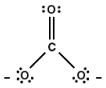
Chapter 7

Electron Delocalization and Resonance

More about Molecular Orbital Theory

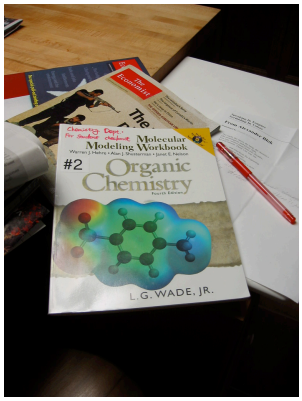
Adapted from Irene Lee
Case Western Reserve University

Resonance

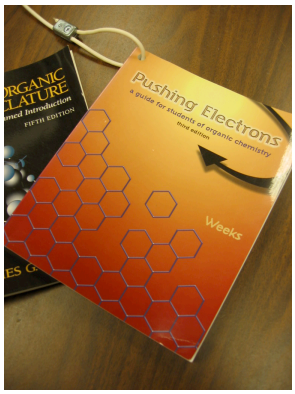


An intellectual explanation for observed differences in bond lengths and energies. The concept of e- delocalization ∝ stability.

Lab: Modeling Exercise

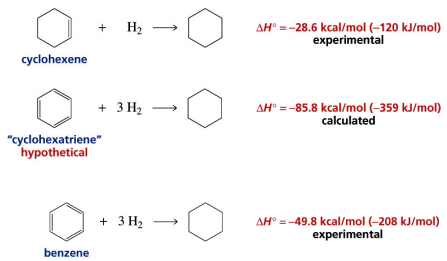


Pushing π electrons: Need double bonds

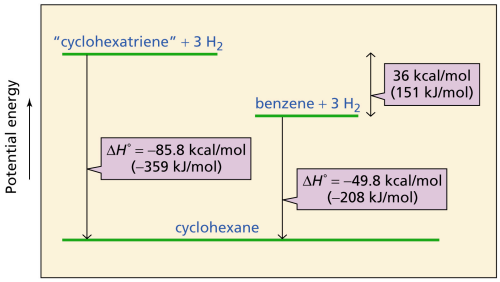


Resonance Energy

- A measure of the extra stability a compound gains from having delocalized electrons

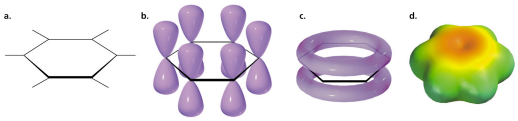


Benzene is stabilized by electron delocalization



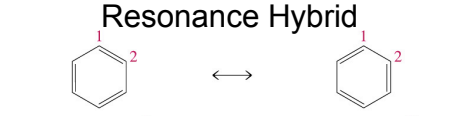
Benzene

- A planar molecule
- Has six identical carbon–carbon bonds



- Each π electron is shared by all six carbons
- The π electrons are delocalized

Resonance Contributors and the Resonance Hybrid

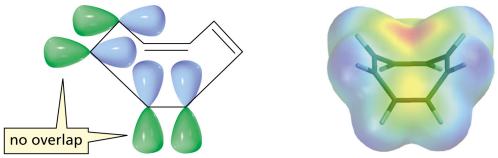


resonance contributor ⟷ resonance contributor

resonance hybrid

Resonance contributors are imaginary; the resonance hybrid is a weighted average that explains experimental observations.

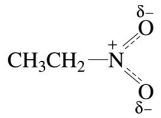
π electrons cannot delocalize in nonplanar molecules



cyclooctatetraene

Drawing Resonance Contributors

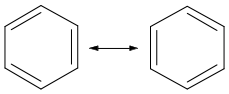
resonance contributor ⟷ resonance contributor



resonance hybrid

Resonance

- Occurs when more than one valid Lewis structure can be written for a particular molecule.

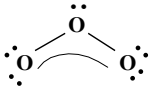


- These are resonance structures. The actual structure is an average of the resonance structures.

Resonance: Delocalized Electron-Pairs

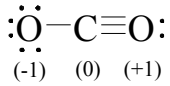
Ozone : O_3

Resonance Hybrid Structure

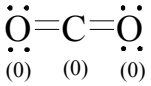


One pair of electron's resonates between the two locations!!

