Chem Factsheet

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Electrophilic Substitution

The term *electrophilic substitution* refers to a chemical reaction involving an *electrophilic species* causing a *substitution reaction* of an organic molecule. More specifically it refers to the *mechanism* for such reactions.

An *electrophile* is an electron-deficient particle which is able to accept a pair of electrons (a lone pair represented by :) from an electron rich region of a molecule (often an alkene or an arene) to form a new covalent bond.

Common examples of electrophiles are the hydrogen ion (H^+), the nitronium ion ($^+NO_2$), the bromonium ion (Br^+), alkyl carbocations ($^+C_nH_{2n+1}$), acyl carbocations ($^+COC_nH_{2n+1}$) and sulphur trioxide ($^{\delta+}SO_3{}^{\delta-}$).

Except for sulphur trioxide and H^+, none of these electrophiles can be obtained directly from a bottle! They are generated in the reaction mixture ("in situ"), usually by mixing two appropriate reagents – see later.

A *substitution reaction* is one in which an atom / group in an organic molecule is *replaced* by another atom / group.

$$A + B \rightarrow C + D$$

Substitution reactions are usually associated with *saturated* molecules – molecules which contain only single bonds. These have "no spare bonding capacity" so reaction usually occurs by substitution.

However, the stability of the delocalised electron system in the six carbon ring (see below) in benzene (C_6H_6), and related arenes, means that, even though such molecules are highly unsaturated, only the C-H bonds tend to react. Hence, substitution of these H atoms usually occurs resulting in the stable C-ring remaining intact.

Also, because of the delocalised electrons in arenes, they are electron-rich and therefore prone to reaction with electrophiles. Hence, arenes are prone to electrophilic substitution reactions. This is the subject of this Factsheet.

The structure of benzene

Benzene was first isolated and identified by Michael Faraday in 1825. Its empirical formula (CH) and molecular formula (C_6H_6) were easily determined but its structure was debated for several decades! This was because it has an unusually high C to H ratio making it highly unsaturated even though it was found to be generally unreactive.

In 1865, the German chemist Friedrich August Kekulé suggested that the structure contained a six-membered carbon ring with alternating single and double bonds as shown in Fig 1.

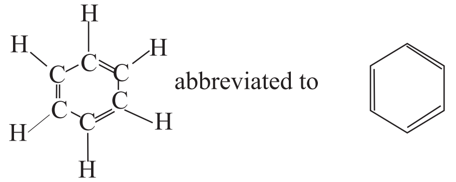


Fig 1

Although this structure is often used in textbooks and scientific papers, it is recognised that it does not represent a structure that is consistent with the actual properties of benzene. Some of these contradictions are summarised in table 1.

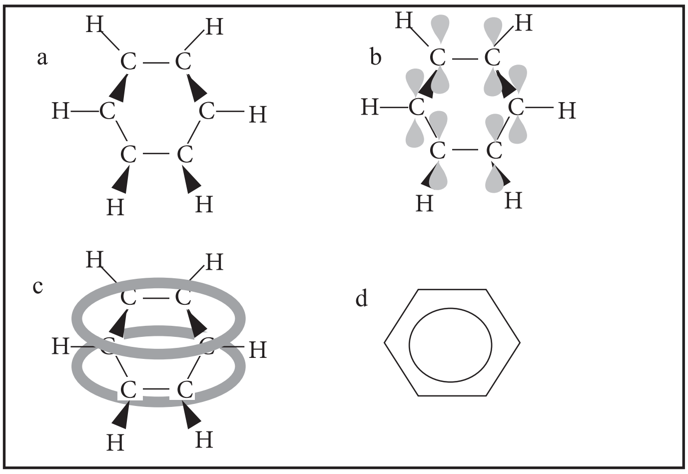
Table 1 : Comparing Kekule Properties and Actual Properties of Benzene

