UNDERSTANDING BENZENE STRUCTURE

LESSON 2 **CONSIDERING POSSIBLE STRUCTURES**

From LESSON 1 we have discovered that the **molecular formula of benzene is C_6H_6**

At the end of the last activity, I asked you to consider **possible structures for benzene** that could fit with this molecular formula.

The first question that you should always ask yourself when you look at any organic formula is,

"Does it look unsaturated?"

Well, does it? Think about the C:H ratio compared to alkanes.

Also, remember that **carbon must always form 4 bonds** in organic compounds.

Sketch some structures below.

Draw 4 possible structures that could have the formula **C_6H_6**. Displayed formulae maybe best for this so that you can count the bonds to each C atom. There is a huge number of isomeric possibilities!

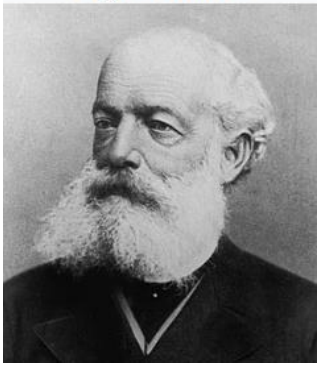
Many chemists worked hard to propose a structure (including *Dewar*[*], *Armstrong* and *Claus*)

One structure that gained most favour was propose by ***Kekulé*** in 1865.

Find out his structure (***Kekulé benzene***) and draw it in the box below.

Kekulé benzene structure

August Kekulé



The next bit of this work on benzene will consider how well the **experimental evidence** supports the ***Kekulé benzene structure***

[*] Dewar was a Scottish chemist and inventor of the Thermos/vacuum flask.

1. Reactivity of Benzene with Bromine water.

The ***Kekulé benzene structure*** appears to have double bonds making it look very much like an alkene.

1. Give the systematic name for ***Kekulé benzene*** ……
2. What is the main ***reaction type*** that alkenes undergo? ……
3. What is the main ***mechanism type*** that alkenes follow when they react? ……
4. Draw the mechanism for the reaction between **but-1-ene** and **HBr** that gives the **major product**.

The major product can be predicted by applying a rule.

5. What is this rule called and why do these addition reactions to **unsymmetrical alkenes** give a major product?

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6. If this reaction in Q4 gives a **75.0% yield** of the major product, calculate the mass of product that would be produced if 11.2g of **but-1-ene** reacted with excess HBr.

   mass of major product = ……..

7. Does **but-1-ene** exhibit ***E/Z*** **isomerism**? YES/NO (circle)
8. Using **skeletal formulae**, draw the **structural isomers** of **but-1-ene**

9. Describe the simple chemical test for the presence of an alkene.

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When bromine water is added to a sample of benzene, there is no obvious reaction.

This strongly suggests that benzene is not a typical alkene and it casts doubt on *Kekulé benzene* structure.

2. Bond Length Evidence

Atoms have different radii.

10. As one progresses across a period of the periodic table, from left to right, what are the trends in **atomic number** and **atomic radius**?
    i) Trend in atomic number INCREASES /DECREASES
    ii) Trend in atomic radius INCREASES /DECREASES
11. What is the reason for the trend in question 10(ii)?

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12. Given that atoms have different sizes, the covalent bonds that hold atoms together in molecules must have different lengths. These can be found out using an analytical technique called **x-ray diffraction** which establishes where nuclei are in the solid state.

    Find the length of the following bonds: **C-C** bond length = ……

    C=C bond length = ……

The x-ray diffraction of benzene derivatives* was carried out in 1929, the results of which finally proved the structure of benzene. It showed that benzene was

i) flat (planar)
ii) all the bonds between carbons were the same length
iii) The **C to C** bond lengths were all 139 *p*m

You should consider this evidence and compare it to the bond lengths that would have expected to see in ***Kekulé benzene***

So, **in conclusion**,

1. benzene does not react with bromine water, like an alkene would.
2. benzene has bonds between carbon atoms that are all the same length AND the length is in-between that of a single C-C and a double C=C.

You should now be feeling even less confident about Kekule's proposed structure for benzene.

* This work 'game-changing' work was actually done on *hexamethylbenzene*.

It was carried out by ***Dame Kathleen Lonsdale, DBE, FRS***. Just like ***Dorothy Mary Crowfoot Hodgkin OM FRS HonFRSC,*** another legend in the world of x-ray crystallography, Lonsdale had very strong political and ethical views. Interestingly, Hodgkin was Margret Thatcher's chemistry teacher at Oxford! Thatcher has a portrait of Hodgkin in her office in Downing Street because she held her in such high regard! Hodgkin was a lifelong supporter of the Labour Party!

