Anderson Serangoon Junior College

JC1 H2 Chemistry

ARENES

CONTENT

Learning Outcomes

Candidates should be able to:

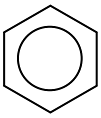
(a) explain, in terms of delocalisation of π electrons, the difference between benzene and alkene:
  (i) reactivity towards electrophiles
  (ii) preference of benzene to undergo substitution rather than addition reaction
(b) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:
  (i) electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalysts)
  (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Bronsted-Lowry acid catalyst)
  (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)
(c) (i) describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example
  (ii) describe the effect of the delocalisation of electrons in arenes in such reactions
(d) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
  (i) free-radical substitution by chlorine and by bromine
  (ii) complete oxidation to give benzoic acid
(e) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions
(f) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes.

References

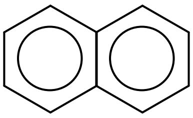
1. A-Level Chemistry by E.N. Ramsden
2. Understanding Chemistry for Advanced Level by Ted Lister and Janet Renshaw
3. Chemistry in Context by Graham Hill and John Holman

1 Introduction

Arenes, also known as aromatic hydrocarbons, are hydrocarbons which are derivatives of benzene, C_6H_6. The word 'aromatic' was initially associated with pleasant smell, but it was later accepted as structures that are stabilised by a ring of delocalised π electrons. The simplest arene is benzene itself.



Benzene



Naphthalene

2 Benzene

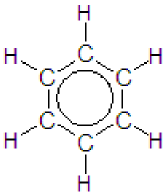
2.1 Properties

- A colourless liquid at room temperature with a characteristic smell.
- C:H ratio is 1:1.
- Burns with a smoky and luminous flame due to its high carbon content.
- Non-polar in nature hence is immiscible with water but mix with other hydrocarbons and other non-polar solvents.
- Toxic and found to carcinogenic and may harm reproductive organs.

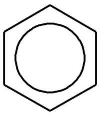
2.2 Structure of Benzene

- The benzene is a flat, symmetrical molecule with the shape of a regular hexagon. All C-C-C bond angles are 120°.
- Each carbon atom is bonded to a hydrogen atom.
- Cloud of ___________________________________ lying above and below the ring.

Displayed formula (Full)



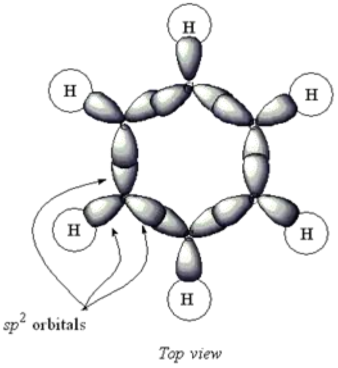
Usually represented as

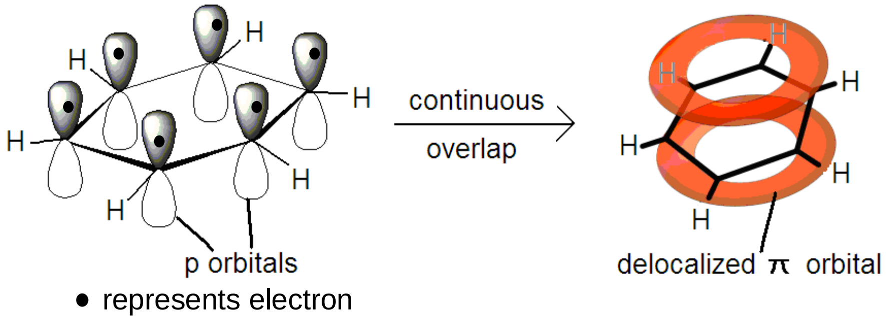


Note: the ring denotes delocalisation of electrons

- All the C–C bonds have the same length (intermediate between those expected for a C–C bond and a C=C bond)

How is the structure formed? (Molecular Orbital Model)





- Each carbon atom has three sp^2 orbitals and one p orbital.
- The three sp^2 orbitals are arranged in trigonal planar shape giving a bond angle of 120°.
- The p orbital is perpendicular to the plane of the ring and contains a single electron.
- For the formation of **σ bonds** in benzene,
  - Each C atom uses two sp^2 hybrid orbitals to ______________________________ with the sp^2 hybrid orbitals of two adjacent C atoms to form two C–C **σ bonds**
  - Each C atom also uses the remaining sp^2 hybrid orbital to **overlap head-on** with the 1s orbitals of the H atoms to form a C–H **σ bonds**.
- For the formation of **π bonds** in benzene,
  - Each unhybridised p orbital overlap equally well with both neighbouring p orbitals above and below the plane of ring, leading to a ____________________________. Hence, benzene has two doughnut-shaped clouds of electrons, one above and one below the ring.
- The six electrons in the π electron cloud are free to move throughout the system. So these electrons are said to be ***delocalised***.
- This delocalisation gives benzene its ***extra*** _________________.

Resonance in benzene

Due to the delocalisation of π electrons, benzene is said to have resonance. The concept of resonance is explained in Appendix A1 on page 19 of your lecture notes. Though you do not need to describe what resonance is, you will need to identify molecules that can exhibit resonance as it affects chemical reactivity of compounds.

What molecules can exhibit resonance?

- Resonance exists in molecules with extensive π bonding. They have more than two consecutive atoms with unhydridised p orbitals orientated in the same direction.
- A typical π bond such as in C=C in ethene is formed by the sideways overlap of the p orbitals of two carbon atoms. For molecules that show resonance, the π bonding can be across multiple consecutive atoms in the structure (e.g. across six C atoms in benzene).
- Their p orbitals merge into one large overlapping region and electrons from these orbitals spread out over the entire overlapping region (i.e. they do not belong to any one specific atom). Hence, they are **delocalised**.
- The electron density is spread out, rather than being concentrated between two atoms as in a typical C=C. This leads to stabilisation of the molecule and there are experimental evidences of such stabilisation as explained in Section 2.3.

2.3 Experimental Evidence of Resonance in Benzene

Benzene has three experimental evidence that shows resonance in benzene:

1. All carbon-carbon bonds in benzene are equal and intermediate in length between single and double carbon-carbon bonds.
2. The enthalpy change of hydrogenation of benzene is less exothermic than expected.
3. Benzene undergoes substitution reactions rather than addition reactions.

2.3.1 Carbon-carbon bond lengths

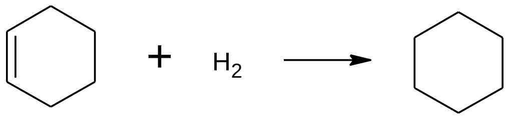
- X-ray diffraction studies show that **all the carbon-carbon bonds in benzene are ____________ and __________ in length.**

Compound	Bond	Bond length / nm
cyclohexane	C—C	0.154
cyclohexene	C═C	0.133
benzene	C$\underset{\cdots}{\text{—}}$C	0.139

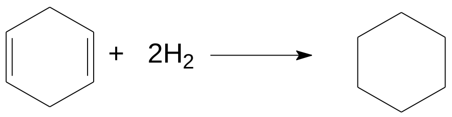
- Carbon-carbon bond in benzene have ____.

2.3.2 Enthalpy Change of Hydrogenation of Benzene

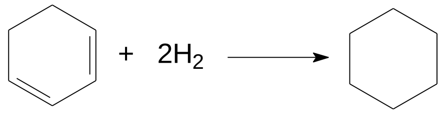
- The actual structure of benzene is ____ than what is expected of hypothetical cyclohexa-1,3,5-triene structure. This can be shown using enthalpy changes of hydrogenation.
- When hydrogen is added to cyclohexene, cyclohexane, C_6H_{12}, is formed. The enthalpy change during this reaction is –120 kJ mol^{-1}. In other words, when 1 mole of cyclohexene reacts, 120 kJ of heat energy is evolved (to saturate one C=C).