Property expected for Kekule's structure	Actual property shown by benzene
VERY REACTIVE because it has three reactive double bonds	Generally SLOW to react and then only under severe reaction conditions with catalysts required
React by ELECTROPHILIC ADDITION reactions - like any alkene	Addition reactions are RARE - most are SUBSTITUTION reactions
Have three SHORTER (135pm) C=C and three LONGER (147pm) C-C bonds	All six C to C bonds are SAME LENGTH (140pm) and intermediate between C-C and C=C bond lengths
Production of FOUR disubstituted isomers (e.g. $C_6H_4Br_2$) – 1,2-dibromo-, 1,3-dibromo-, 1,4-dibromo- and 1,6-dibromobenzene	ONLY THREE disubstituted isomers are produced – 1,2-dibromo-, 1,3-dibromo-, and 1,4-dibromobenzene
REACT WITH HYDROGEN GAS TO LIBERATE 125 × 3 = -375 kJ mole^{-1} because any C=C bond [e.g. CH_2=CH_2] liberates 125 kJ mole^{-1} when reacted with hydrogen	ONLY 208 kJ mole^{-1} is released when reacted with hydrogen

Following development of "molecular orbital theory" during the 1900's, the preferred model for the structure of benzene is now the "delocalised structure of benzene".

(a) Each C has four outer bonding electrons. Three of these are used to form "ordinary" sigma covalent bonds – 2 to neighbouring C's and 1 to an H atom. This gives a planar ring of 6 C's, each bonded to an H. This is shown in Fig 2a.

Fig 2. Building the Delocalised Structure of Benzene



(b) The remaining six electrons (one per C) are in p-orbitals (grey dumbbell shapes) above and below the plane of the carbon atoms as shown in Fig 2b.

(c) These six p-orbitals overlap sideways to produce a delocalised Pi orbital (circular grey shapes), positioned above and below the plane of the carbon atoms as shown in Fig 2c.

(d) The delocalised structure is represented by the abbreviated form shown in Fig 2d. The hexagon represents the 6C ring and the circle represents the delocalised electrons in the Pi orbital. The H atoms are not shown – don't forget them!

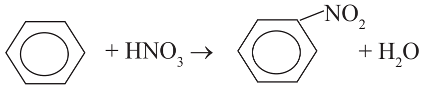
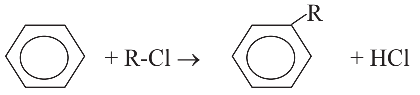
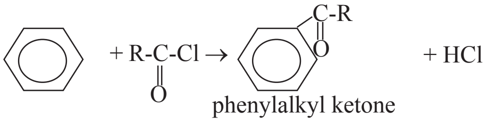
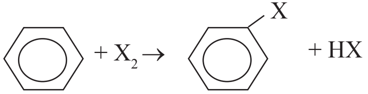
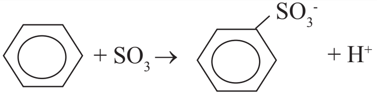
> Calculation shows this delocalized structure to be about 180 kJ mole^{-1} lower in energy (more stable) than the Kekule structure. This corresponds approximately to the difference between the enthalpy change of hydrogenation of benzene and the hydrogenation of Kekule's structure – see table 1.

Electrophilic substitution of benzene – how to carry them out

As already stated, the electron-rich nature of benzene's carbon ring favours attack by electrophiles and the stability of the delocalised structure favours substitution reactions. Hence, electrophilic substitutions are the characteristic reactions of benzene. How to carry out the common electrophilic substitution reactions of benzene are summarized in table 2.

> Your particular A-level specification will involve just *some* of these reactions. The appropriate examples are indicated for each of the major exam boards.

Table 2 : Electrophilic Substitution Reactions of Benzene

Nitration	 + HNO_3 → + H_2O ; NO_2 nitrobenzene
AQA, Edexcel, OCR & WJEC	Add c. HNO_3 + c. H_2SO_4 catalyst at 50°C.
Alkylation	 + R-Cl → + HCl ; R alkyl benzene
Edexcel & WJEC	Add a chloroalkane ($C_nH_{2n+1}Cl$) + anhydrous $AlCl_3$ catalyst
Acylation	 + R-C(=O)-Cl → + HCl ; C(=O)-R phenylalkyl ketone
AQA and Edexcel	Add an acyl chloride ($C_nH_{2n+1}COCl$) + anhydrous $AlCl_3$ catalyst
Halogenation	 + X_2 → + HX ; X (X= Cl or Br) halobenzene
Edexcel & WJEC	Add liquid bromine or gaseous chlorine + anhydrous $FeBr_3$ or $FeCl_3$ catalyst
Sulphonation	 + SO_3 → + H^+ ; SO_3^- benzene sulphonic acid
Edexcel	Add "fuming" sulphuric acid (also called oleum – $H_2S_2O_7$ = SO_3 dissolved in c. H_2SO_4) at 40°C.