Resonance and Formal Charge

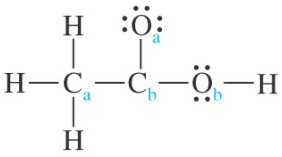


Not as good



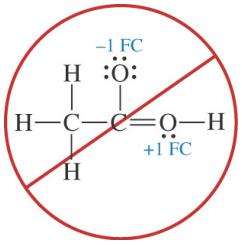
Better

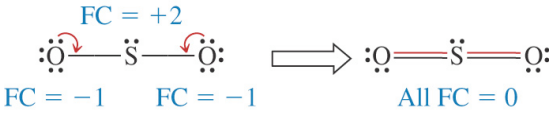
Acetic acid



Complete the Lewis Structure.

Acetic acid





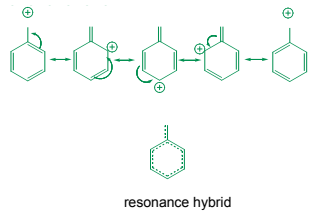
Rules for Drawing Resonance Contributors

1. Only electrons move
2. Only π electrons and lone-pair electrons move
3. The total number of electrons in the molecule does not change
4. The numbers of paired and unpaired electrons do not change

The electrons can be moved in one of the following ways:

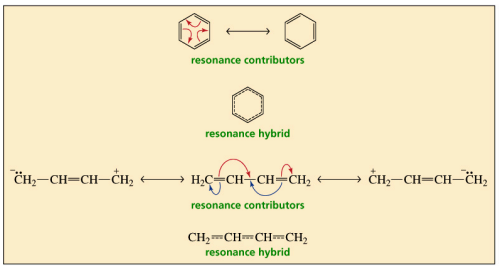
1. Move π electrons toward a positive charge or toward a π bond
2. Move lone-pair electrons toward a π bond
3. Move a single nonbonding electron toward a π bond

Resonance contributors are obtained by moving π electrons toward a positive charge:

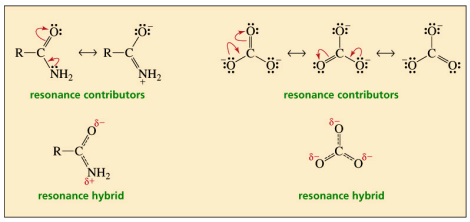


resonance hybrid

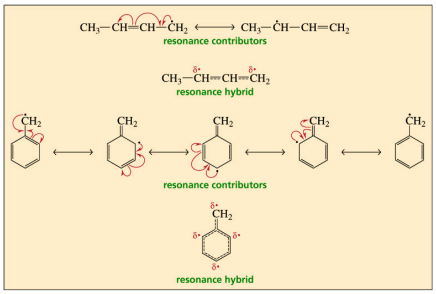
Moving π electrons toward a π bond



Moving a nonbonding pair of electrons toward a π bond



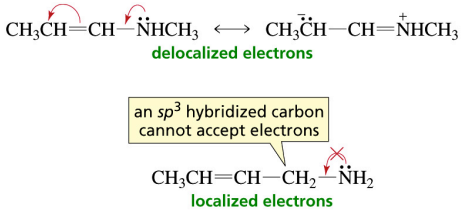
Resonance Structures for the Allylic Radical and for the Benzyl Radical



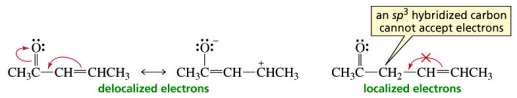
Note

- Electrons move toward an sp^2 carbon but never toward an sp^3 carbon
- Electrons are neither added to nor removed from the molecule when resonance contributors are drawn
- Radicals can also have delocalized electrons if the unpaired electron is on a carbon adjacent to an sp^2 atom

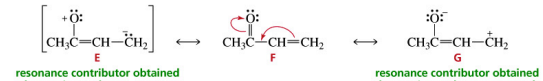
The Difference Between Delocalized and Localized Electrons



Resonance contributors with separated charges are less stable



Electrons always move toward the more electronegative atom



resonance contributor obtained by moving π electrons away from the more electronegative atom

resonance contributor obtained by moving π electrons toward the more electronegative atom

When there is only one way to move the electrons,

movement of the electrons away from the more electronegative atom is better than no movement at all

because electron delocalization makes a molecule more stable

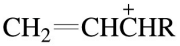
Features that decrease the predicted stability of a contributing resonance structure …

