on overlap of **$2p_z$ orbital** of each C **laterally**
  Pi electron cloud forms a cylindrical sheath around the axis joining the carbon atoms.



sigma bond formation



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^3, sp^2 and sp.
Answer: sp^3: **4 regions** of electron densities and **tetrahedral** in electron pair geometry
sp^2: **3 regions** of electron densities and **trigonal planar** in electron pair geometry
sp: **2 regions** of electron densities and **linear** in electron pair geometry

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]

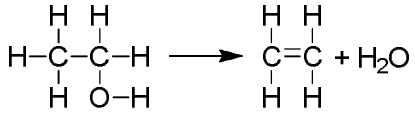
- **Addition** reaction: Two or more molecules combine to form a **single** product. Usually occurs in unsaturated compound where the multiple bond is broken to form a saturated compound.

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

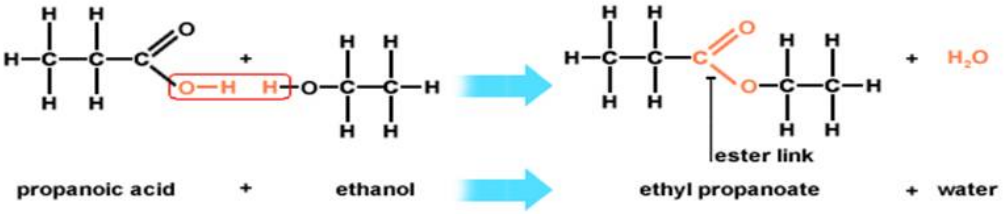
- **Substitution** reaction: An atom or group of atoms **replaces** another atom or group of atoms.

  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. 

- **Condensation** reaction: Two or more molecules or functional groups **combine** to form another molecule, together with the **loss of a small molecule** such as H_2O or HCl.

  E.g. 

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

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

- **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 Thinking Visible		
Question:	How do you know when a reaction is substitution, addition, elimination or condensation?	
Answer:	Substitution:	two reactants form two products by replacing one group with another
	Addition:	two reactants form one product only
	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: ……

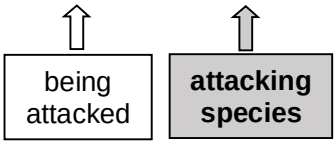
7 Reaction Mechanisms

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 → product(s)

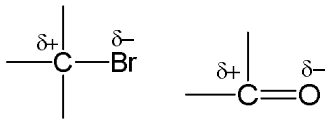
  Depending on their nature, the **carbon atom of the functional group** of organic molecules are attacked by different types of reagents. There are three main classes of reagents.

- **Nucleophiles (Lewis bases)**
  - are **electron-rich** species with a **lone pair of electrons** which can be **donated** to form a new bond.
  - can be anions, e.g. OH^-, CN^-, Cl^-, Br^-, I^- or neutral molecules, e.g. NH_3, H_2O, RNH_2, ROH.

- **Electrophiles (Lewis acids)**
  - are **electron-poor** species capable of **accepting an electron pair** to form a new bond.
  - can be cations, e.g. H^+, Br^+, Cl^+, NO_2^+, R^+ or neutral molecules, e.g. H–Cl, H–Br, H–I, H_2SO_4 (H and S atoms have $\delta+$ charge, which render the reagent electrophilic).

- **Free radicals**
  - are species with an **unpaired** electron, e.g. •Cl, $•CH_3$ (methyl radical).
  - are **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 **carbon bonded to an electronegative atom**. E.g. 	nucleophile
Organic reactant contains electron–rich centre, typically a **carbon that forms pi bonds**. E.g. C=C, benzene	electrophile
All organic compounds which contain C–H bonds. **Note:** While all organic compounds can be attacked by free radicals, this type of reaction is only of importance for **alkanes** 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.)

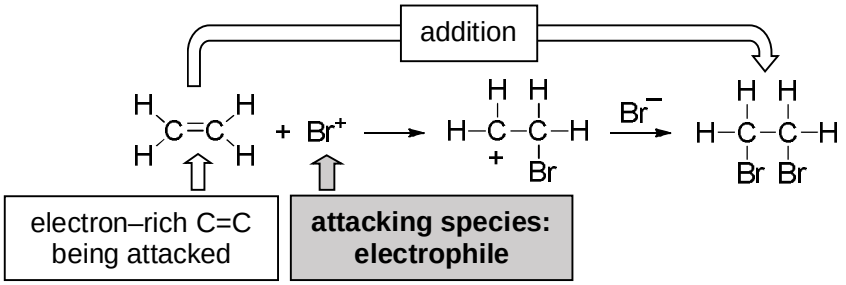
- In particular, the **mechanism for substitution and addition** reactions are classified according to the type of attacking species that initiates the reaction. The name of an organic mechanism typically comprises two components.

