

**ASSIGNED READINGS:**

**TODAY'S CLASS:**

- 1.18 Effect of structure on pKa
- 1.19 Introduction to delocalized electrons & resonance
- 7.2-7.5 Understanding & drawing resonance structures
- 7.10 Effect of electron delocalization on pKa

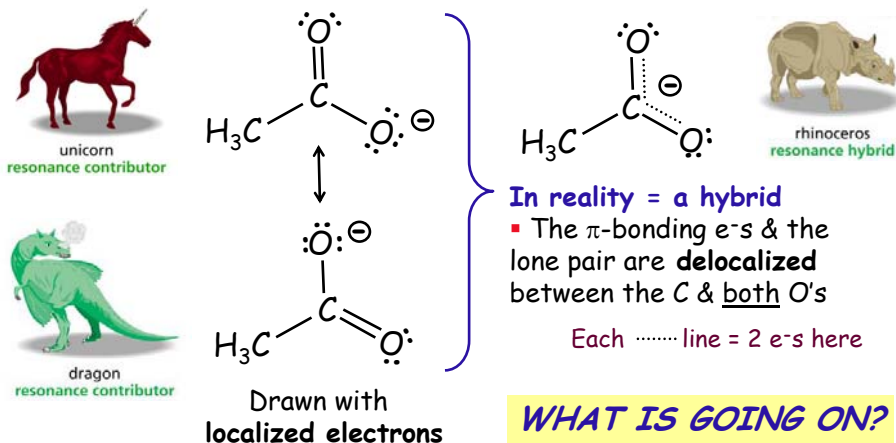
**NEXT CLASS: finish Ch.1, start Ch.2 (?)**

<http://artsandscience.concordia.ca/facstaff/P-R/rogers>

(1)

**Resonance Contributors and the Resonance Hybrid**

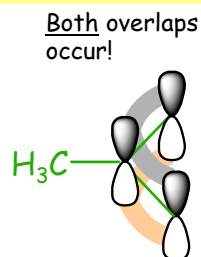
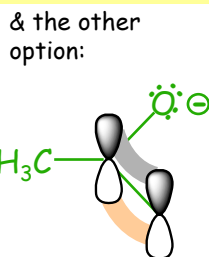
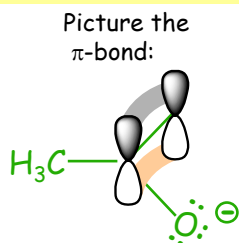
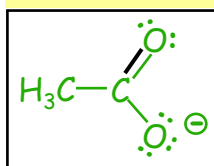
Resonance contributors are imaginary, but the resonance hybrid is **real**



**WHAT IS GOING ON?**

(2)

## Resonance requires an "extended $\pi$ -system"



An extended  $\pi$ -system

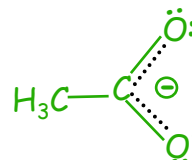
= 3 or more adjacent atoms with aligned p-orbitals

Atoms must be:

- $sp^2$  or  $sp$  hybridized (need unhybridized p-orbitals)
- directly  $\sigma$ -bonded to each other

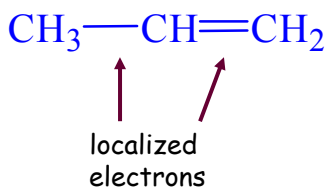
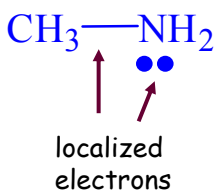
Result: a very stable, *delocalized*  $\pi$ -bond

- parallel p-orbitals WILL overlap (*E-favourable*)
- e<sup>-</sup>s become spread over several atoms
- more stable than a 2-atom  $\pi$ -bond

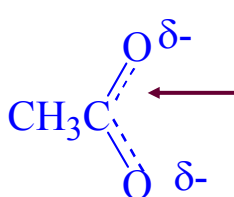


(3)

