Chapter 7. Delocalized Electrons and Their Effect on Stability, Reactivity, and p*Ka*

Learning objectives:

1. Know what is resonance and delocalization.
2. Draw resonance structures by moving electron(s), and predict the order of stability for these resonance structures.
3. Know the effect of resonance on stability, reactivity, and p*Ka* of compounds.

Sections to be covered (in the order of delivery):

7.1 The structure of benzene
7.2 Benzene has delocalized electrons
7.3 Resonance contributors and the resonance hybrid
7.4 How to draw resonance contributors
7.5 The predicted stabilities of resonance contributors
7.6 Delocalization energy is the additional stability delocalized electrons give to a compound
7.7 Examples that illustrate how delocalized electrons affect stability
7.8 Examples that illustrate how delocalized electrons can affect the product of a reaction
7.9 Examples that illustrate how delocalized electrons can affect p*Ka*
7.10 Ultraviolet and visible spectroscopy[#]
7.11 the λ_{max} increases as the nuber of conjugated double bonds increases[#]
7.12 A compound that absorbs visible light is colored[#]

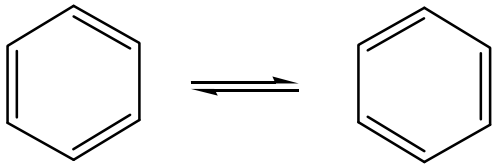
[#] Sections that will be skipped

Recommended additional problems

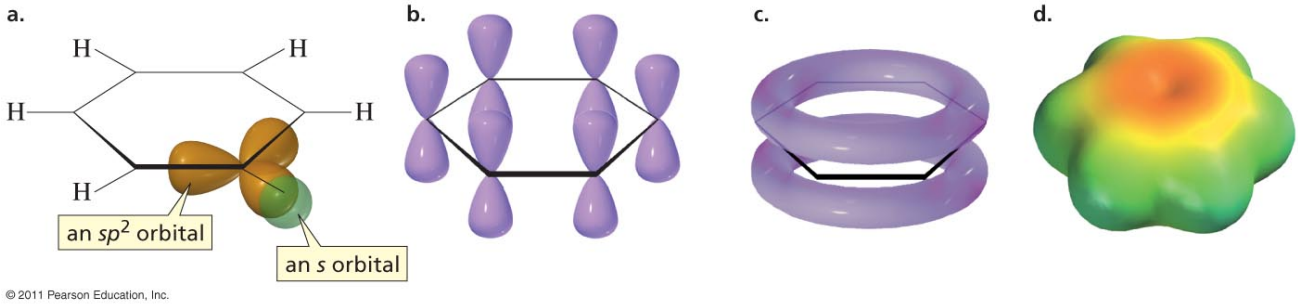
23-27, 31, 33, 34, 38,

7.1 The structure of benzene
7.2 Benzene has delocalized electrons

A. The Kekulé's Model of Benzene



B. The Orbital Model of Benzene



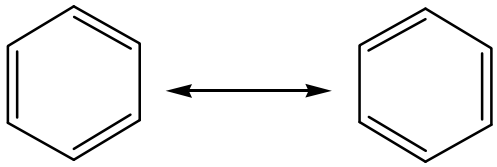
7.3 Resonance contributors and the resonance hybrid

Molecule that has more than one structures, and the real property of this molecule is depicted by the combination of these structures (resonance contributors or resonance structures).

Use ⟷ to represent resonance.

Use ⇌ to represent an equilibrium.

Resonance contributors:



7.4 How to draw resonance contributors

A. Tips for drawing resonance structures

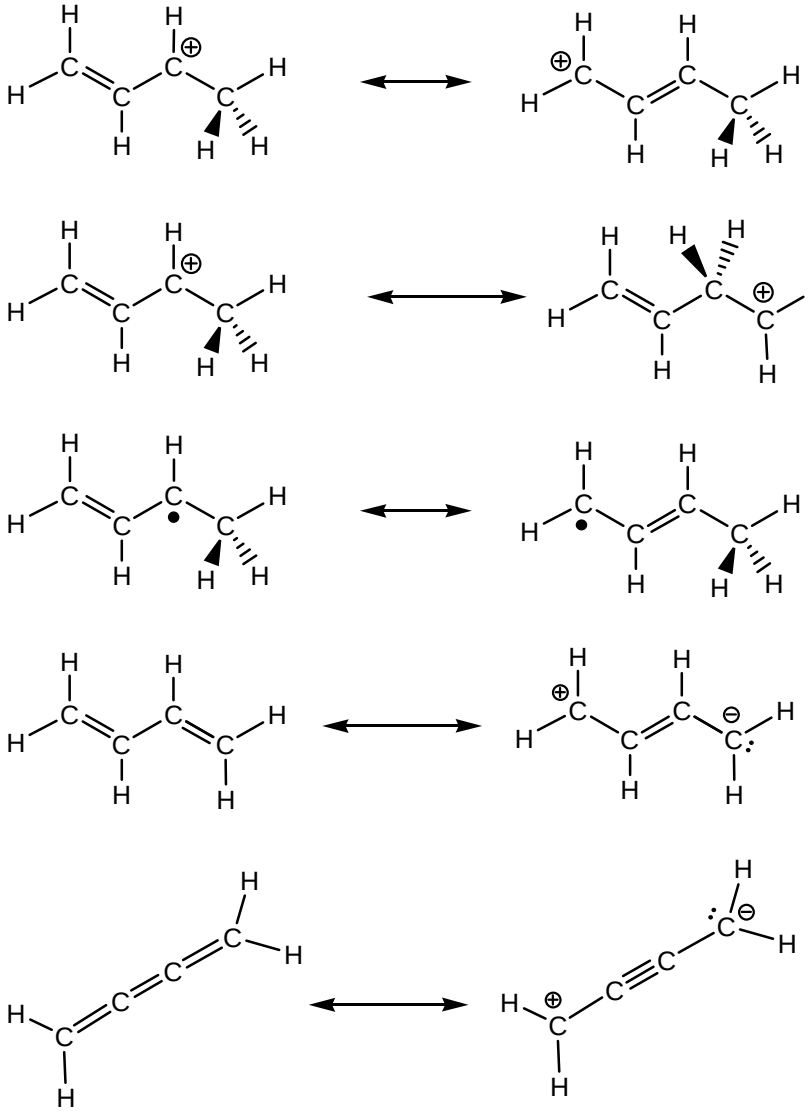
(i) Orbital interaction (overlapping) is essential.