		(1)		(2)
Mechanism name	=	nature of attacking species	+	substitution or addition

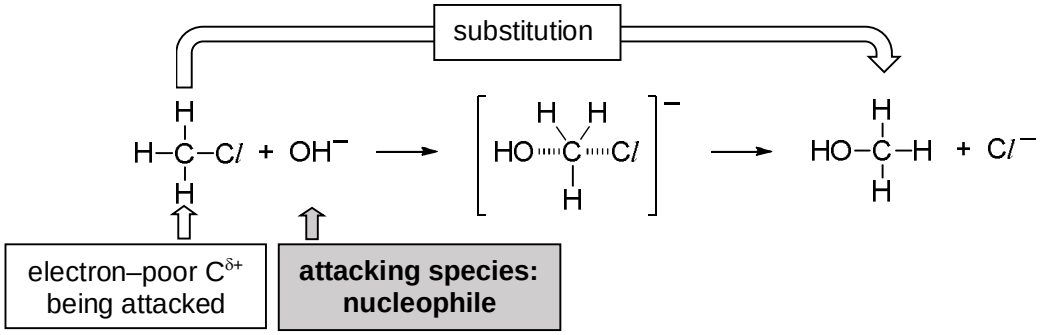
Examples		
	electrophilic	addition
	nucleophilic	substitution
	free radical	substitution

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

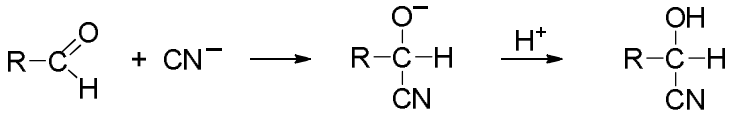
- Mechanism: ……



- Mechanism: ……



Exercise
State the name of the mechanism for the following reaction.



Mechanism: ……

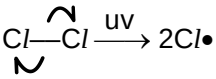
7.3 Bond Fission (breaking of covalent bonds)

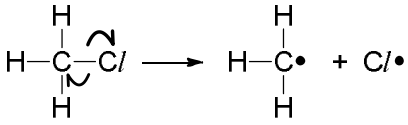
Candidates should be able to: (b) interpret, and use the following terminology associated with organic reactions: (iii) homolytic and heterolytic fission (iv) carbocation (v) free radical, initiation, propagation, termination (h) recognise that the mechanisms of polar reactions involve the flow of electrons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

- **Homolytic fission**

  - Two shared electrons in the covalent bond are split **equally** between the two atoms. Products formed are **free radicals**.

  - 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. 

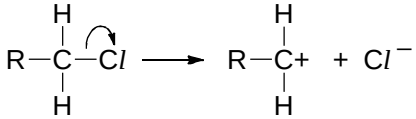
  - The free radical substitution mechanism involving the initiation, propagation and termination steps will be covered in the topic, Alkanes.

- **Heterolytic fission**

  - 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.

  - 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.

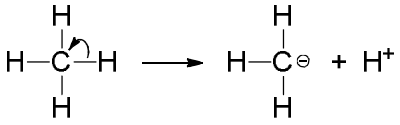
  E.g.

  (**I**)

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

  E.g.



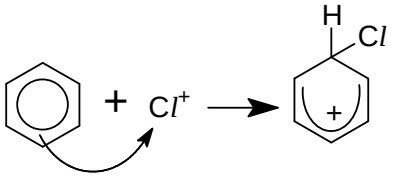
(II)

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

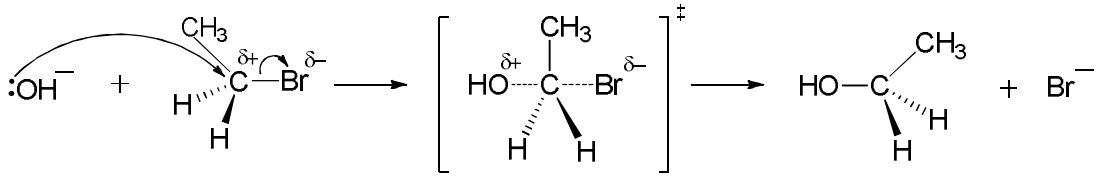
- **Movement of electrons in reaction mechanisms**

  ↳ For mechanisms involving electrophiles and nucleophiles, the flow of electrons is from electron-rich to electron-poor sites.