- For both cyclohexa-1,4-diene and cylcohexa-1,3-diene, you would expect the enthalpy change of hydrogenation of both C=C to be –240 kJ mol^{-1} (twice the amount of energy to saturate one C=C). While this is true for cyclohexa-1,4-diene, the enthalpy change of hydrogenation for cyclohexa-1,3-diene is less exothermic than expected (–232 kJ mol^{-1}).

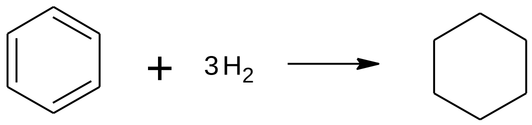


cyclohexa-1,4-diene

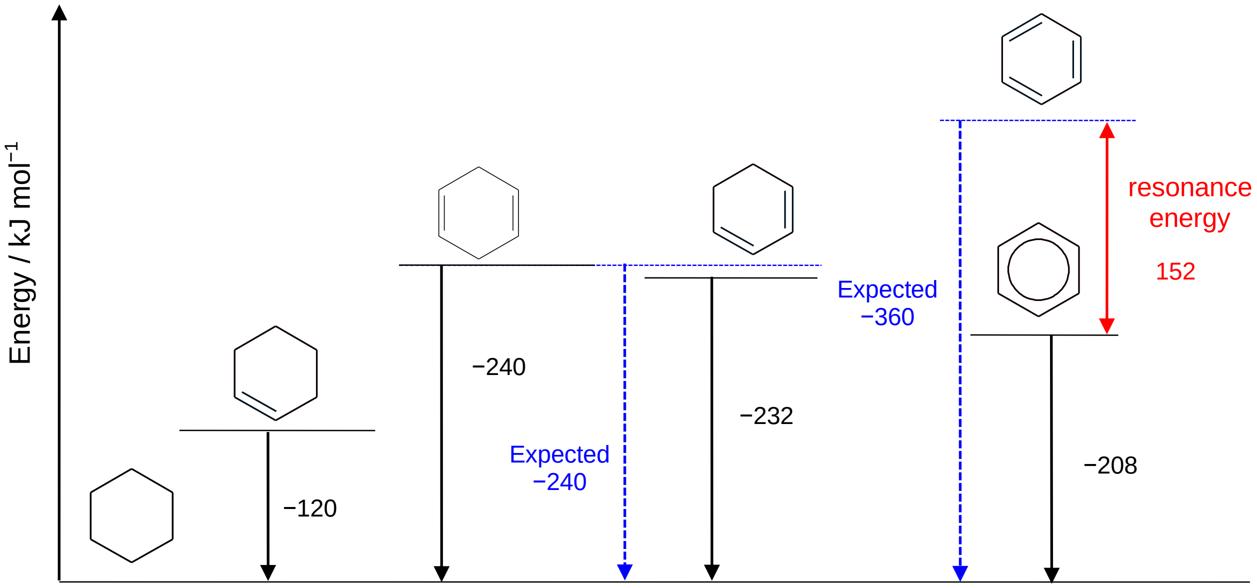


cyclohexa-1,3-diene

- For benzene, you would expect the enthalpy change of hydrogenation to be –360 kJ mol^{-1} (to saturate three C=C). However, what you get is *–208 kJ mol^{-1}*.



- This is easier to visualise on an enthalpy diagram. Notice that in each case heat energy is released, and the hydrogenation product is the same (cyclohexane).

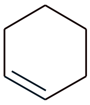
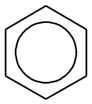


- The real benzene is about 150 kJ mol^{-1} more stable than the expected structure with three C=C. This increase in stability of benzene is known as the ______________________ or ***resonance energy*** of benzene. The first term (delocalisation energy) is more commonly used.

> FYI
> Similarly, cylcohexa-1,3-diene gives a less exothermic than expected enthalpy change due to the presence of conjugated diene (in which two carbon-carbon double bond are connected to each other by a single bond). This increased stability is the delocalisation energy.

2.3.3 Benzene undergoes Substitution rather than Addition Reactions

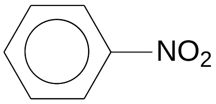
- Comparing cyclohexene and benzene, it is noted that under conditions whereby cyclohexene undergo reaction readily, benzene either react slowly or remains unreactive.

Reagent	**Compound**	
	Cyclohexene 	Benzene 
Br_2 in CCl_4 (in the dark)	Addition	No reaction
HBr(g)	Addition	No reaction
H_2(g), Ni catalyst	Reduction at high temperature	Reduction at high temperature and pressure

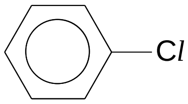
- Addition reactions on benzene will destroy the extra stability brought about by the delocalisation of the π electrons in the benzene ring, thus losing its **aromatic character**.
- Benzene undergo ______________ **reactions** under suitable conditions because such reactions retain its resonance-stabilised ring system (contributing to its aromatic character).

2.4 Nomenclature

- Monosubstituted benzene derivatives are systematically named with *-benzene* as the parent name.

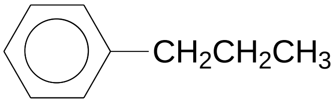


nitrobenzene

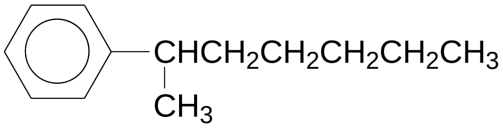


chlorobenzene

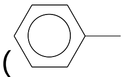
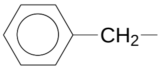
- Alkyl-substituted benzenes (arenes) are named in 2 ways depending on the size of the alkyl group. If alkyl substituent has six or fewer carbons, the arene is named as an alkyl substituted benzene. If alkyl substituent is larger than the ring (i.e. more than six carbons), the arene is named as a phenyl-substituted alkane.

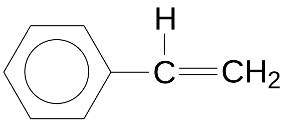


propylbenzene

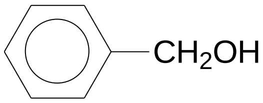


2-phenylheptane

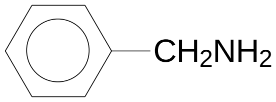
- When a benzene ring is regarded as a side chain, the C_6H_5 group () is called the phenyl group and $C_6H_5CH_2$— group () is called benzyl group.



phenylethene

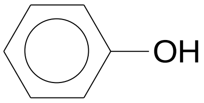


phenylmethanol
(benzylalcohol)

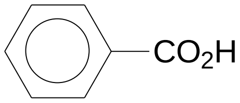


benzylamine

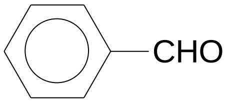
- Some groups on the benzene ring retain their traditional names.



phenol

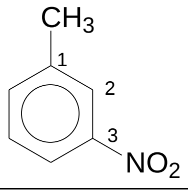


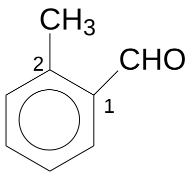
benzoic acid

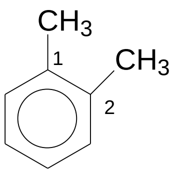


benzaldehyde

- A second group on benzenes with traditional names (e.g. phenol, methylbenzene) will be named as a substituent and its position number will be with reference from the group with traditional names. If there are more than one substituent, substituents will be listed alphabetically when writing the name of the molecule.







*You need to be able to work from the name to the correct structure.

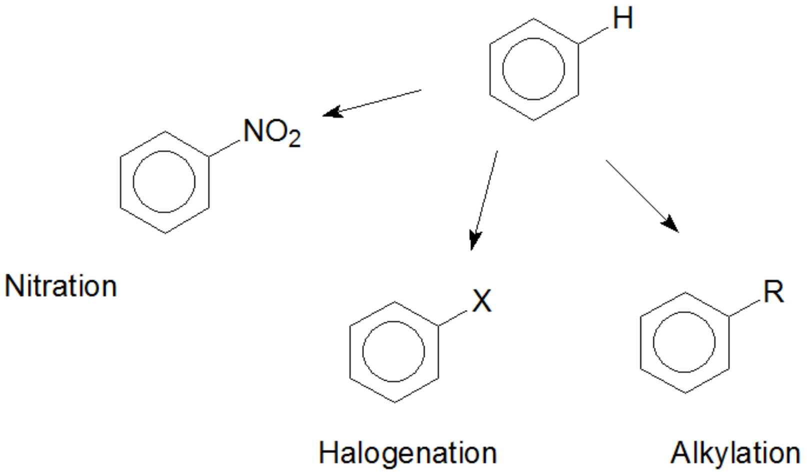
3 Reactions of Benzene

- Benzene readily undergo **substitution reactions** under suitable conditions to retain its resonance-stabilised ring system.