> Under appropriate conditions, continued substitution can occur because the mono-substituted product still has 5H atoms which can be substituted. Most A-level specifications restrict consideration to mono-substitution.

Electrophilic substitution of benzene – the mechanism

The mechanism is best considered in three steps.

Step 1 : The "in situ" formation of the electrophile (E^+) from the main reactant and the catalyst (except sulphonation where the SO_3 electrophile is already present in fuming sulphuric acid).

Step 2 : The bonding of the electrophile (E^+) to benzene to form the substituted product.

Step 3 : The reforming of the catalyst and formation of the second product.

Step 1

Nitration: $HNO_3 + 2H_2SO_4 \rightarrow {}^+NO_2 + 2HSO_4^- + H_3O^+$; ${}^+NO_2$ = nitronium ion

Alkylation : $C_nH_{2n+1}Cl + AlCl_3 \rightarrow {}^+C_nH_{2n+1} + AlCl_4^-$; ${}^+C_nH_{2n+1}$ = alkyl carbocation

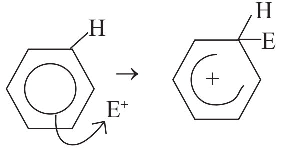
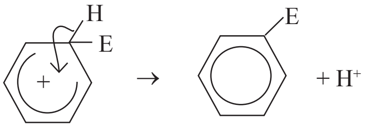
Acylation : $C_nH_{2n+1}COCl + AlCl_3 \rightarrow C_nH_{2n+1}C^+O + AlCl_4^-$; $C_nH_{2n+1}C^+O$ = acyl carbocation

Halogenation: $X_2 + FeX_3 \rightarrow X^+ + FeX_4^-$; X^+ = chloronium or bromonium ion

Sulphonation: not applicable - SO_3 already in fuming sulphuric acid.

> In the cases of alkylation and acylation, make sure the positive charge is shown on the C atom.

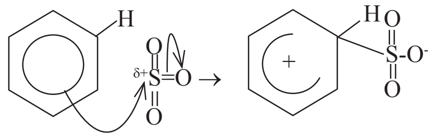
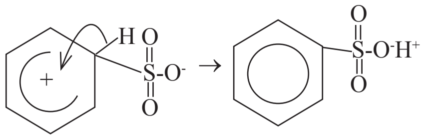
Step 2

<table>
<tr><td>E^+ =</td><td>${}^+NO_2$</td><td>${}^+C_nH_{2n+1}$</td><td>$C_nH_{2n+1}C^+O$</td><td>Cl^+ or Br^+</td></tr>
<tr><td colspan="3"> </td><td colspan="2">Two electrons from benzene's 6-electron delocalised system form a bond to the electrophile (E^+). This gives an intermediate with a positively charged benzene ring and the remaining 4 electrons delocalised over the other 5 carbon atoms.</td></tr>
<tr><td colspan="3"> </td><td colspan="2">Two electrons from the C-H bond of the intermediate restore the full 6 electron delocalised system, forming the final substitution product and releasing an H^+ ion.</td></tr>
</table>

Step 3

Reaction	From step 2		From step 1		Catalyst reformed		Second product
Nitration	H^+	+	HSO_4^-	→	H_2SO_4		
Alkylation	H^+	+	$AlCl_4^-$	→	$AlCl_3$	+	HCl
Acylation	H^+	+	$AlCl_4^-$	→	$AlCl_3$	+	HCl
Chlorination	H^+	+	$FeCl_4^-$	→	$FeCl_3$	+	HCl
Bromination	H^+	+	$FeBr_4^-$	→	$FeBr_3$	+	HBr

The sulphonation mechanism is essentially the same as the others but will be stated explicitly here to highlight the slight differences.

	Two electrons from benzene's 6-electron delocalised system form a bond to the δ+ S of the SO_3. This gives an intermediate with a positively charged benzene ring and the remaining 4 electrons delocalised over the other 5 carbon atoms. One of the O atoms becomes negative as a result of electrons moving from a S=O bond to O.
	Two electrons from the C-H bond of the intermediate restore the full 6 electron delocalised system, forming the final substitution product and releasing an H^+ ion. The benzene derivative and the H^+ ion together constitute the product, benzene sulphonic acid.