  E.g. Electrophile, Cl^+, in electrophilic substitution of benzene



  E.g. Nucleophile, OH^-, in nucleophilic substitution of halogenoalkane



transition state

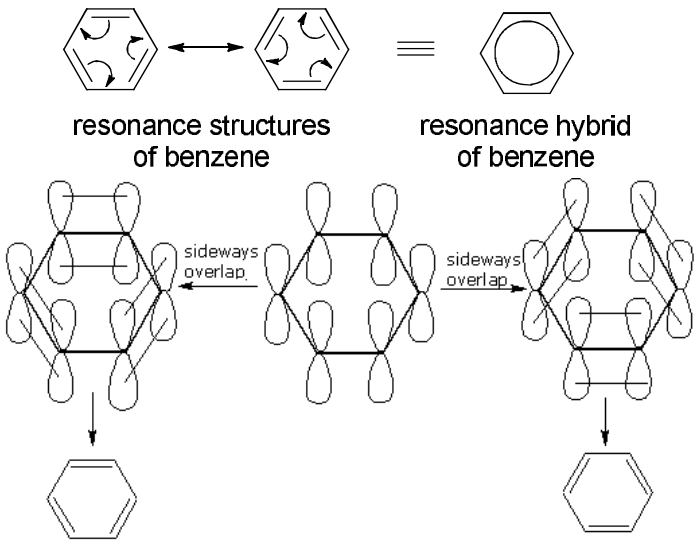
Making Thinking Visible
Question: Can C*l*–C*l* undergo heterolytic cleavage? Answer: Yes. When Cl_2 reacts with an alkene, it undergoes heterolytic cleavage.
Question: Can HC*l* undergo homolytic cleavage? Answer: Yes.
Question: How would I know if a bond can undergo homolytic or heterolytic cleavage? Answer: If the right amount of energy is supplied for heterolytic cleavage, then the bond will not undergo homolytic cleavage and vice versa.

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)

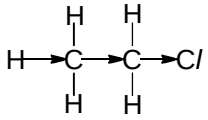
- **Delocalisation of pi electrons (resonance effect)**

  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



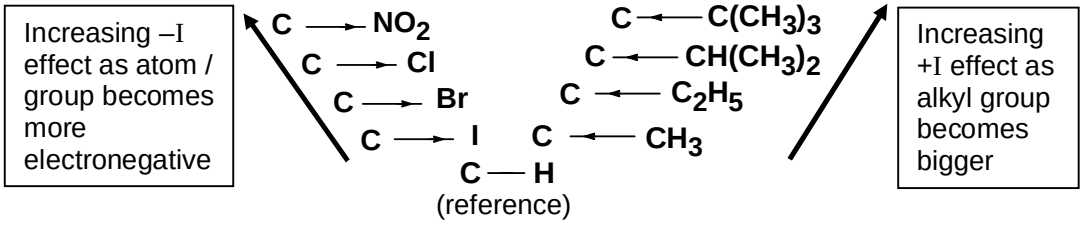
- **Electronic effect (electron–donating and electron–withdrawing inductive effect)**

  - 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 δ– charge. This, in turn, will **induce** a shift of electrons in the **neighbouring bonds**.

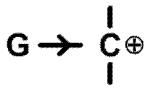
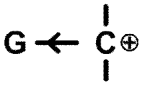
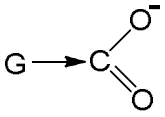
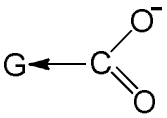
E.g. 

  - The direction of the arrow represents the movement of electrons and C*l* 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).



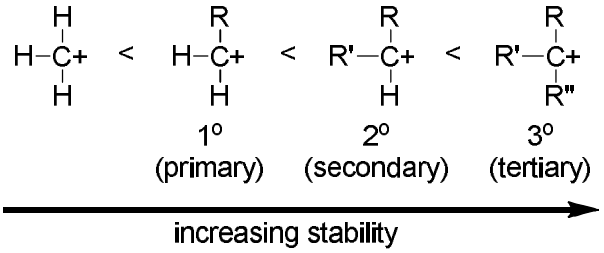
  - The **stability** of a charged system is **increased by the dispersal of the charge**.