## Localized Versus Delocalized Electrons



Do not have an extended array of adjacent p-orbitals



delocalized electrons

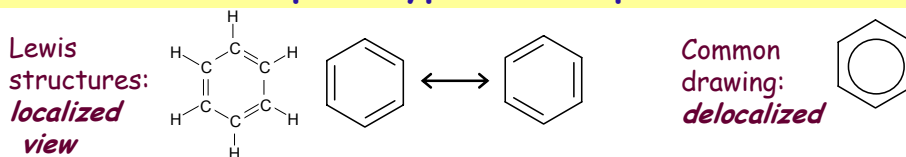
p-orbitals on 3 atoms in a row are able to align parallel  
 → overlap occurs over multiple atoms  
 → makes a bonding M.O.

TYPICAL DELOCALIZATION SCENARIOS:  $-sp^2-sp^2-sp^2-\dots$

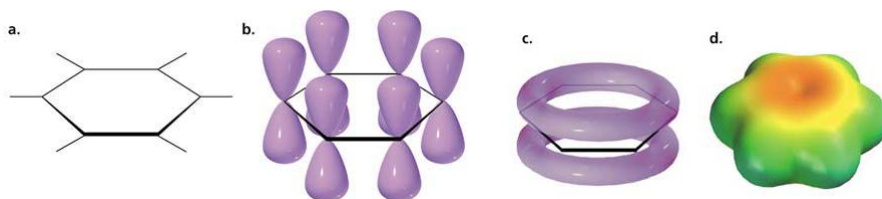
1. Lone pair on atom next to a  $\pi$ -bond
2. Alternating double & single bonds in a structure

(4)

## Benzene: the prototypical example of resonance

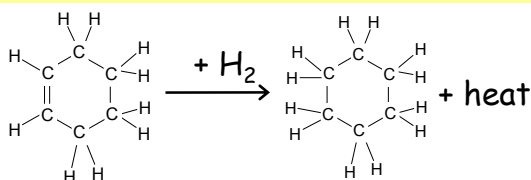


- A planar molecule with “alternating” single & double bonds
- All carbon atoms are  $sp^2$  hybridized  $\rightarrow$  all p-orbitals actually overlap!
- From experiment: all 6 C-C bond distances are same between single & double bond (B.O. = 1.5)
- The 6  $\pi$ -electrons are delocalized: each  $\pi$ -electron shared by every C



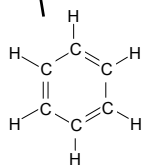
(5)

## How much stabilization does resonance provide?



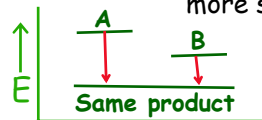
Observed  $\Delta H_{rxn}$  for 6-C ring with 1 localized C=C bond:  
 $\Rightarrow \Delta H_{rxn} = -120 \text{ kJ/mol}$

Expected  $\Delta H_{rxn}$  for 6-C ring with 3 localized C=C bonds:  
 $\times 3 \Rightarrow \Delta H_{rxn} = -359 \text{ kJ/mol}$



Experimental evidence: heat of reaction with  $H_2$

- Compounds with C=C bonds react exothermically with  $H_2$
- Less heat  $\Rightarrow$  reactant was more stable



Measured  $\Delta H_{rxn}$  for benzene (3 delocalized C=C bonds):  
 $\Rightarrow \Delta H_{rxn} = -208 \text{ kJ/mol}$

Difference in E between localized vs. delocalized = resonance energy

- larger resonance E  $\Rightarrow$  greater stabilization due to delocalization

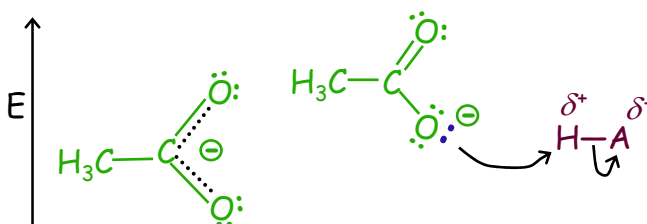
(6)

## Why is a resonance-stabilized anion a rather weak base?

See 7.10

Remember the mechanism of deprotonation:

- a base attacks a  $\delta^+$  H using its lone pair
- to form a bond: pair of e<sup>-</sup>s must localize between two atoms
- a delocalized lone pair must be "rounded up" into one orbital first!
- In terms of energetics: delocalized e<sup>-</sup>s are stabilized  
→ lower in energy than if localized  
→ less driving force for reaction



(7)

### Larger # resonance structures (resonance contributors)

⇒ more extensive delocalization ⇒ greater stabilization

How do we know how many to draw?