(ii) π electrons and lone-pair electrons are potentially delocalizable (movable) but **not** the σ electrons.

(iii) Indication of electron movement using curved arrow.

Using electron-pushing or arrow-pushing

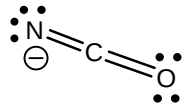
B. Examples: which of the following represent a pair of resonance structures?

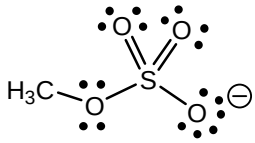


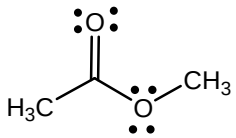
C. Rules for writing acceptable resonance structures

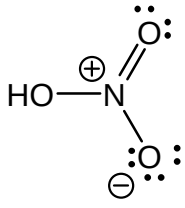
(i) Same number of valence electrons
(ii) Same position (connectivity) of atoms
(iii) Obey rule of covalent bonding:
No more than 2 valence electrons for 1st row elements (H, He).
No more than 8 valence electrons (octet rule) for 2nd row elements.
3rd row elements (P, S) may have more than 8 valence electrons.
(iv) Avoid having positively charged O, N, or halogen with less than 8 valence electrons.

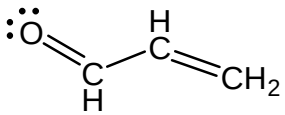
Examples:











7.5 The predicted stabilities of resonance contributors

(i) More (nearly equivalent) resonance structures, better stability

(ii) Prediction of electron density distribution based on the stability among resonance structures (in order of significance):

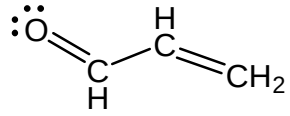
- Neutral molecule is generally more stable than charged molecule.
- Molecule having all the 2nd row atoms meet the octet rule is more stable than the one that does not.
- Negative charge locates on the atom with high electronegativity is preferred.
- Wider separation of positive and negative charges is preferred.

(iii) Chemical properties of molecules can be predicted by resonance effect

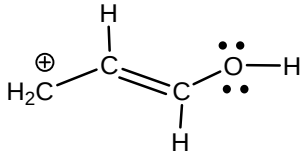
Examples:

(i) Why sulfate (SO_4^{2-}) has more delocalization enery than acetate ($CH_3CO_2^-$)?

(ii) Which atom in the structure below has the highest (or lowest) electron density?



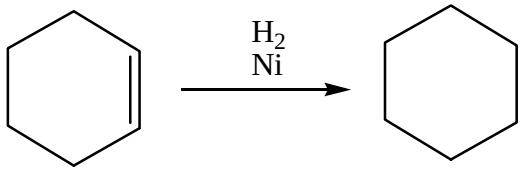
(iii) Outline the possible resonance structures and predict the order of stability.