	G: electron-donating group	**G: electron-withdrawing group**
cation	Charge is dispersed ⇒ cation is **stabilised** 	Charge is intensified ⇒ cation is **destabilised** 
anion	 Charge is intensified ⇒ anion is **destabilised**	 Charge is dispersed ⇒ 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.

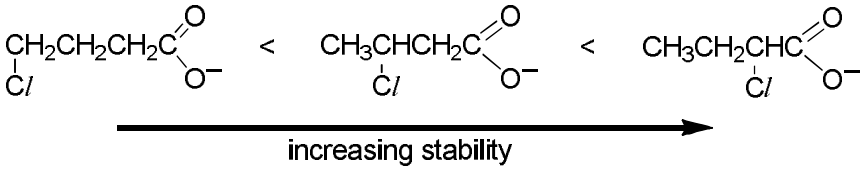
E.g. **Electron–donating** inductive effect of alkyl group **disperses positive charge** of carbocation, thus **stabilising** it.

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 –C*l* **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**.

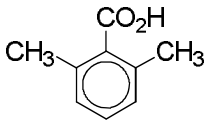


Making Thinking Visible	
Question:	With reference to the above example, arrange $CH_2ClCH_2CH_2CO_2H$, $CH_3CHClCH_2CO_2H$ and $CH_3CH_2CHClCO_2H$ in increasing K_a value.
Answer:	Increasing K_a value: $CH_2ClCH_2CH_2CO_2H < CH_3CHClCH_2CO_2H < CH_3CH_2CHClCO_2H$ The more stable the anion, the stronger is the acid, the greater the K_a value (or smaller the pK_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 $-CO_2H$ group.



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_3O^- $CH_3CH_2CH_2O^-$ $CH_3CH_2O^-$

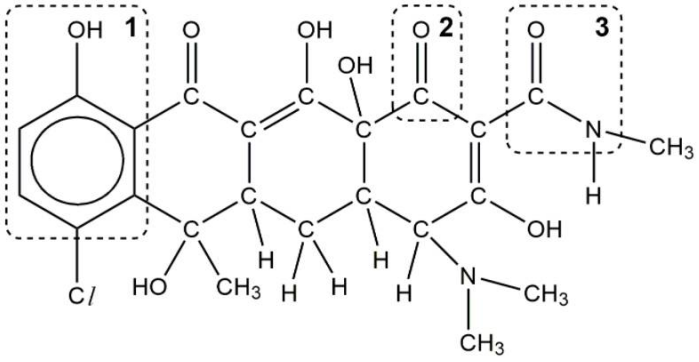
……

(ii) $CH_3CH(NO_2)CH_2O^-$ $CH_3CH_2CH(NO_2)O^-$ $CH_2(NO_2)CH_2CH_2O^-$

……

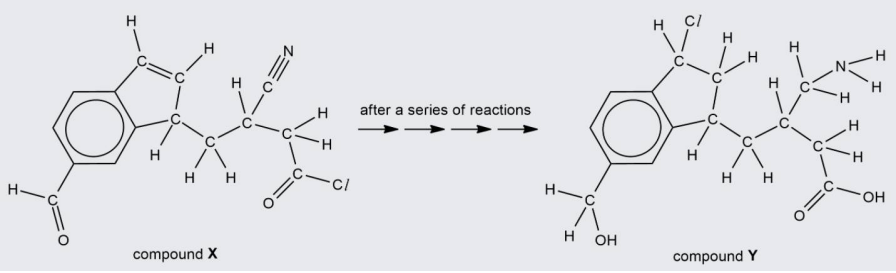
Additional Exercises: Check your answers on SLS

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 → phenol	**B**	alkene → chlorobenzene
C	nitrile → amine	**D**	acyl chloride → 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)	sp^3	tetrahedral, 109.5°	methane (CH_4) ethane (CH_3–CH_3)
3 sigma and 1 pi bonds (1 double bond present) (3 regions of electron densities)	sp^2	trigonal planar, 120°	ethene (CH_2=CH_2) benzene
2 sigma and 2 pi bonds (triple bond or 2 double bonds present) (2 regions of electron densities)	sp	linear, 180°	ethyne (HC≡CH) carbon dioxide (O=C=O)