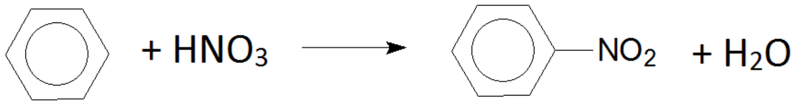
- The ***cloud of delocalised π electrons*** of the ring is a region of ***high electron density*** susceptible to attack by electrophiles.

- Hence majority of the reactions of aromatic systems are ***electrophilic substitution*** reactions. The hydrogen atom is substituted by the electrophile.

Electrophilic Substitution



3.1.1 Electrophilic Substitution - Nitration (Substitution of H atom by NO_2 group)



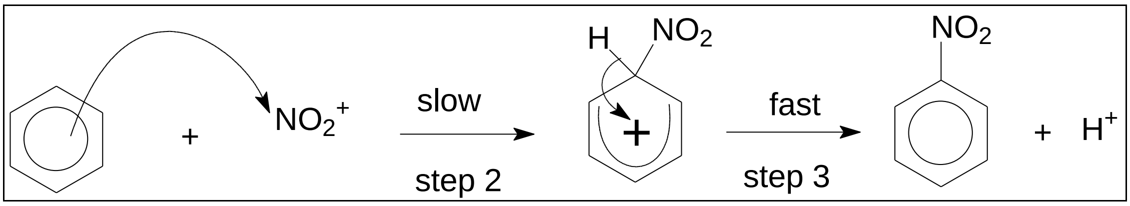
nitrobenzene (dense pale yellow liquid)

Reagent: <u>conc. HNO_3</u>
Condition: <u>conc. H_2SO_4 catalyst, heat under reflux</u>

FYI: Temperature is maintained at 55 °C (or below) to minimise further nitration to form di– or tri–nitrobenzene.

Mechanism:

Step 1: $HNO_3 + 2\,H_2SO_4 \longrightarrow NO_2^+ + 2\,HSO_4^- + H_3O^+$



Step 4: $H^+ + HSO_4^- \longrightarrow H_2SO_4$

<u>Explanation of the mechanism:</u>

Step 1: Generation of strong electrophile, NO_2^+ (nitronium ion).
This can be seen as a Bronsted-Lowry acid-base reaction. H_2SO_4 is a stronger acid and acts as the proton (H^+) donor. HNO_3 acts as a base to accept the proton to give nitronium ion, NO_2^+ and H_2O as products. Due to the acidic environment, H_2O is protonated to give H_3O^+.

Step 2: NO_2^+ is strongly attracted to the cloud of delocalised π electrons of benzene. It accepts an electron pair from the delocalised π electrons and forms a carbocation intermediate which is stabilised by delocalisation of the remaining four electrons and positive charge over the other five carbon atoms.

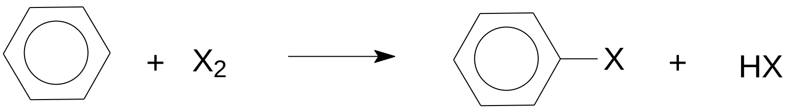
The shape of the reactive carbon atom changes from trigonal planar (sp^2 hybridised) in benzene to tetrahedral in carbocation intermediate (sp^3 hybridised) to which the NO_2 group is attached.

Step 3: The intermediate rapidly loses a proton (H^+), restoring the symmetry and stability of the benzene ring. The shape with respect to the reactive carbon atom changes back to trigonal planar (sp^2) in the product.

Step 4: Regeneration of catalyst

[FYI: Nitration of aromatic rings is important because the product nitrobenzene can be reduced to yield phenylamine. Attachment of a nitrogen atom to an aromatic ring by the two-step nitration/reduction sequence is a key part of the industrial synthesis of dyes and many pharmaceutical agents.]

3.1.2 Electrophilic Substitution – Halogenation (Substitution of H atom by X atom)



, where X = C*l*, Br

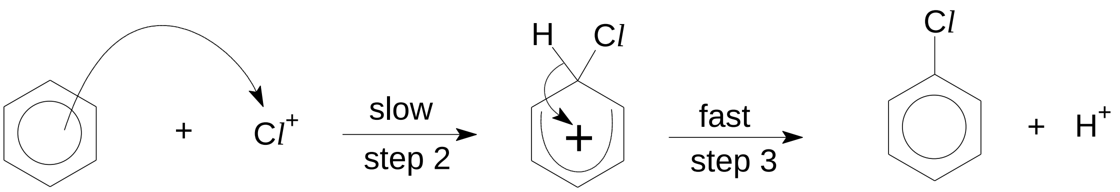
Reagent: X_2 (X = C*l* or Br)
Condition: Room temperature, anhydrous, $\mathrm{FeX_3}$ or $\mathrm{AlX_3}$ or Fe catalyst

Note:

- $\mathrm{FeCl_3}$ or $\mathrm{AlCl_3}$ is used for chlorination; and $\mathrm{FeBr_3}$ or $\mathrm{AlBr_3}$ is used for bromination.
- $\mathrm{FeX_3}$ or $\mathrm{AlX_3}$ are catalysts and are regenerated in step 4.
- Fe filings with halogen (X_2) can be used. Reaction of Fe with halogen forms the catalyst, $\mathrm{FeX_3}$ *in situ*. i.e. $2\mathrm{Fe} + 3\mathrm{X_2} \rightarrow 2\mathrm{FeX_3}$ (This equation should be written when Fe is the catalyst.)
  (*When a reactant/catalyst is produced in the reaction vessel, it is said to be made "**in situ**".)*
- Anhydrous condition is needed as $\mathrm{AlX_3}$ or $\mathrm{FeX_3}$ can undergo side reactions with water (JC 2 Topic: Periodicity - $\mathrm{AlCl_3}$ reaction with water)

Mechanism:

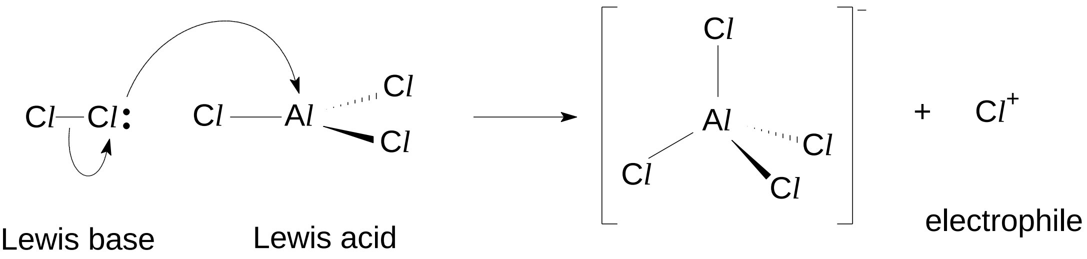
Step 1: $\mathrm{Cl_2} + \mathrm{AlCl_3} \longrightarrow \mathrm{Cl^+} + \mathrm{AlCl_4^-}$



Step 4: $\mathrm{H^+} + \mathrm{AlCl_4^-} \longrightarrow \mathrm{HCl} + \mathrm{AlCl_3}$

Note:

- Step 1 can be seen as a Lewis acid-base reaction.