Will they all contribute the same to the resonance hybrid?

### Rules for Drawing Resonance Contributors: Part 1

1. The molecule's  $\sigma$ -framework stays the same:  
atoms do not move, & their  $\sigma$ -bonds don't change.
2. Only  $\pi$ -electrons and lone-pair electrons move.
3. The total number of e<sup>-</sup>s in the molecule does not change.
4. The numbers of paired e<sup>-</sup>s and unpaired e<sup>-</sup>s do not change.
5. The total charge on the molecule does not change.

Remember why the e<sup>-</sup>s move:

being delocalized via overlapping p-orbitals

(8)

## Rules for Drawing Resonance Contributors: Part 2

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

1. Move  $\pi$  e<sup>-</sup>s toward a positive charge or toward a  $\pi$  bond
2. Move lone-pair electrons toward a  $\pi$  bond
3. Move a single nonbonding electron toward a  $\pi$  bond

WHY?

→ towards an  $sp^2$ -hybridized atom (p-orbital)

*Atoms with a lone pair are often  $sp^3$ -hybridized.*

*How can they participate in resonance???*

- Remember: p-p ( $\pi$ -type) overlap is energetically favourable
- Thus: atom can actually change to  $sp^2$ -hybridization
  - the e<sup>-</sup> repulsion that normally forces it to go  $sp^3$  will be compensated for by the stabilization provided by the  $\pi$  overlap

(9)

Draw resonance structures (if appropriate!)



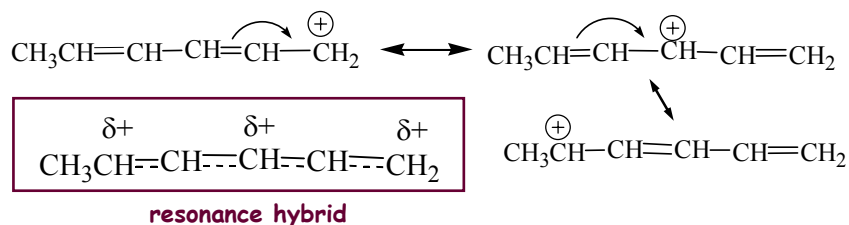
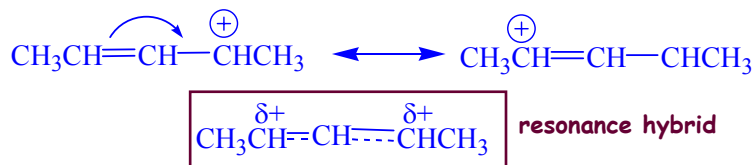
If the atom carrying lone pair were to **rehybridize** so it had an unhybridized p-orbital, could delocalization then occur?

Note: "push arrows" ( $1 \rightarrow = 2e^-$ ) to indicate path e<sup>-</sup>s must "travel" to make transitions between your localized resonance structures

So: which of these will be the stronger base?