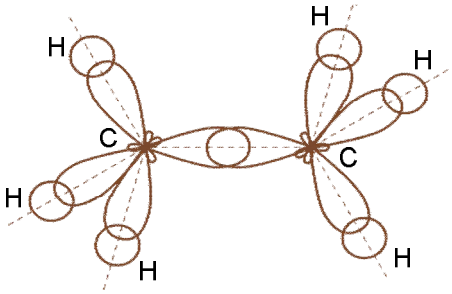
Overlapping of orbitals

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.

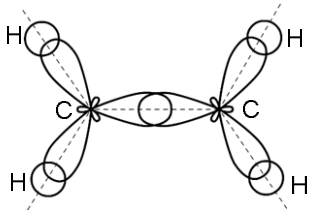
Pi bonds are formed from the side-on overlap of **p orbitals**.

Drawing of orbitals

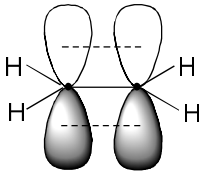
sp^3 hybridisation (as illustrated by ethane):



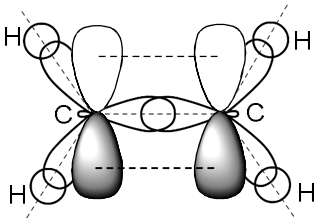
sp^2 hybridisation (as illustrated by ethene):



sigma bond formation

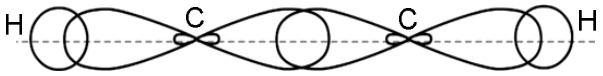


pi bond formation

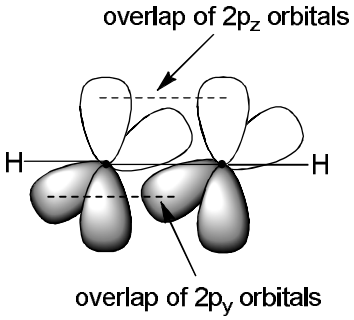


sigma and pi bonds superimposed together

sp hybridisation (as illustrated by ethyne):



sigma bond formation



pi bond formation
(the two pi bonds can be formed by any two of the three p 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. $Cl\bullet$, $\bullet NO_2$

Types of mechanisms

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

Approach for recognising mechanisms

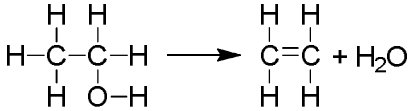
Examine first step to determine nature of species attacking organic reactant.
Note: Electron–rich C=C or benzene C is usually attacked by electrophiles and C with $\delta+$ charge is usually attacked by nucleophiles.

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**.

E.g. 

- **Condensation** reaction: Two or more molecules or functional groups **combine** to form another molecule, together with the **loss of a small molecule** such as water or HC*l*.

E.g. $CH_3CH_2CO\boxed{OH + H}OCH_2CH_3 \rightarrow CH_3CH_2COOCH_2CH_3 + H_2O$

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

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

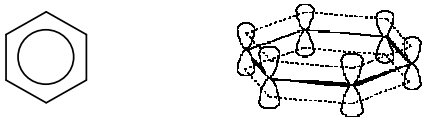
- **Oxidation** reaction: It involves a **gain of oxygen or loss of hydrogen** in a compound.
  E.g. $CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$

- **Reduction** reaction: It involves a **gain of hydrogen or loss of oxygen** in a compound.
  E.g. $CH_3CH_2COCH_3 + 2[H] \rightarrow CH_3CH_2CH(OH)CH_3$

(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.



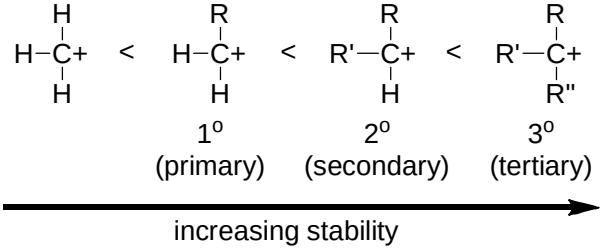
(ii) Electronic effect (electron–donating and electron–withdrawing inductive effect)

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.