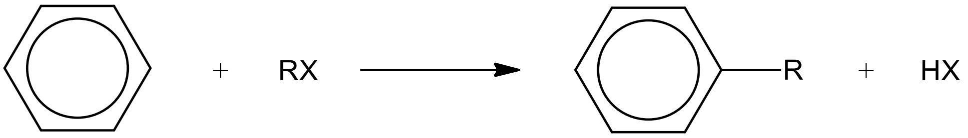


Depiction of electrons flow as shown above is for illustrative purpose and not required for mechanism unless question demands it.

- Although halogens can act as electrophiles due to their instantaneous dipoles $X^{\delta+} - X^{\delta-}$, they are not good enough electrophiles to react with benzene without the presence of a catalyst.

- Conditions for further halogenation: prolonged condition and in the presence of a higher proportion of the halogen.

3.1.3 Electrophilic Substitution (Friedel-Crafts alkylation)



, where X = Cl, Br

Reagents: RX (The R group depends on intended substituted product)
Condition: Room temperature, anhydrous, FeX_3 or AlX_3 catalyst (X = Cl or Br)

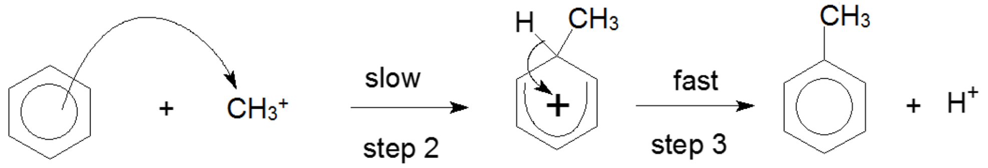
Note:

- For the RX reagent, different alkyl R group can be used. E.g. CH_3Cl, CH_3CH_2Cl
- However, the reaction **does not** occur if the RX reagent is an aryl halide or vinylic halide ($CH_2{=}CHX$).

Mechanism:

E.g. $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$
$CH_3CH_2Br + FeBr_3 \rightarrow CH_3CH_2^+ + FeBr_4^-$

Step 1: $CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$



Step 4: $H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

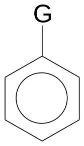
Exercise 1:

Which of the following statements about the nitration of benzene by concentrated nitric acid and concentrated sulfuric acid are correct?

1 If concentrated sulfuric acid is replaced with dilute sulfuric acid, the reaction will still proceed at the same rate.
2 The attacking electrophile is the nitronium ion, NO_2^+.
3 The shape about the carbon atom where electrophilic attack occurs is different in the intermediate and product.
4 The intermediate has 5 electrons delocalised over 6 carbon atoms.

A **1**, **2** and **3** only
B **1** and **2** only
C **2** and **3** only
D **3** and **4** only

4 Substitution of Monosubstituted Benzene Derivatives

Consider a benzene ring containing a substituent G as in .

The presence of G has **two effects** on the aromatic ring:

(1) Reactivity towards further electrophilic substitution

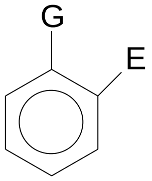
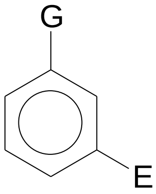
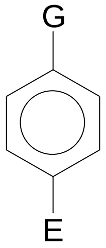
(a) Substituent G may ***release electrons*** into the benzene ring

- Increases electron density of the ring compared to an unsubstituted benzene
- Electrophiles more attracted towards the benzene ring
- Rate of electrophilic substitution is faster compared to unsubstituted benzene
- Such substituent is called an ***activating group***

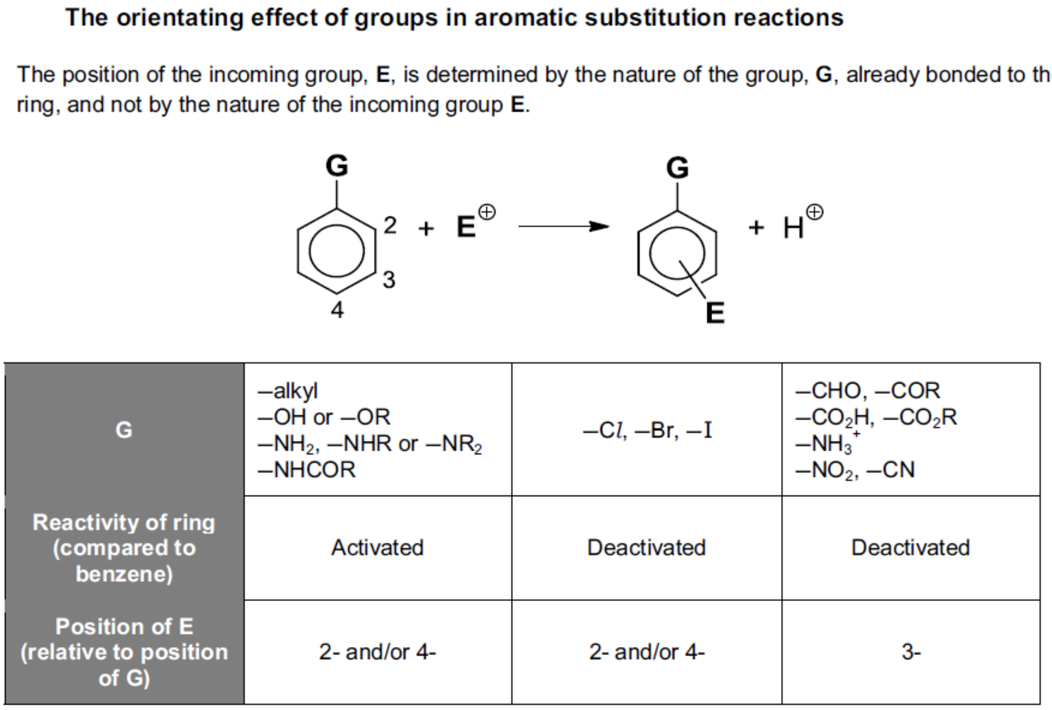
(b) Substituent G may ***withdraw electrons*** from the benzene ring

- Decreases electron density of the ring compared to unsubstituted benzene
- Electrophiles less attracted towards the benzene ring
- Rate of electrophilic substitution is slower compared to unsubstituted benzene
- Such substituent is called a ***deactivating group***

(2) Position of further substituents (such as E below) on the benzene ring

		
Electrophile E^+ attacks 2nd position (same as 6th position)	Electrophile E^+ attacks 3rd position (same as 5th position)	Electrophile E^+ attacks 4th position

- Overview of the orientating effect of substituent is found in Table 8 of *Data Booklet* as seen below.



The orientating effect of groups in aromatic substitution reactions

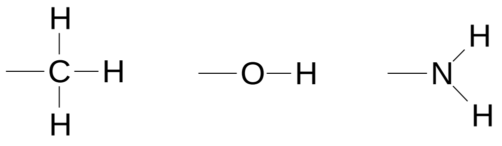
The position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.

G	–alkyl –OH or –OR $-NH_2$, –NHR or $-NR_2$ –NHCOR	–C*l*, –Br, –I	–CHO, –COR $-CO_2H$, $-CO_2R$ $-NH_3^+$ $-NO_2$, –CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

4.1 Activating and 2– and/or 4– directing substituents

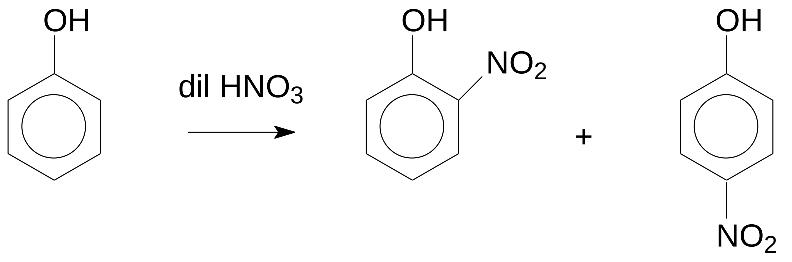
- substituents: $-CH_3$, $-OH$, $-NH_2$, $-OR$, $-NHR$, $-NR_2$

Structure of some substituents:



- they are electron-donating groups
- ***increases electron density*** in the π electron cloud of the ring and thus ***increases attraction of electrophiles***
- ***increases rate of electrophilic substitution*** of benzene ring compared to unsubstituted benzene
- direct incoming electrophile to the **2nd and 4th positions**.