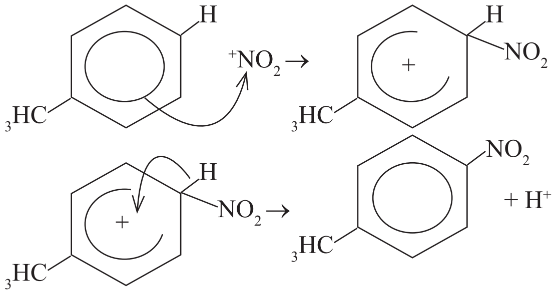
Practice Questions

1. What is an electrophile?
2. What is a substitution reaction?
3. Explain briefly why benzene preferentially undergoes substitution reactions rather than addition reactions.
4. Outline the mechanism for the reaction of (a) methylbenzene to form 4-nitromethylbenzene (b) benzene to form ethylbenzene (c) benzene to form phenylpropan-1-one (d) nitrobenzene to 3-chloronitrobenzene.
5. Why can iron plus excess liquid bromine rather than iron(III) bromide with liquid bromine be used to brominate benzene?

Answers

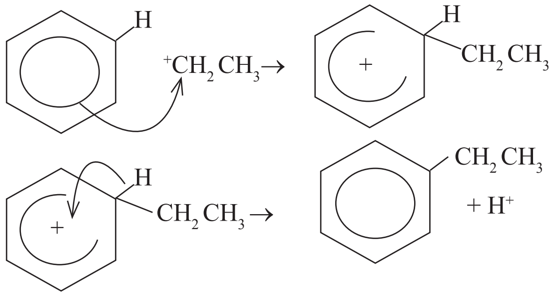
1. An electrophile is an electron pair acceptor. An electron deficient atom in an electrophile accepts an electron pair to form a covalent bond.
2. A substitution reaction is one in which an atom or a group of atoms in a molecule is replaced by another atom or a group of atoms.
3. The stable delocalised structure is retained if substitution occurs but lost if addition occurs.

4 (a) $HNO_3 + 2H_2SO_4 \rightarrow {}^+NO_2 + 2HSO_4^- + H_3O^+$



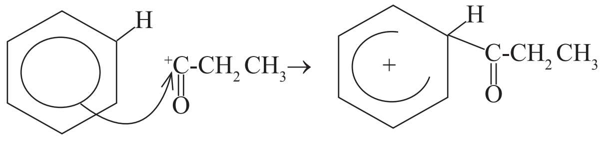
$HSO_4^- + H^+ \rightarrow H_2SO_4$

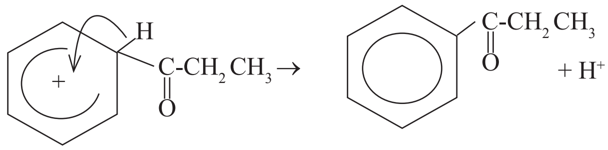
4 (b) $CH_3CH_2Cl + AlCl_3 \rightarrow {}^+CH_2CH_3 + AlCl_4^-$



$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

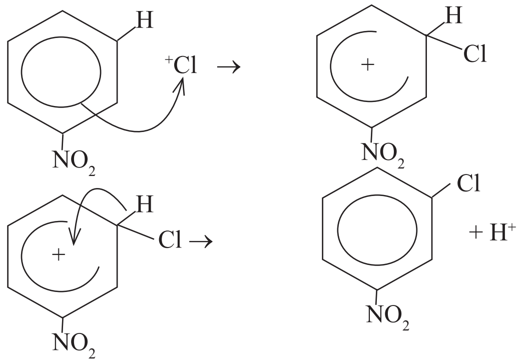
4 (c) $CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2C^+O + AlCl_4^-$





$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

4 (d) $Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$



$H^+ + FeCl_4^- \rightarrow FeCl_3 + HCl$

5. Iron metal reacts with bromine to form iron(III) bromide.

   $2Fe(s) + 3Br_2(l) \rightarrow 2FeBr_3(s)$

   Hence, the required catalyst is produced *in situ*.

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