(10)

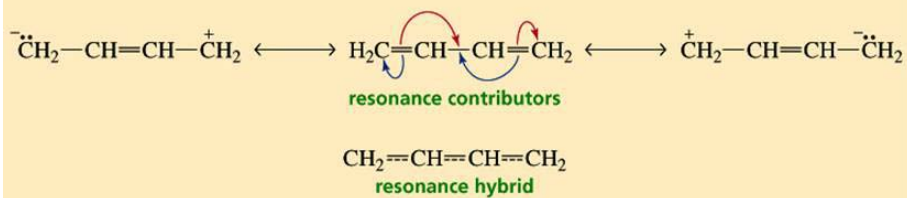
Resonance contributors are obtained by moving  $\pi$  electrons toward a positive charge:



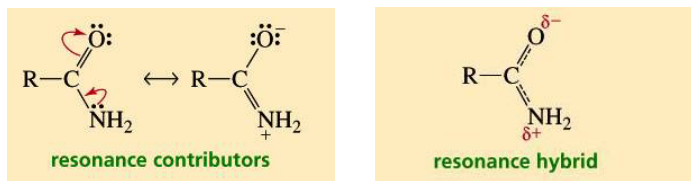
More resonance contributors, so more stable hybrid

(11)

Resonance contributors also obtained by moving  $\pi$ -electrons toward a  $\pi$ -bond (an  $sp^2$  atom!):

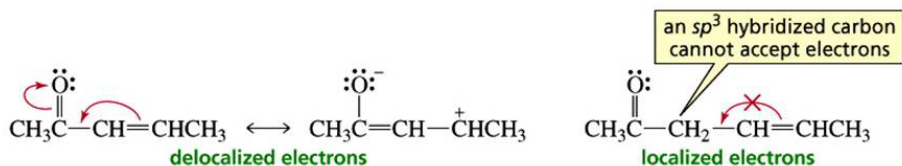


Resonance contributors also obtained by moving lone pair  $e^-$ s toward a  $\pi$ -bond (an  $sp^2$ -atom):



(12)

BUT: Never move p-electrons toward an  $sp^3$  atom:



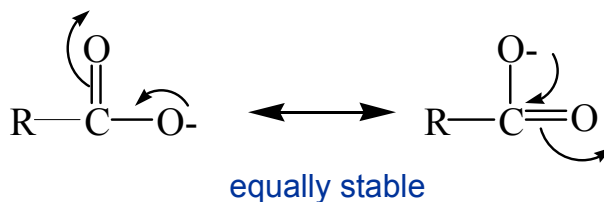
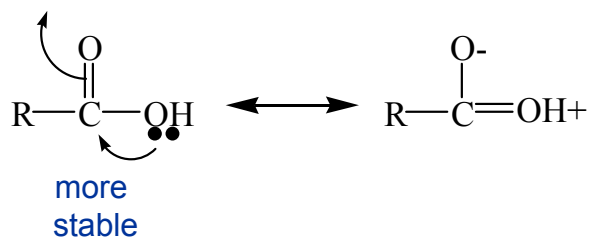
(13)

### Features that decrease the predicted stability of a contributing resonance structure ...

1. An atom with an incomplete octet ("open shell")
  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
- } Same idea...

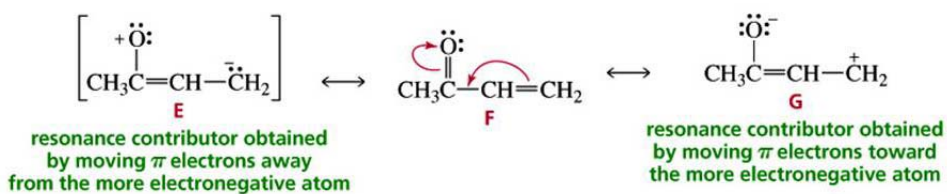
(14)

Resonance contributors with separated charges are less stable



(15)

Electrons prefer to move toward the more electronegative atom (as you might expect...)



- 1 open-shell atom
- charge separation
- -ve charge on less electroneg. atom
- Least stable
- Does not contribute very much

- all atoms closed shell
- no charge separation
- Most stable
- Contributes most to character of hybrid

- 1 open-shell atom
- charge separation
- -ve charge on more electroneg. atom
- Moderately stable
- Contributes somewhat to hybrid

(16)



## ASSIGNED READINGS

### BEFORE NEXT LECTURE:

**Read:** Ch.1: 1.20-1.21  
Ch.7: 7.2-7.5, 7.10

**Practice:** Lewis structures, resonance structures