E.g.



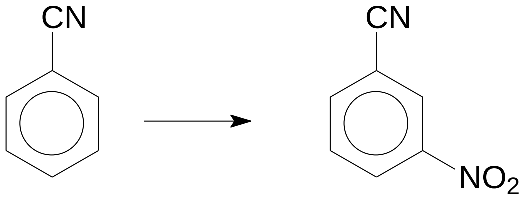
Note that milder conditions are employed than in the nitration of benzene.

4.2 Deactivating and 3– directing substituents

- substituents: $-NO_2$, –CN, −COOH, –CHO (aldehyde), $-CO_2R$ (ester), –COR (ketone)
- Structure of some substituents:

- they are electron-withdrawing groups
- ***reduces electron density*** in the π electron cloud of the ring and thus ***reduces attraction towards electrophiles***
- ***decreases rate of electrophilic substitution*** of benzene ring compared to unsubstituted benzene
- direct incoming electrophile to the **3rd position** (because deactivating substituents tend to withdraw electrons from the 2nd and 4th positions, so further substitution tends to be at the 3rd position)

E.g.



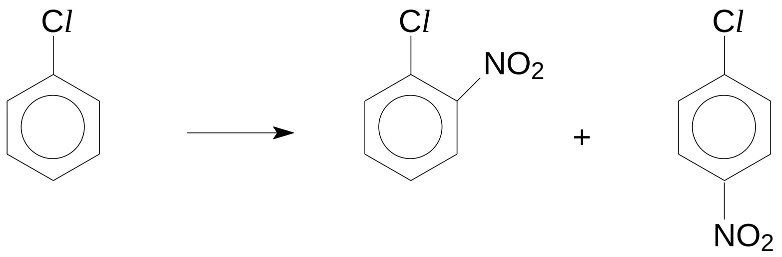
Here, would you expect milder conditions than in the nitration of benzene?

4.3 Deactivating but 2– and/or 4– directing substituents

Halogens are an exception:
They **deactivate the ring** by *electronic effect (induction)* **but** direct further substitution to the **2nd and 4th positions** due to its ability to stabilise the carbocation intermediate via *resonance effect* (delocalisation of lone pair of electrons on halogen)

[Refer to Appendix A3 for explanation on induction and resonance effect]

E.g.

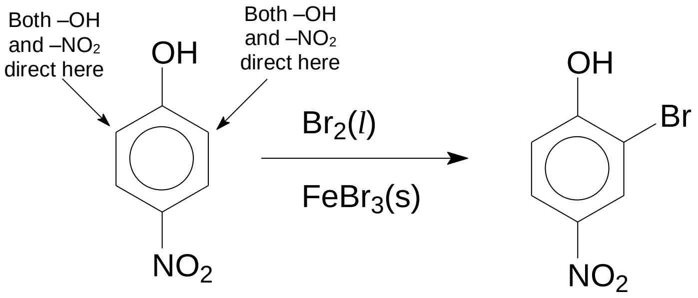
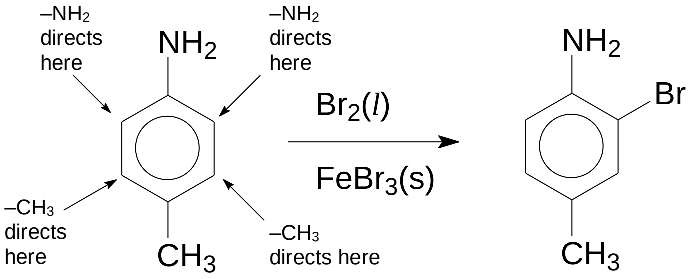


Here, would you expect milder conditions than in the nitration of benzene?

In practice, a mixture of all possible isomers is obtained, but the above 3 rules give the main products.

Self-reading (to discuss further during tutorial)

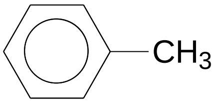
When there are more than one substituent on the ring,

If both groups are directing to the same position on the ring, that is where electrophilic substitution will occur predominantly.	
If both groups are directing to different positions, the directing effect of the **stronger activating group dominates**. –NH_2 and –CH_3 directs to different positions. The directing effect of –NH_2 dominates since it is a stronger activating group.	

5 Methylbenzene

5.1 Structure of Methylbenzene (Toluene)

Methylbenzene has an aromatic portion (the benzene ring) and an aliphatic portion (the methyl (−CH_3) group).



5.2 Reactions of Methylbenzene

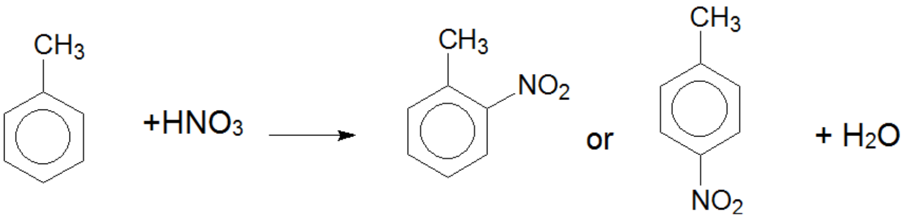
Aromatic compounds that have substituents will show the reactions of the substituents as well as those of the aromatic system.

Thus for methylbenzene there are 2 sets of reactions, involving the
- benzene ring
- methyl group (‘side chain’)

5.2.1 Reaction of the Ring

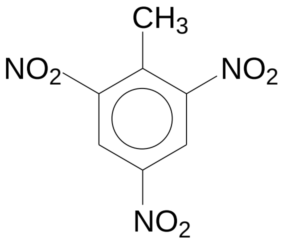
–CH_3 is an activating group and 2–, 4– and 6– directing
⇒ compared to benzene, electrophilic substitution of the ring is easier and faster

(a) Electrophilic Substitution (Nitration)



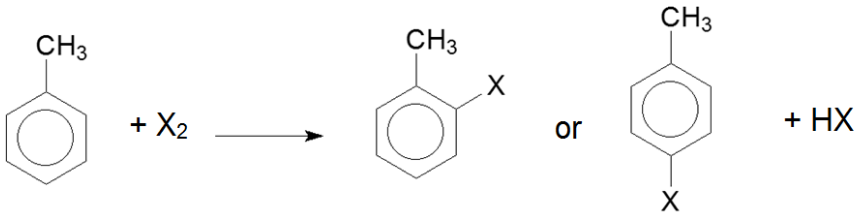
Reagents: conc. HNO_3
Condition: Heat under reflux (30 °C), conc. H_2SO_4 catalyst

Note:
- A **lower temperature** is used as compared to 55 °C for benzene mono-nitration
- A higher temperature leads to further nitration where two or three groups are introduced. E.g.



(b) Electrophilic Substitution (Halogenation)

Example:

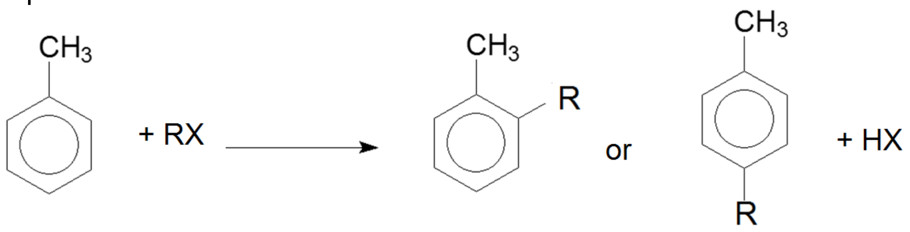


Why is it necessary to perform the reaction in the dark/absence of UV light?