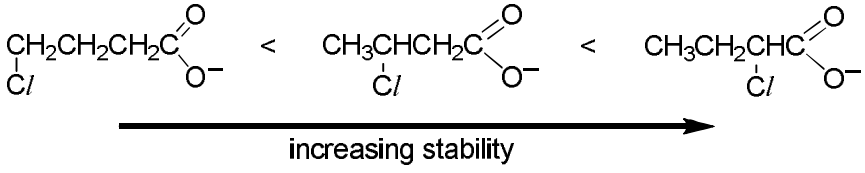
Examples:

(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:



–C*l* exerts **electron–withdrawing inductive effect**, hence **disperses negative charge** and **stabilises anions**. As –C*l* 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.

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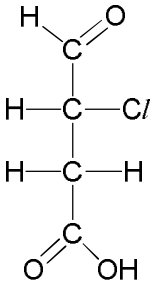
Introduction to Organic Chemistry Tutorial

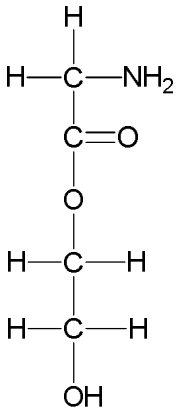
Classes of compounds

1 Circle the functional groups present in the following structural formulae and name the class of compounds to which the functional groups belong.

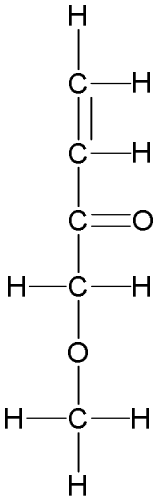
(a)



(b)



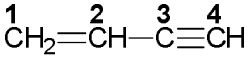
(c)



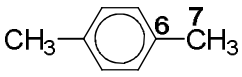
Hybridisation of carbon

2 For each of the organic molecules below, state the type of hybridisation for the numbered carbon atoms.

Hence, state whether the molecule is planar with respect to
- carbon atoms only, or
- all atoms in the molecule.

(a) 

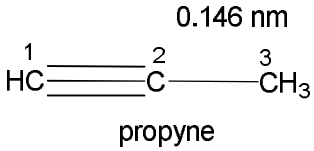
(b) 

(c) 

3 N2010 / P1 / Q19 (modified)

The bond lengths in propyne differ from those which might be expected.

The carbon–carbon bond length in ethane (CH_3CH_3) is 0.154 nm and in ethyne ($CH{\equiv}CH$) is 0.120 nm. The single C2–C3 bond in propyne, however, is shorter than the single bond in ethane: it is 0.146 nm.



propyne

What helps to explain this C2–C3 bond length in propyne?

A It has a partial sp^2–sp^2 character.
B It is an sp–sp^3 overlap.
C The sp^3–sp^3 bonding is pulled shorter by a p–p (π–bond) overlap.
D The electrons in the C3 carbon atom are attracted towards the π–bonds between C1 and C2.

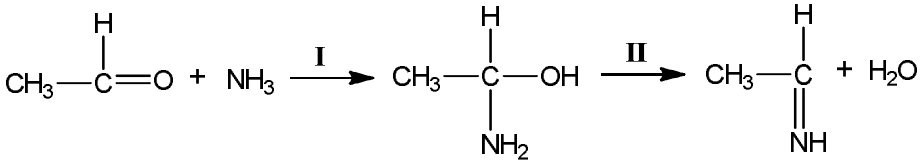
Reaction types and mechanisms

4 N2018 / P1 / Q21

Which pair of species are carbocations?

A $[CH_3CO]^+$, $[CH_3OH_2]^+$
B $[(CH_3)_3C]^+$, $[(CH_3)_4N]^+$
C $[CH_3CO]^+$, $[(CH_3)_3C]^+$
D $[(CH_3)_4N]^+$, $[CH_3OH_2]^+$

