

Chapter 21: Benzene and the Concept of Aromaticity

Lecture Outline

I. The Structure of Benzene

A. Introductory information

1. Benzene (MP = 6° ; BP = 80°) was first isolated by Michael Faraday in 1825

2. Even though C_6H_6 has a IHD of 4 we would expect it to be reactive like an ~~alkene~~ alkene or alkyne, but ~~it~~ it doesn't!

a. Does not react with bromine, hydrogen bromide, oxidized by chromic acid (oxidation of alkenes and alkynes)

b. ~~*~~ When it does react, it undergoes substitution ~~*~~

3. Aromatic - use to classify benzene and its derivatives because most of these groups have very distinctive smells

a.

4. Arenes are used to describe aromatic hydrocarbons (abbreviation is Ar-)

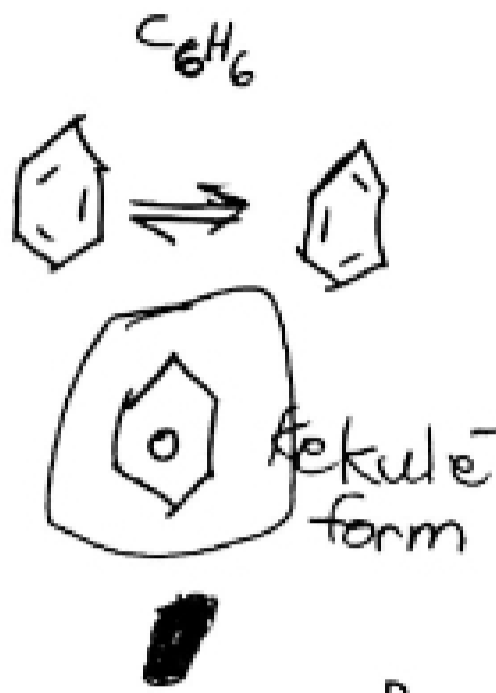
B. It was found that in order to do a substitution reaction, we had to add one mole of Br_2 gas in the presence of a Lewis acid catalyst ($FeCl_3$) - we would form bromobenzene - because of this, scientists concluded that all 6 H's are equivalent

1. If we treat bromobenzene under the same conditions, we get three isomeric dibromobenzenes.

2. So how do we put this together with the fact that carbon is tetravalent?

C. First Theory: Kekulé Model

1. 1865 - August Kekulé \rightarrow 6-membered ring with one H on each C



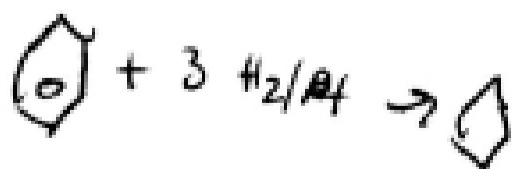
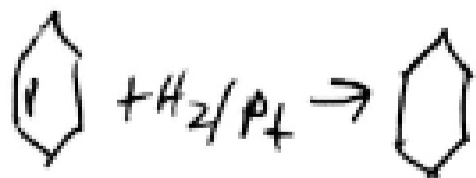
- Advantages: all C-C and C-H bonds are equivalent
- Disadvantages: carbon is tetravalent, not trivalent.
- In 1822, Kekulé proposed that the ring contains 3 double bonds that shift back and forth so rapidly that the 2 forms cannot be separated (an equilibrium) — that's how we get a Kekulé structure
- This definitely explained the experimental results but was still contested for years — remember that this was proposed before electrons were even thought of!
- It also didn't account for the unusual stability of benzene.

D. Second Theory: Molecular-Orbital Model

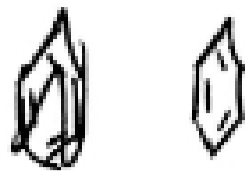
- All C-C-C bonds are 120° . All C's are sp^2 hybridized
- Two sp^2 orbitals will overlap to form the C-C bonds, one sp^2 orbital will form the C-H bond
- All the C-C bonds are 139 pm (halfway between a — and =)
- Each carbon contains a 2p orbital that's perpendicular — we can put these together to form π -bonding orbitals.
- Advantage: explains delocalization of e's, MO theory agrees with Kekulé
- Disadvantages: If both π_2 and π_3 are used, that means that there's some sort of node — how does that work?

E. Third Theory: Resonance (Valence-Bond) Model

- Remember that one of the postulates of resonance theory was that when a molecule can be represented by 2 or more contributing structures, it is not adequately represented by any single structure (Kekulé structure)



- We can estimate the resonance energy of benzene by comparing the heats of hydrogenation of cyclohexene and benzene.
 ΔH (cyclohexene) = -119.7 kJ/mol (1 mol H_2)
 ΔH (benzene) = -208 kJ/mol (3 mol H_2)



3. What if we found the ΔH for a hypothetical molecule: 1,3,5-cyclohexatriene? $\Delta H = 3 \times -119.7 \text{ kJ/mol}$
 $\Delta H (\text{cyclohexatriene}) = -359 \text{ kJ/mol}$

4. Resonance Energy

$$\Delta RE = -359 \text{ kJ/mol} - (-208 \text{ kJ/mol}) = -150.6 \text{ kJ/mol}$$

a.

5. Figure 21.5 explains what we just discussed.



II. The Concept of Aromaticity

- A. If valence bond theory said that benzene has to have alternating single and double bonds, does that mean that cyclobutadiene and ~~□~~ cyclooctatetraene are aromatic compounds?

1. The answer is NO!!!

2. In order to determine aromaticity, we have to use the Hückel Criteria from Aromaticity

B. MO calculations were done by Erich Hückel in the early 1930's for monocyclic, planar molecules in which each atom has a 2p orbital available to form MO's. — He found that if these molecules contain 2, 6, 10, 14, 18, etc πe^- 's, the system should be aromatic

★ ON FINAL ★



1. This is known as Hückel's rule $(4n + 2)\pi$ electrons where n is a positive integer.

C.

In order for a compound to be aromatic, it must meet the following criteria:

1. Has to be cyclic

2. Each atom has a 2p orbital on the ring

3. Be planar (or nearly planar) so that there is continuous overlap of all 2p orbitals of the ring