Reagents: X_2 (X = Cl or Br)
Condition: Room temperature, anhydrous, in the dark/absence of UV light, FeX_3 or AlX_3 or Fe catalyst

(c) Electrophilic Substitution (Alkylation)

Example:

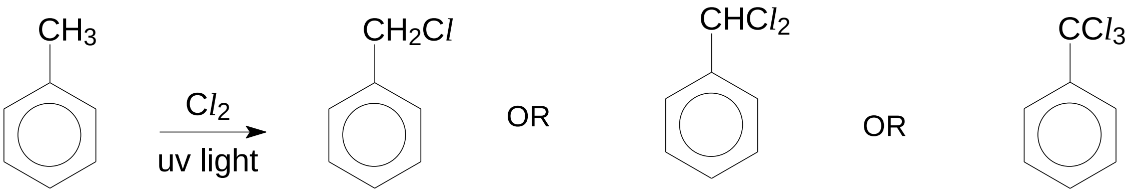


Reagents: CH_3X
Condition: Room temperature, anhydrous, FeX_3 or AlX_3 catalyst (X = Cl or Br)

5.2.2 Reaction of the Side Chain

(a) Free Radical Substitution

The $-CH_3$ group in methylbenzene shows some reactions we would expect of an alkyl group. For example, it can undergo free radical substitution like those seen in halogenation of aliphatic alkanes:



(chloromethyl)benzene (dichloromethyl)benzene (trichloromethyl)benzene

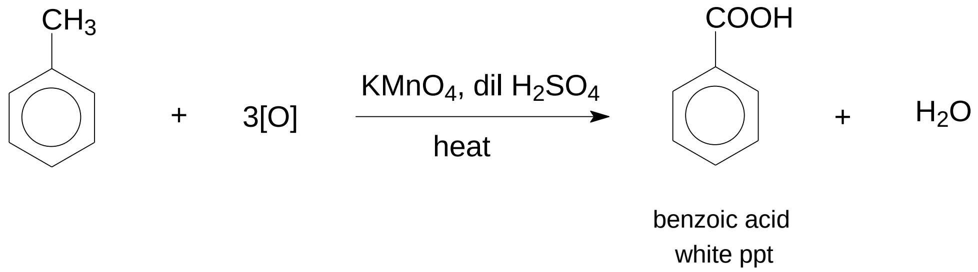
Recall: Such reactions are very difficult to control and results in many products being formed. Note the difference between *free radical substitution* in the side chain (in the presence of uv light) and *electrophilic substitution* of the aromatic ring (in the presence of a halogen carrier).

(b) Oxidation (or 'side-chain' oxidation)

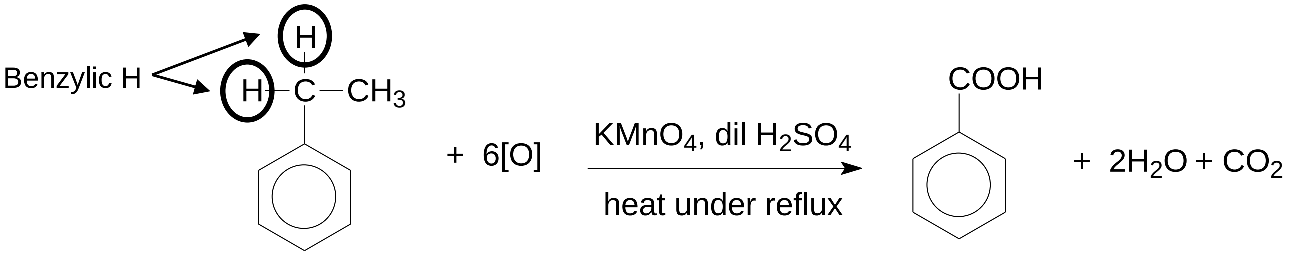
Reagent: $KMnO_4$
Condition: dil. H_2SO_4, heat under reflux

The benzene ring with its region of high electron density has a modifying effect on any group that is attached to it. Thus the $-CH_3$ group in methylbenzene does not always behave as a typical alkyl group in its reactions.

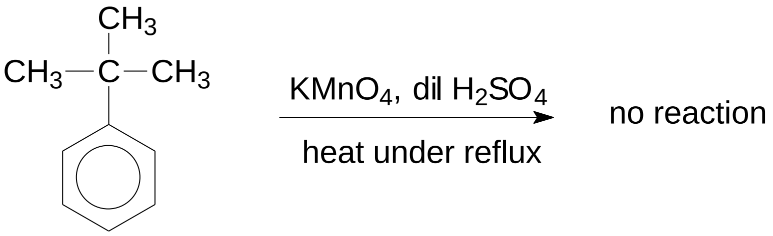
- For instance, alkanes and benzene are inert to oxidation, but the $-CH_3$ group in methylbenzene can be oxidised to give benzoic acid.



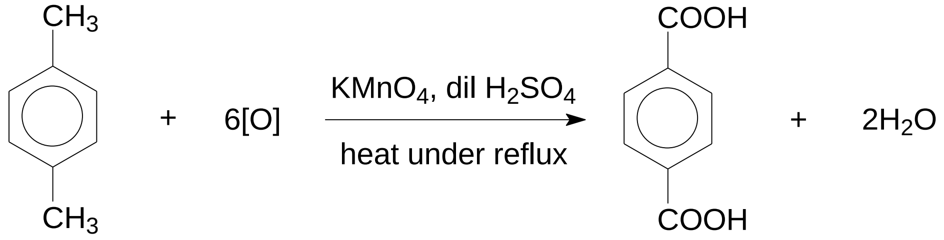
- Note that potassium dichromate, $K_2Cr_2O_7$ is unable to oxidise the alkyl side chain as it is a weaker oxidising agent than $KMnO_4$.
- For oxidation to occur, the side chain must have at least one ***benzylic H*** – a hydrogen atom bonded to the C directly bonded to the benzene ring.



- Tert-butylbenzene has **no benzylic H atom** and hence inert to oxidation.

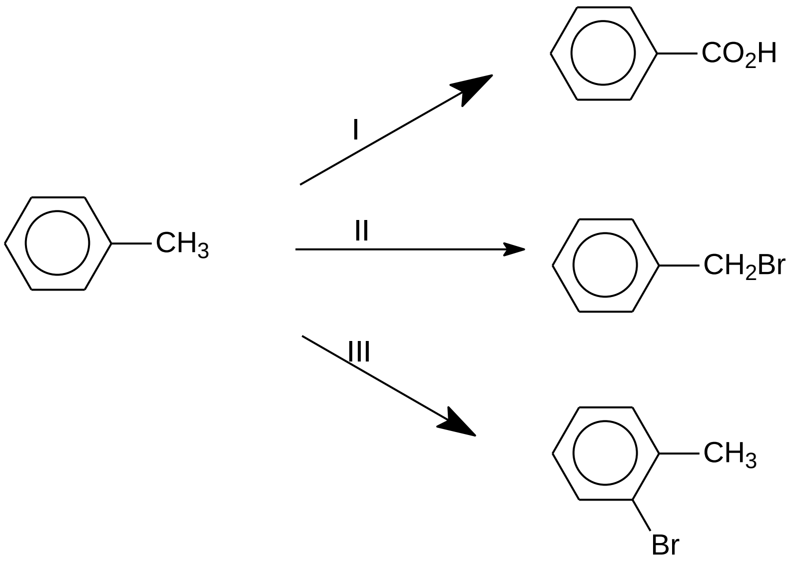


- When the benzene ring contains more than one alkyl group, each one is oxidised in the same way.



Exercise 2:

Methylbenzene can be used as an additive in unleaded petrol. Some chemical transformations of methylbenzene are given below.

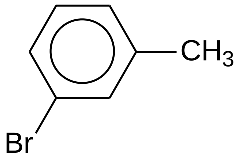


A

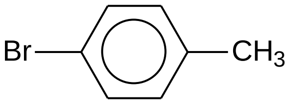
(a) Suggest reagents and conditions for each of the reactions, I, II and III, and describe as fully as you can the type of reaction undergone in each case.