Stretch & Challenge

Please feel free to attempt this but don't be put off if you struggle with it!

a) Define ***enthalpy of atomisation for an element*** $\Delta_a H$

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b) Define ***enthalpy of atomisation for a compound*** $\Delta_a H$

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c) Define ***mean bond enthalpy***

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d) Look up values for the following

$\Delta_a H$ (hydrogen) = …… *k*Jmol^{-1}

$\Delta_a H$ (carbon) = …… *k*Jmol^{-1}

mean bond enthalpy **C=C** = …… *k*Jmol^{-1}

mean bond enthalpy **C-C** = …… *k*Jmol^{-1}

mean bond enthalpy **C-H** = …… *k*Jmol^{-1}

Using these ***mean bond enthalpies,*** calculate

$\Delta_a H$ ('*Kekule'* benzene) = …… *k*Jmol^{-1}

e) Why is there often (but not always) a very significant* difference between the **enthalpy of atomisation of a molecular substance** and the **sum of the mean bond enthalpies within the molecule**. This is tied into the definitions in 2 and 3 and **not** because of the mean nature of bond enthalpies. (Clue: states!)

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f) You have already calculated the $\Delta_f H$ for benzene from experimental (real) $\Delta_f H$ data. This was done in WEEK 1

What value did you obtain? $\Delta_f H$('real' benzene).....*k*Jmol^{-1}

Now let's assume that Kekule's structure for benzene is correct, i.e. a structure that is the triene 1,3,5-cyclohexatriene. If so, the $\Delta_f H$ (benzene) should be the same, according to *Hess's Law*

We will recalculate the $\Delta_f H$ **using mean bond enthalpies benzene** and the **enthalpy of atomisation** $\Delta_a H$ for carbon and hydrogen. Surely the $\Delta_f H$ (benzene) should be the same, according to *Hess's Law*.

* the English that I used there is poor. You can't say *very significant* in the same way you can't say *very black* or *very unique.* (Black, unique and significant are **non-gradable adjectives**)

g) To do this you will need to draw another Hess Cycle for $\Delta_f H$ (*'Kekule'* benzene). This has been started for you. **BUT** there is another enthalpy change that you need to complete the cycle. What is this enthalpy change? You can describe this in words.

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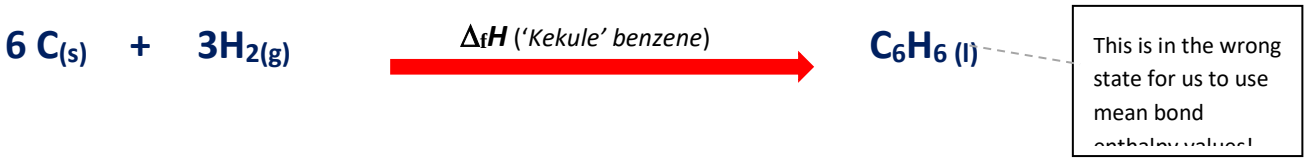
The enthalpy change that you need it the enthalpy change that will convert $C_6H_{6\,(l)}$ into $C_6H_{6\,(g)}$. It's only when it is in the gaseous phase that we can break all the bonds and then use the mean bond enthalpy values (according to the definition!)

This missing enthalpy change is the ***enthalpy of vaporisation***, $\Delta_{vap}H$(benzene)

h) Look up a value for this.

$\Delta_{vap}H$(benzene) = …… *k*Jmol^{-1}



i) Calculate the $\Delta_f H$ (*'Kekule' benzene*) $\Delta_f H$ (*'Kekule' benzene*) = …… *k*Jmol^{-1}

Now you have $\Delta_f H$ for the theoretical *'Kekule'* benzene, you can compare it to $\Delta_f H$ for the *'real'* benzene (a value that was obtained by **doing experiments with the real stuff**).

j) What is the value for the difference in values? Difference = …… *k*Jmol^{-1}

The significant discrepancy between the **real** value and the **theoretical** value that you just calculated suggests that Kekule's structure can't be correct. It is too large to blame the average nature of bond enthalpies!

k) Assume that the universe seems to favour processes that have negative a $\Delta_{reaction}H$ (or as small a positive value as possible) because it leads to ***more stable*** compounds being formed. What does this suggest about the ***stability*** of real benzene compared to the theoretical one?

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Next year, we will learn that there is more to the **feasibility** of a process than is associated solely with the enthalpy change of a reaction/process. **But**, the exothermicity of a process is a big contribution and is usually helpful hint about feasibility.