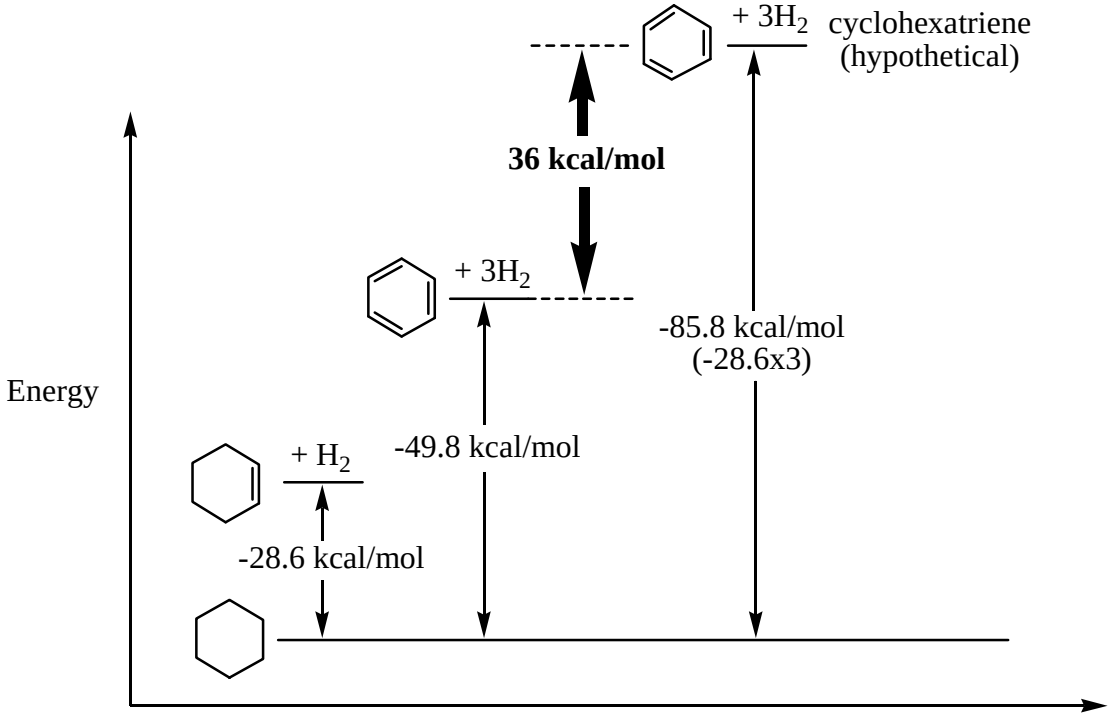
7.6 Delocalization energy is the additional stability delocalized electrons give to a compound

7.7 Examples that illustrate how delocalized electrons affect stability

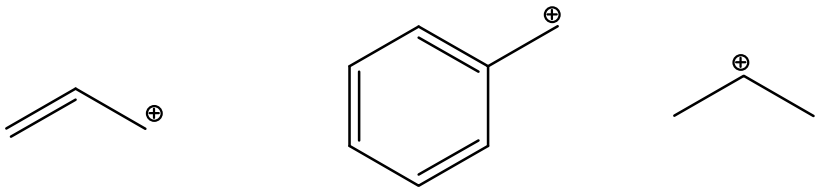
A. The resonance of benzene provides additional stabilization.



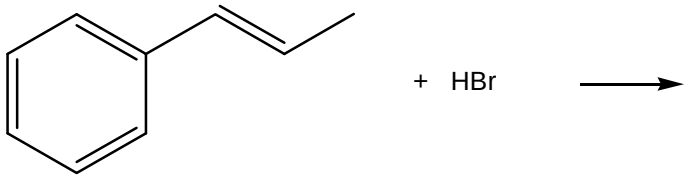
ΔH = -28.6 kcal/mol

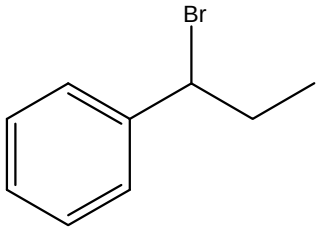


B. Why allylic and benzylic cations are more stable than a secondary alkyl cations?



7.8 Examples that illustrate how delocalized electrons can affect the product of a reaction





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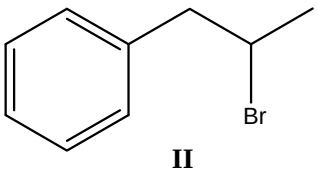

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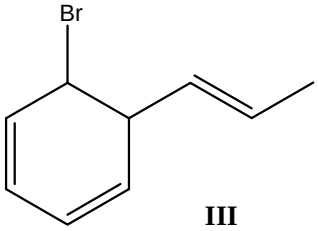


III

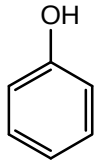
7.9 Examples that illustrate how delocalized electrons can affect p*Ka*

Know resonance effect vs. inductive effect

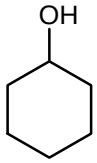
A. Why ethanoic acid (acetic acid), CH_3CO_2H is a stronger acid than methanol, CH_3OH?

B. Why methanesulfonic acid (CH_3SO_3H) is a stronger acid than ethanoic acid (acetic acid), CH_3CO_2H?

C. Why phenol is ore acidic than cyclohexanol?

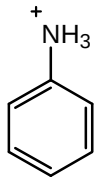


phenol

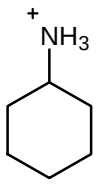


cyclohexanol

D. Why protonated aniline is more acidic than protonated cyclohexylaine?

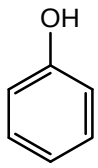


protonated aniline



protonated cyclohexylaine

E. What is the order of acidity for the following compounds?



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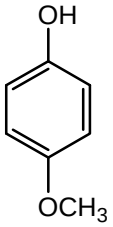

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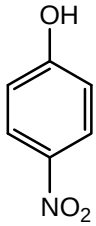
III



IV