	Reagents	**Conditions**	**Type of reaction**
I	$KMnO_4$, dilute H_2SO_4	heat under reflux	
II	Br_2	ultraviolet light/high temperature	
III	Br_2, $AlBr_3$ catalyst	Room temperature, anhydrous, in the dark/absence of UV light	

(b) There are two other positional isomers of **A**. Draw their structural formulae, and suggest which one is more likely to be formed along with **A** in reaction III.



B



C

(c) Explain why the other isomer you have drawn in **(b)** is least likely to be formed in reaction III.

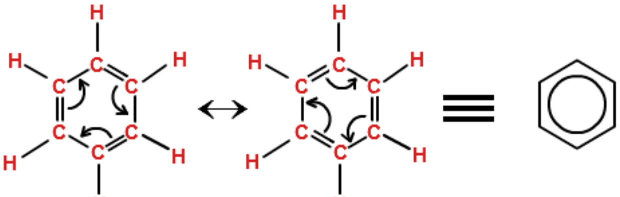
(*refer to* ***A4 Effect on the position of incoming electrophile*** *for stability of carbocation*)

APPENDIX

A1 Resonance in Benzene

- Resonance is present in a molecule when it can be represented by two or more structures that differ only in the arrangement of electrons, and the molecule in reality is a hybrid of all these structures.

- The **resonance hybrid** is intermediate between any of the representation structures and is **not a mixture** of them. It does not oscillate between any of the representation structures.



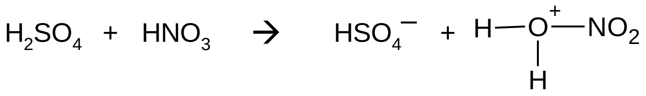
Kekulé structures of benzene
“cyclohexa-1,3,5-triene”
structures

Resonance hybrid of benzene
The delocalised electrons are
represented as a circle.
(Accepted displayed formula for benzene)

- The resonance hybrid is **more stable** than any of the representation structures, and this extra stability of benzene resulting from delocalisation of the π electrons is linked to the concept of ‘resonance energy’; which corresponds to the difference in potential energy between the actual molecular entity and the contributing structure of lowest potential energy. The resonance energy cannot be measured, but only estimated, since contributing structures are not observable molecular entities.

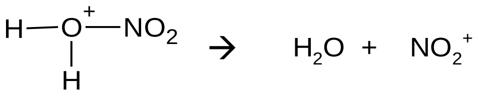
A2 Formation of the nitronium ion in the nitrating mixture

1) In the nitrating mixture, HNO_3 acts as a base and accepts a proton from the stronger acid, H_2SO_4.



$$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H-\overset{+}{\underset{\underset{H}{|}}{O}}-NO_2$$

2) The protonated nitric acid then splits up to form a H_2O molecule and the nitronium ion.



$$H-\overset{+}{\underset{\underset{H}{|}}{O}}-NO_2 \rightarrow H_2O + NO_2^+$$

3) The H_2O molecule is protonated by a second molecule of sulphuric acid.

$$H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^-$$

Adding up the three steps gives the overall equation.

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

The concentrated H_2SO_4 is said to be a catalyst in the nitration reaction since it is regenerated at the end of the reaction. (Refer to mechanism of nitration of benzene)

A3 Effect of the Substituent on the Rate of Electrophilic Substitution

A substituent on the benzene ring can be **electron-donating** or **electron-withdrawing** due to two effects,

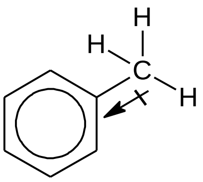
- **inductive effect**
- **resonance effect**

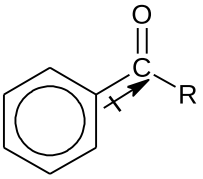
a) Inductive effect

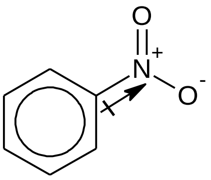
- Inductive effect is the donation or withdrawal of electrons through σ bonds due to **electronegativity difference** between atoms.

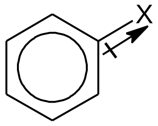
- Substituents like –R (alkyl groups e.g. CH_3, CH_2CH_3) can inductively **donate electron density** into the benzene ring and thus causes an **electron-donating via inductive effect**.

- Substituents like $–NH_2$, –OR, $–NO_2$, –OH, –CHO, –COR and halogens (e.g. C*l*, Br) can inductively **withdraw electron density** from the benzene ring (see below) and thus causes an **electron-withdrawing via inductive effect**.





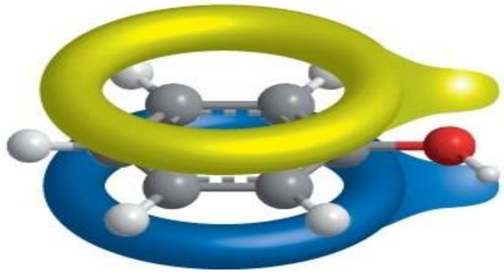




b) Resonance effect

- When electron flow occurs through the pi bond, it is termed as ***resonance effect***. This is possible when there is overlapping of p orbitals between the sp^2 hybridised carbon atom of the benzene ring and the substituent that it is bonded to.

- Substituents like $–NH_2$, –OR, –OH and halogens have at least a lone pair of electrons on the atom directly attached to the benzene ring. This **lone pair is usually in a p-orbital which overlaps with the π electron cloud of the benzene ring**. This results in the **delocalisation** of a lone pair electrons into the π electron cloud of benzene ring (see below), increasing electron density resulting in the substituent being **electron-donating via resonance effect**.



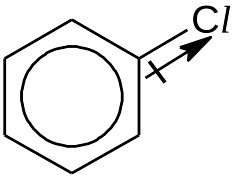
Shape of the electron cloud when –OH group delocalises a lone pair of electrons into the benzene ring

- Substituents like $–NO_2$, –CHO and –COR has an atom that is directly attached to the benzene ring which is double or triple bonded to a more electronegative atom. This results in the **withdrawal** of electrons from the π electron cloud of benzene ring, reducing electron density resulting in the substituent being **electron-withdrawing via resonance effect**.

c) Overall effect

- In some situations, competition between the inductive and resonance effect require consideration of the more dominant effect.

- For example, aryl halides like chlorobenzene has an electron-withdrawing via inductive effect and also, electron donating via resonance effect. In this case, the inductive effect is stronger than the resonance effect.
  - C*l* is in period 3. The 3p orbital of C*l* atom overlaps less effectively with the 2p orbital of the carbon atom (due to different sized p orbitals)



electron-withdrawing via inductive effect

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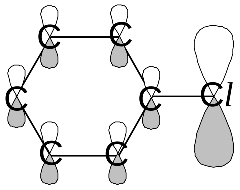
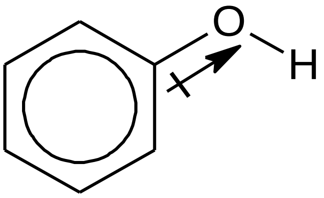


electron donating via resonance effect

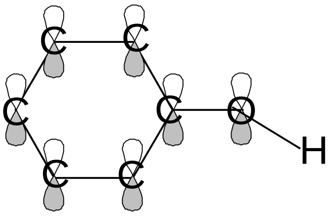
  - **Overall effect** of –C*l* is **electron-withdrawing via inductive effect**.
  - –C*l* substituent is considered **<u>deactivating</u>**.

- In contrast, substituents such as –OH, $–NH_2$ and –OR have effective 2p–2p overlap between the orbitals on O (or N) atom and the 2p orbital of carbon atom in the benzene ring.



electron-withdrawing via inductive effect

<



Electron-donating via resonance effect

  - the electron-donating resonance effect outweighs the electron-withdrawing effect.
  - **Overall effect** of –OH, $–NH_2$ and –OR substituents are **electron-donating via resonance effect**.
  - Thus, –OH, $–NH_2$ and –OR substituents are **<u>activating</u>**.

