Chem Factsheet

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Chemistry of Benzene

You need to know AS organic chemistry especially the terms electrophile, carbocation, substitution, addition, the bonding and structure of alkenes and the IUPAC naming system.

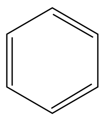
After working through this Factsheet with reference to benzene your knowledge should include:
(i) the Kekulé and delocalised models and evidence for and against them,
(ii) examples of electrophilic substitution reactions, the reaction mechanisms and the importance of these reactions in synthesis,
(iii) examples of addition reactions.

1. Introduction

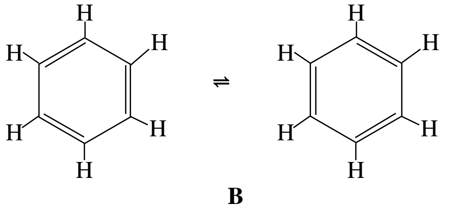
Benzene is the simplest member of a class of hydrocarbons called ***arenes*** or ***aromatic hydrocarbons***. Benzene was first isolated in 1825 by Michael Faraday and its molecular formula C_6H_6 was determined in1834. The chemists of this period knew that hydrogen atoms and carbon atoms could join to 1 and 4 other atoms respectively and thus suggested structural formulae such as $CH_2{=}C{-}CH{=}CH{-}CH{=}CH_2$. The electron was not discovered until 1897 and the word *orbital* was introduced by Robert Mulliken in 1932.

2. The Kekulé Structure of Benzene (1865)

Kekulé suggested that the structure of benzene was a regular hexagon of carbon atoms with alternating single and double bonds, each carbon being bonded to a hydrogen atom – structure A. Later he modified this model and considered benzene as a mixture of two cyclohexa-1,3,5-trienes in rapid equilibrium – structures B.



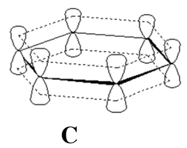
A



B

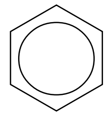
The Kekulé model proved to be *unacceptable* on many levels, but especially, it could not explain the unreactive nature of benzene compared to the high reactivity of C=C bonds in alkenes. Alkenes typically undergo electrophilic ***addition*** reactions under mild reaction conditions whereas benzene tends to react by electrophilic ***substitution*** under severe conditions including the need for catalysts.

3. The Delocalised Structure of Benzene



C

D



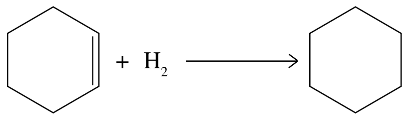
E

Delocalized electrons are electrons in a molecule that are not associated with any particular atom or to any particular covalent bond. These electrons are contained within an orbital that extends over several adjacent atoms.

In benzene, each carbon atom uses three outer electrons to form three sigma (single covalent) bonds, one to a hydrogen atom and two to two carbon atoms so that a flat regular hexagon of carbon atoms is formed each with a hydrogen atom pointing away from the ring. This leaves six p-orbitals (see diagram C), one per carbon atom, which are able to overlap all around the ring to form pi (π) orbitals above and below the carbon plane (see diagram D). These pi orbitals contain six delocalised electrons; this delocalisation is responsible for benzene's stability and decreased reactivity.

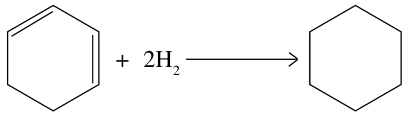
The delocalised model (commonly represented as shown in diagram E) means that the electron density between carbon atoms in the ring is equal, hence all C-C bond lengths are equal and all bond angles are 120°. The experimental technique of X-ray diffraction confirms this with all C-C bond lengths being 0.139 nm which is intermediate between a C-C single (0.154 nm) and C=C double (0.134 nm). The IR spectrum only shows one peak due to C-H stretch (3100-3000 cm^{-1}) so all C-H bonds are identical. There is also one peak due to C-C stretch (≈1500 cm^{-1}) since all C-C bonds are identical.

4. Thermochemical evidence that the delocalised structure is more stable than the Kekulé structure.



F G

ΔH = -120 kJ $mole^{-1}$



H

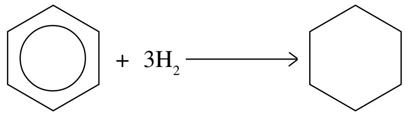
ΔH = -240 kJ $mole^{-1}$

Experiment shows that the heat of hydrogenation of cyclohexene (F) to form cyclohexane (G) is -120 kJ mol^{-1} and that of cyclohexa-1,3-diene (H) to also form cyclohexane (G) is -240 kJ mol^{-1}.

If benzene had the Kekulé structure, the heat of hydrogenation should be (3 × -120) = -360 kJ mol^{-1}.

Benzene does react with hydrogen under vigorous conditions resulting in *loss of delocalisation*, e.g. 150°C in the presence of a nickel catalyst.