1. An atom with an incomplete octet
2. A negative charge that is not on the most electronegative atom
3. A positive charge that is not on the most electropositive atom
4. Charge separation

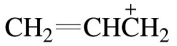
Summary

- The greater the predicted stability of a resonance contributor, the more it contributes to the resonance hybrid
- The greater the number of relatively stable resonance contributors, the greater is the resonance energy
- The more nearly equivalent the resonance contributors, the greater is the resonance energy

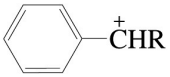
Resonance-Stabilized Cations



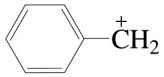
an allylic cation



the allyl cation

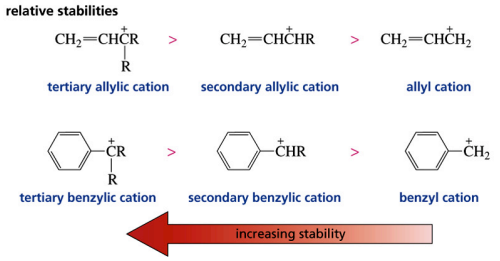


a benzylic cation

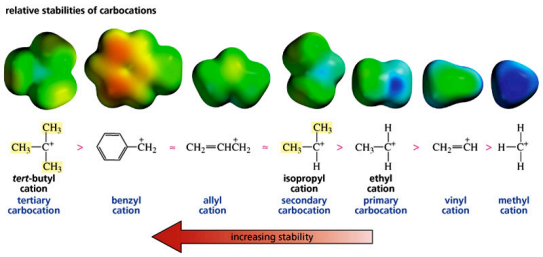


the benzyl cation

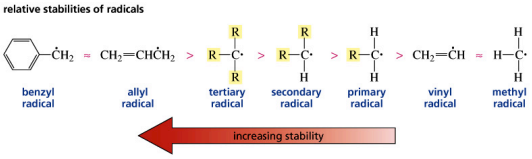
Relative Stabilities of Allylic and Benzylic Cations



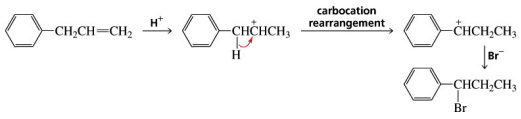
Relative Stabilities of Carbocations



Relative Stabilities of Radicals



Some Chemical Consequences of Electron Delocalization



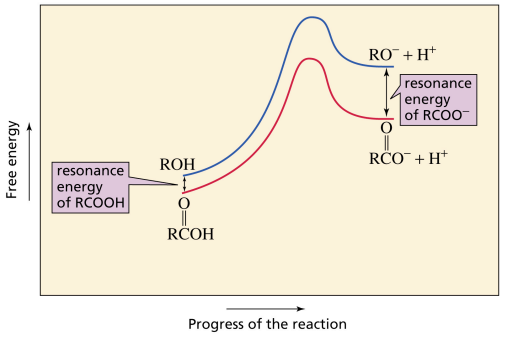
Why is RCO_2H more acidic than ROH?

Table 7.1 Approximate pK_a Values

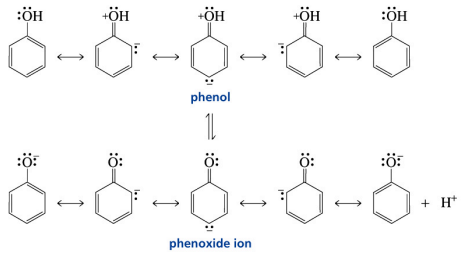
$pK_a < 0$	$pK_a \approx 5$	$pK_a \approx 10$	$pK_a \approx 15$
ROH_2^+	$RCOH$	RNH_3^+	ROH
$RCOH$ (+OH)	NH_3^+	OH	H_2O
H_3O^+			

Electron withdrawal by the double-bonded oxygen decreases the electron density of the negatively charged oxygen, thereby stabilizing the conjugated base (the carboxylate)

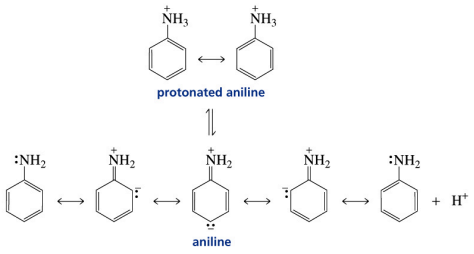
Increased resonance stabilization of the conjugated base