A4 Effect on the position of incoming electrophile

The positions of the incoming electrophile by substituents can be explained by examining the structure and stability of the intermediates. The fundamental principle is that,

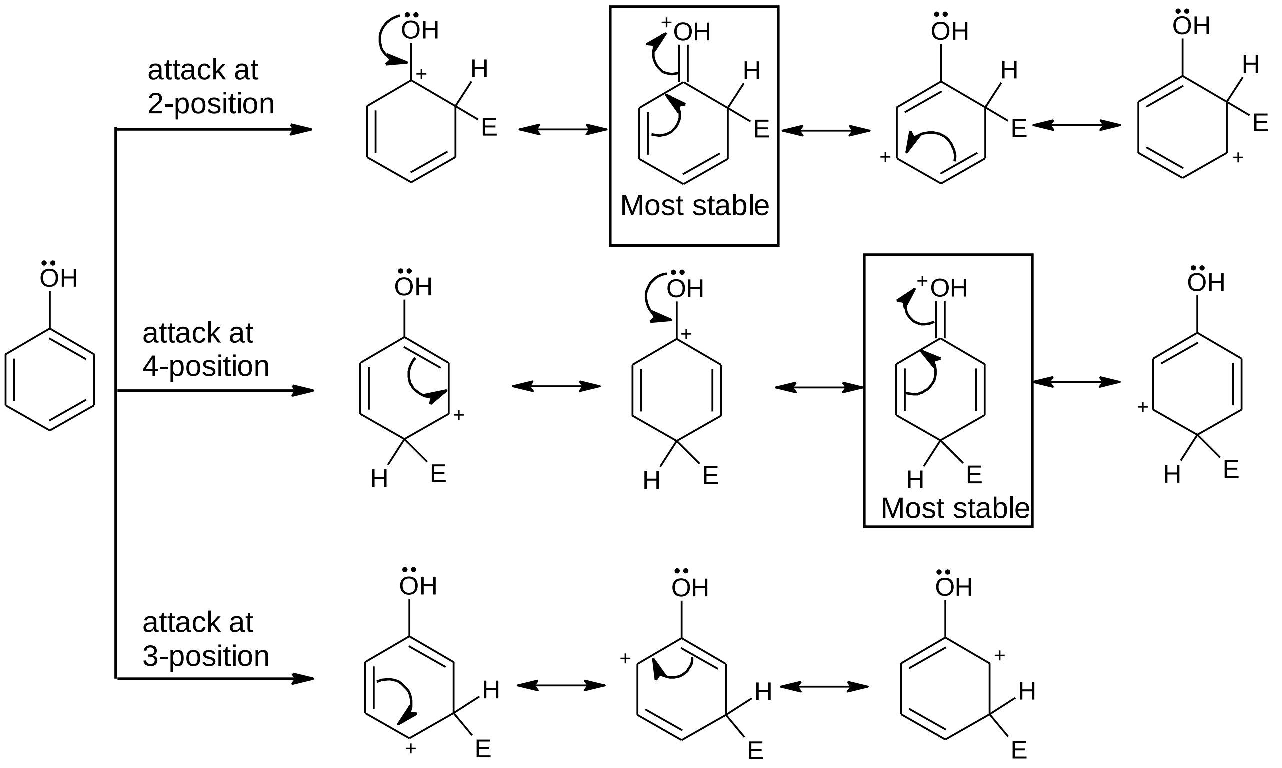
"a more stable carbocation intermediate is formed faster than a less stable one."

The flow chart on the next two pages shows how the –OH groups in phenol acts as a 2,4-directing group and the –CHO group in benzaldehyde acts as a 3-directing group.

2,4-directing groups

Activating groups and halogens are 2,4-directing. The carbocation intermediates formed from attack at 2- and 4-position are stabilised more than the intermediate formed from the attack at 3-position. Consider phenol in the example below.

Resonance structures of carbocation intermediates



The incoming electrophile can occupy the 2-, 3- or 4-position, forming different carbocation intermediates.

Attack at 2- and 4-position: positive charge resides on the carbon atom bonded to the -OH group. As the p-orbital of the O atom overlaps with the p-orbital of the sp^2-hybridised C atom with positive charge, the lone pair of electrons on the O atom can also be delocalised to the carbon to disperse the positive charge, further stabilising the carbocation.

Attack at 3-position: positive charge always rest on a sp^3-hybridised C atom that does not allow delocalisation of the lone pair on O atom to disperse the positive charge on C+.

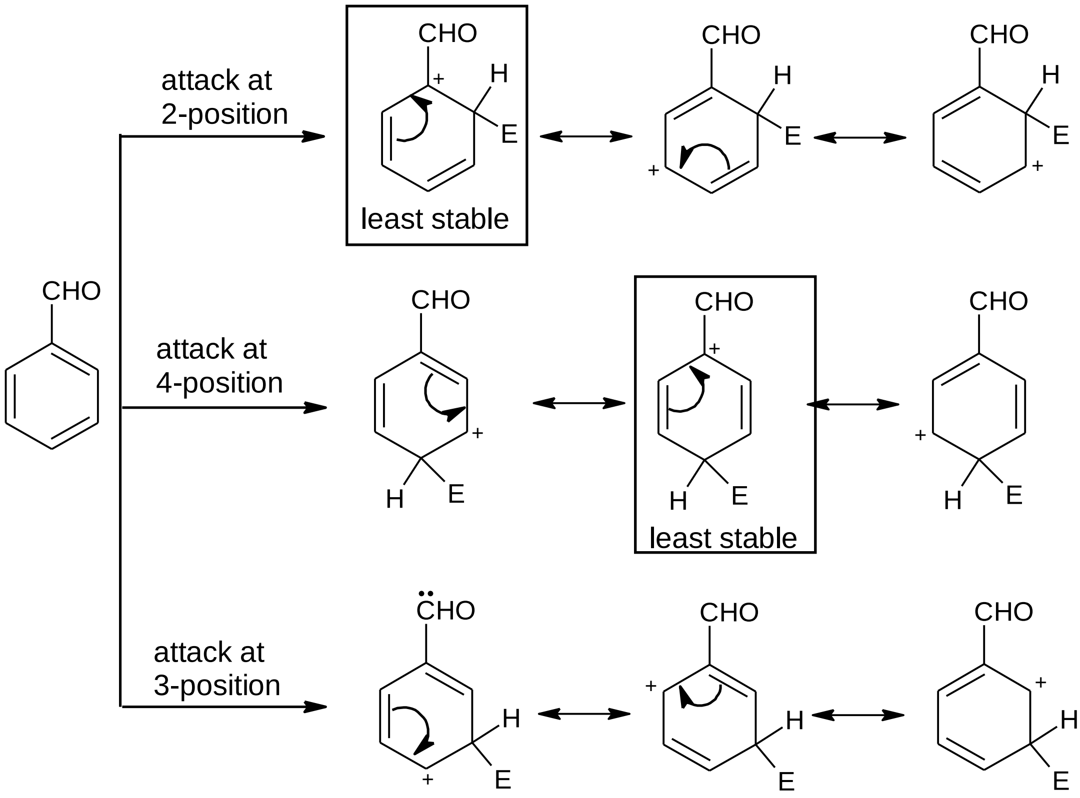
Hence, phenol is **2,4-directing** since the incoming electrophiles occupy positions that result in the more stable carbocation intermediate formed.

Note: Even though halogens are deactivating, they are 2,4-directing as well since the lone pair of electrons on the halogens can be donated via resonance to the benzene ring just like the O atom.

3-directing groups

Deactivating groups (except halogens) are 3-directing. The carbocation intermediates formed from attack at 2- and 4-position are destabilised more than the intermediate formed from attack at 3-position. Consider benzaldehyde in the example below.

Resonance structures of carbocation intermediates



The incoming electrophile can occupy the 2-, 3- or 4-position, forming different carbocation intermediates.

Attack at 2- and 4- position: positive charge on the C atom containing electron-withdrawing –CHO group. This intensifies the positive charge of the carbocation, thereby destabilising the carbocation.

Attack on 3- position: there is no destabilising effect.

Hence, benzaldehyde is **3-directing**.