However, the ACTUAL experimental value for benzene is only – 208 $kJmol^{-1}$.



ΔH = -208 kJ $mole^{-1}$

Thus benzene is, as a result of delocalisation, 152 $kJmol^{-1}$ (360 – 208) *more stable* than the Kekulé structure. This energy is called the *stablisation energy* or *delocalisation energy* of benzene.

5. Electrophilic Substitution Reactions of Benzene (Arenes)

(a) Reagents, catalysts, temperatures, electrophiles and types of products

Reaction Type	Reagent	Catalyst	Temp. /^{0}C	Electrophile	Type of product
Nitration	Conc. HNO_3	Conc. H_2SO_4	≈ 50	Nitronium ion / $^+NO_2$	Nitroarene
Friedel-Crafts Acylation	An acyl chloride e.g. CH_3COCl	Anhydrous $AlCl_3$	Room	Acyl carbocation / RC^+O	Phenylketone
Halogenation	Cl_2 for chlorination	e.g. $FeCl_3$	Room	Chloronium ion Cl^+	Chloroarene
	Br_2 for bromination	e.g. $FeBr_3$	Room	*Bromonium ion* Br^+	Bromoarene
Friedel-Crafts Alkylation	An alkyl halide e.g. CH_3CH_2Br	Anhydrous $AlCl_3$	≈ 50	Alkyl carbocation / e.g. $CH_3C^+H_2$	Alkylarene
Sulphonation	Fuming H_2SO_4	None used	≈ 40	$^{\delta+}SO_3^{\delta-}$	Sulphonic acid

Note: Catalysts such as $AlCl_3$ and $FeBr_3$ are *Lewis acids* (electron pair acceptors). They are also called *Friedel-Crafts catalysts* and *halogen carriers*.

(b) Equations and Names of Organic Products

Reaction Type	Equation	Name of organic product
Nitration	$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$	Nitrobenzene
Friedel-Crafts Acylation	e.g. $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$	Phenyl ethanone
Halogenation (Chlorination or Bromination)	$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$	Chlorobenzene
	$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$	Bromobenzene
Friedel-Crafts alkylation	e.g. $C_6H_6 + CH_3CH_2Br \rightarrow C_6H_5CH_2CH_3 + HBr$	Ethyl benzene
Sulphonation	$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$	Benzenesulphonic acid

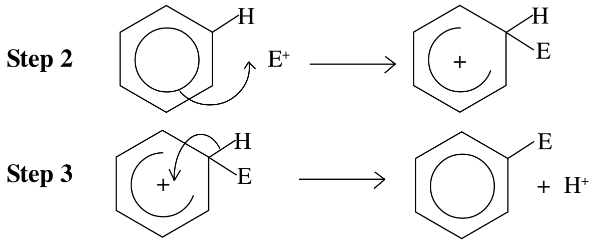
(c) Mechanisms

Step 1. Production of the electrophiles.

Nitration	$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
Friedel-Crafts Acylation	e.g. $CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2^+CO + AlCl_4^-$
Chlorination	$Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$
Bromination	$Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-$
Friedel-Crafts Alkylation	$CH_3CH_2Br + FeBr_3 \rightarrow {}^+CH_2CH_3 + FeBr_4^-$

Step 2. The electrophile (represented by ^+E in general) attacks the benzene ring and accepts a pair of electrons from the 6 delocalised ring electrons.

Step 3. The two C-H bond electrons move into the ring and restore the six electron delocalisation, thus releasing a proton, H^+.



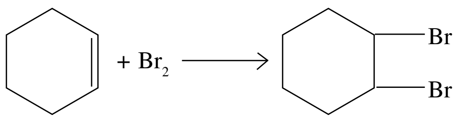
Notes: 1. Make sure the + is shown on the correct atom of the electrophile as required by the question – ^+N for $^+NO_2$, and ^+C for alkyl and acyl carbocations.
2. Make sure the curly arrow in step 1 forms a bond to this + atom..
3. Make sure the + sign on the intermediate is in the centre of the ring.
4. Make sure the partial delocalisation covers all 5 carbons atoms.

Step 4.	The regeneration of the catalyst by the proton reacting with the anion formed during step 1.
Nitration	$HSO_4^- + H^+ \rightarrow H_2SO_4$
Friedel-Crafts acylation	$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ (white fumes seen)
Bromination and Friedel-Crafts alkylation	$FeBr_4^- + H^+ \rightarrow FeBr_3 + HBr$ (white fumes seen)

6. Why does electrophilic substitution occur and not electrophilic addition

Addition would mean loss of delocalisation and delocalisation stabilisation. Substitution retains delocalisation and hence the stability associated with delocalisation.

During bromination of alkenes (e.g. cyclohexene), dilute orange solutions of bromine are rapidly decolourised. The *localised* pi electrons of the double bond allow an *electrophilic addition* reaction to occur producing 1,2-dibromocyclohexane.