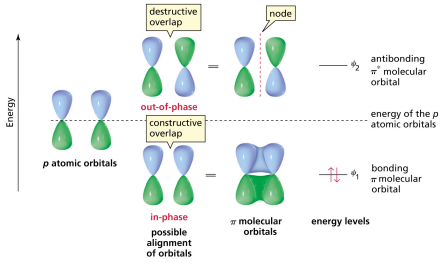
Account for the Acidity of Phenol by Resonance Stabilization



Account for the Acidity of Protonated Aniline by Resonance Stabilization

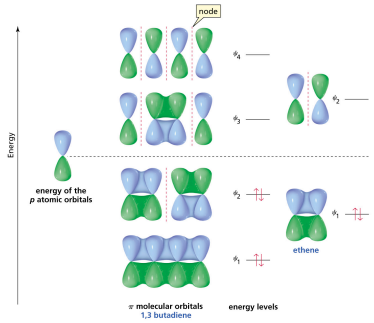


A Molecular Orbital Description of Stability



- Bonding MO: constructive (in-phase) overlap
- Antibonding MO: destructive (out-of-phase) overlap

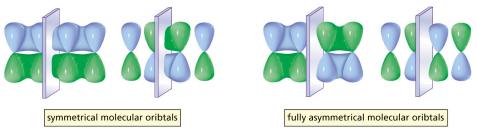
The Molecular Orbitals of 1,3-Butadiene



Symmetry in Molecular Orbitals

ψ_1 and ψ_3 in 1,3-butadiene are symmetrical molecular orbitals

ψ_2 and ψ_4 in 1,3-butadiene are fully asymmetrical orbitals

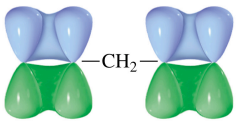


- The highest-energy molecular orbital of 1,3-butadiene that contains electrons is ψ_2 (HOMO)
- The lowest-energy molecular orbital of 1,3-butadiene that does not contain electrons is ψ_3 (LUMO)
- HOMO = the highest occupied molecular orbital
- LUMO = the lowest unoccupied orbital

Consider the π molecular orbitals of 1,4-pentadiene:

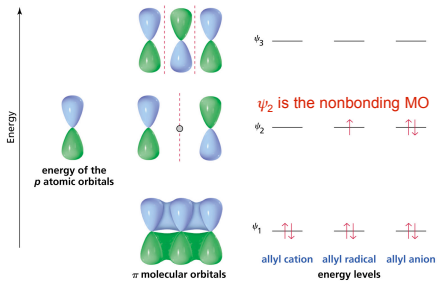
$CH_2{=}CHCH_2CH{=}CH_2$

1,4-pentadiene



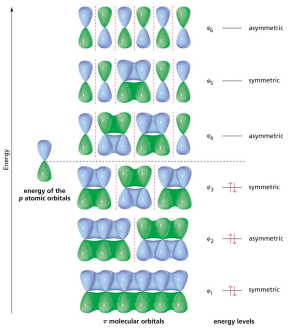
This compound has four π electrons that are completely separated from one another

The Molecular Orbitals of the Allyl System

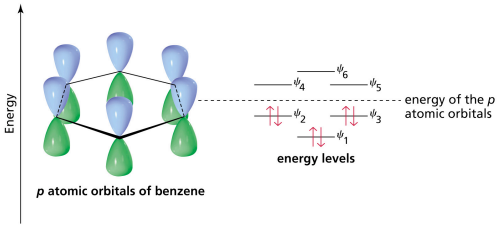


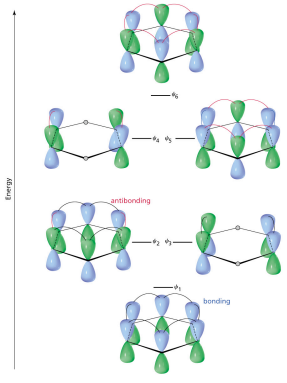
No overlap between the *p* orbitals: the nonbonding MO

The Molecular Orbitals of 1,3,5-Hexatriene



Benzene has six π molecular orbitals





Benzene is unusually stable because of large delocalization energies