5 For the reaction sequence:

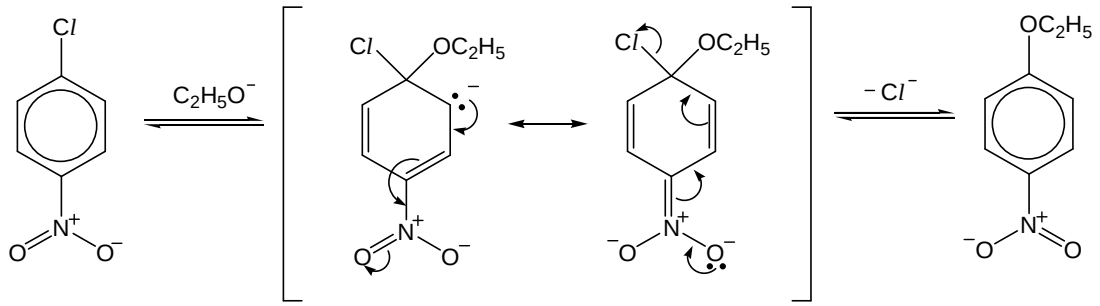


Which of the following statements are true?

1 **I** is a nucleophilic addition reaction.
2 **II** is an elimination reaction.
3 **I** and **II** constitute a condensation reaction.

A **1**, **2** and **3**
B **1** and **2** only
C **2** and **3** only
D **1** only

6 4-nitrochlorobenzene reacts with ethoxide ion via a mechanism shown below.



State the name of the mechanism.

Factors affecting reactivity of organic compounds

7 For each of the following sets, arrange the ions in ascending order of stability and explain your answer.

(a) $(CH_3)_3C^+$ $^+CH_2CH(CH_3)_2$ $CH_3CH_2\overset{+}{C}HCH_3$

(b) $CH_2BrCH_2O^-$ $CH_2ClCH_2O^-$ $CH_2ICH_2O^-$

Integrated question

8 A reactive compound called ketene was discovered by N.T.M. Wilsmore at University College, London, in 1907. He passed propanone (CH_3COCH_3) vapour over a heated platinum filament, and obtained ketene and methane (CH_4) as gaseous products.

(a) A sample of 0.080 g of ketene (contains C, H and O only) measured at 32 kPa and 30 ^oC occupies a volume of 150 cm^3. Calculate the relative molecular mass and suggest a structural formula for ketene.

(b) Ketene reacts rapidly with water and ammonia via an addition reaction. The mechanism involves water or ammonia acting as the electrophile.

Ketene + $H_2O \rightarrow CH_3CO_2H$
Ketene + $NH_3 \rightarrow CH_3CONH_2$

Predict the product of the reaction of ketene with ethanol, C_2H_5OH, and draw its displayed formula.

(c) With respect to each of the carbon atoms in ketene, state the

- type of hybridisation,
- shape, and
- number of sigma and pi bonds.

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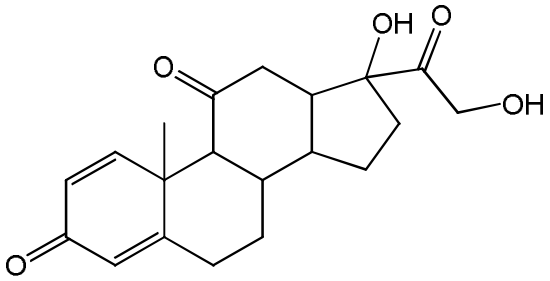
Introduction to Organic Chemistry Tutorial Supplementary Questions

Classes of compounds

1 2011 VJC H1 Prelim / P1 / Q18
Prednisone is an immune suppressant used to prevent rejection after organ transplants.



Which functional group is **not** found in the molecule?

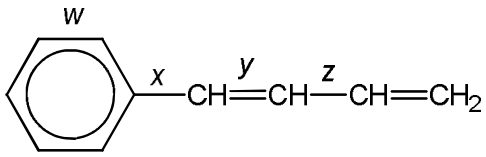
A ester **B** alkene **C** alcohol **D** ketone

2 2013 VJC H1 Prelim / P1 / Q17
A compound with a general formula $C_nH_{2n}O_2$ does **not** contain

A two carbonyl groups
B one carbonyl and one hydroxyl group
C one carboxylic acid group
D one ester group

Hybridisation of carbon

3 N2013 / P1 / Q20
Four carbon–carbon bonds are labelled in the diagram.



Which bonds are made up of an sp^2–sp^2 overlap?

A *w* and *y* only **B** *w*, *x* and *y* only
C *w*, *x*, *y* and *z* **D** *x*, *y* and *z* only

4 N2012 / P1 / Q19
Covalent bonds are formed by orbital overlap. The shape of unsaturated hydrocarbon molecules can be explained in terms of hybridisation of orbitals.