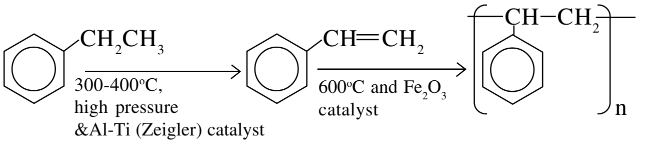


Note 1 The fact that benzene does not rapidly decolourise bromine solution but, under more vigorous conditions (bromine and a catalyst), undergoes substitution rather than addition is chemical evidence for the delocalised model rather than the Kekulé model. The Kekulé structure with three double bonds would be expected to rapidly decolourise bromine solution.

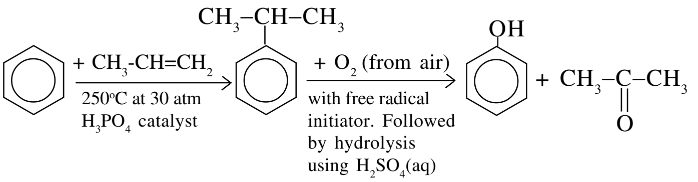
Note 2 Benzene *will* add bromine in the presence of UV light to form 1,2,3,4,5,6-hexabromocyclohexane but this is a free radical addition reaction under much more vigorous conditions.

7. Significance of Nitration, Alkylation & Acylation Reactions

These are very important steps in the *synthesis of other organic compounds*. Nitration leads to the manufacture of explosives such as 2,4,6-trinitromethylbenzene (TNT) and nitro compounds can be reduced to amines from which dyestuffs are manufactured. Ethylbenzene is an alkyl benzene involved in manufacturing phenylethene for making polyphenylethene (polystyrene).



Phenol and propanone are formed via 2-phenylpropane (cumene).



Ketones produced by acylation can be reduced to a secondary alcohols, oxidised to a carboxylic acids, converted to a nitriles, etc.

Practice Questions

1. In general, what type of reagent attacks a benzene ring to form substitution compounds? State the attacking agents during (i) nitration, (ii) alkylation and (iii) acylation of benzene (4 marks)
2. Before Kekulé proposed his structure for benzene, structures such as $CH_2=C=CH-CH=C=CH_2$ were suggested. How do the C-C-C bond angles and C-C bond lengths of this structure compare with the delocalised structure of benzene? (8 marks)
3. An acylium ion has the structure $R-{}^{+}C=O$ where R is any alkyl group. In the conversion of benzene into phenylpropan-1-one, $C_6H_5COCH_2CH_3$, an acylium ion $CH_3CH_2{}^{+}CO$ reacts with a benzene molecule. Write an equation to show the formation of this acylium ion from aluminium chloride and one other substance. Name and outline the mechanism of the reaction of this acylium ion with benzene. (6 marks)
4. Give, in the form of equations, two different examples of electrophilic substitution reactions of benzene. Outline the mechanism for each reaction. (10 marks)
5. A possible synthesis of phenylethene is outlined bellow

$$\text{benzene} \xrightarrow{\text{reaction 1}} \text{phenylethanone} \xrightarrow{\text{reaction 2}} \text{1-phenylethan-1-ol} \xrightarrow{\text{reaction 3}} \text{phenylethene}$$

   Why types of reactions are 1, 2 and 3 and identify a suitable reagent for each reaction. (6 marks)

6. Under what conditions does benzene react with (a) nitric acid, (b) bromine, (c) ethanoyl chloride? (9 marks).

Answers

1. Electrophile ✓
   (i) nitronium ion / ${}^{+}NO_2$ ✓
   (ii) carbocation / R^+ ✓
   (iii) acyl carbocation / $RC^{+}O$✓

2. $CH_2=C=CH-CH=C=CH_2$. Bond angles: both C=C=C = 180^0 ✓and both C=CH-C ≈120^0. ✓
   In all CH_2 angles are 120^0✓. $CH_2=C=CH-CH=C=CH_2$ has 4 ✓ shorter double bonds ✓ (C=C) and 1 longer single bond ✓ (C-C). In the delocalised structure all bond lengths are equal ✓ and between single and double ✓.

3. Electrophilic substitution ✓.
   See 5c using CH_3CH_2COCl ✓, plus one mark for each step ✓✓✓✓.

4. See 5 for equations ✓✓and for mechanisms - one mark for each step ✓✓✓✓ x 2.

5. 1- substitution ✓, 2- reduction ✓, 3- elimination / dehydration ✓.
   1: ethanoyl chloride and anhydrous $AlCl_3$ catalyst ✓,
   2- e.g. $NaBH_4$✓,
   3- Conc. H_3PO_4 / Conc. H_2SO_4 ✓.

6. See 5 for reagents, catalysts and temperatures. (3 x 3 = 9 marks)

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