Which bond is **not** present in $HC{\equiv}CCH_2CH{=}CH_2$?

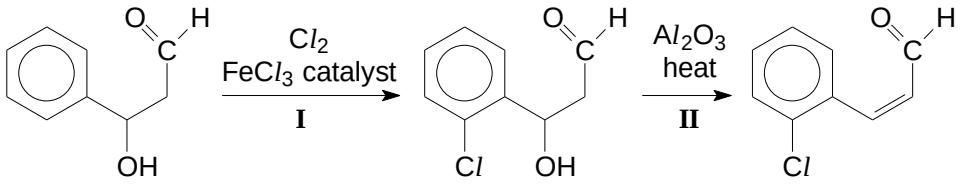
A a π bond formed by 2p–2p overlap
B a σ bond formed by 1s–2sp overlap
C a σ bond formed by 2sp–$2sp^2$ overlap
D a σ bond formed by $2sp^2$–$2sp^3$ overlap

Reaction types and mechanisms

5 **June 2004 / P1 / Q21**
Which of these always applies to a nucleophile?

A It attacks a double bond.
B It has a lone pair of electrons.
C It is a single atom.
D It is negatively charged.

6 **2013 VJC Promo (modified)**
Consider the reaction scheme shown below.



Which of the following best describes the types of reaction involved in **I** and **II**?

	I	**II**
A	substitution	reduction
B	addition	reduction
C	addition	elimination
D	substitution	elimination

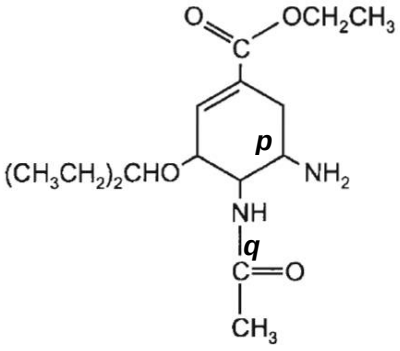
Factors affecting reactivity of organic compounds

7 By considering the number of inductive groups and their proximity, explain the relative stability of the following ions.

$CH_3CCl_2CO_2^-$ > $CH_3CHClCO_2^-$ > $ClCH_2CH_2CO_2^-$ > $CH_3CH_2CO_2^-$

Integrated question

8 *Tamiflu*® is an anti-viral drug that is used widely to treat swine flu. The structure of this drug is shown below.



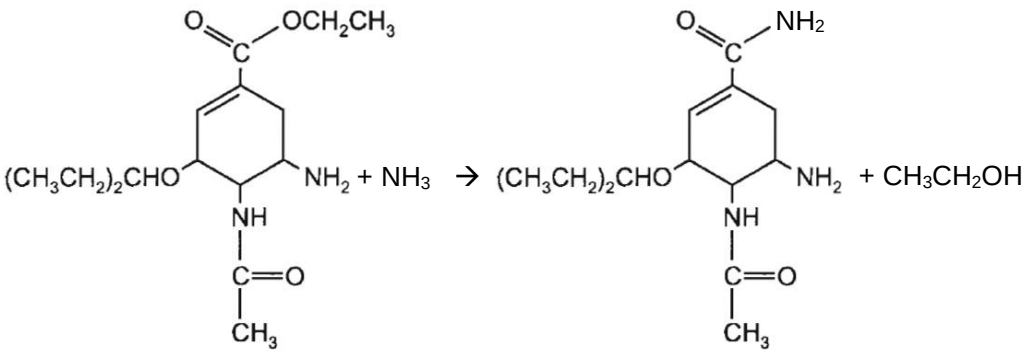
Tamiflu®

(a) Name any four functional groups present in this drug.

(b) State the hybridisation undergone by the carbon atoms labelled ***p*** and ***q***. Hence, draw the hybrid orbitals of these two carbon atoms, showing clearly the spatial arrangement of the orbitals around each carbon atom.

(c) The bond length of carbon–carbon single bond between C=O and C=C bonds in *Tamiflu*® is 0.148 nm while the carbon–carbon single bond in propanone, CH_3COCH_3 is 0.154 nm. Explain the difference in the bond length.

(d) *Tamiflu*® can react with liquid ammonia as shown.



Tamiflu®

State the name of the mechanism for the above reaction.

Answers for Supplementary Questions: (1) A (2) A (3) C (4) C (5) B (6) D