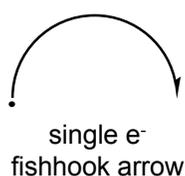
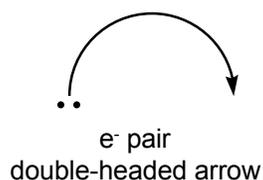


Representing Change in Elec. Configuration

Curved Arrow Notation

shows “movement” of electrons (electron flow)

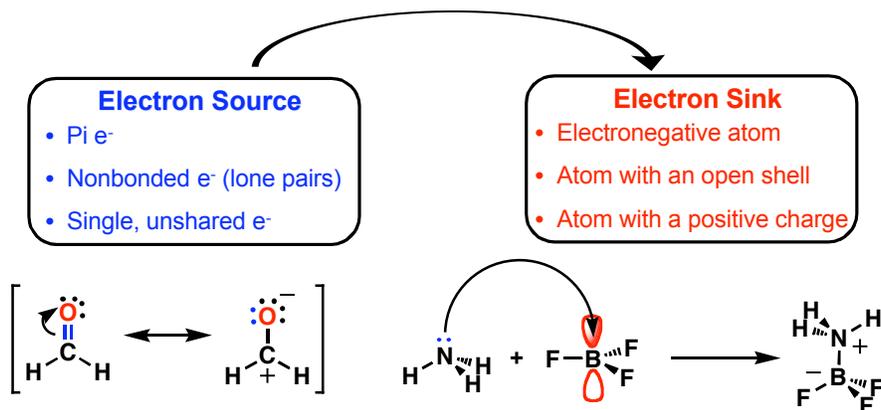
Electrons move from a “source” to a “sink”



Electron redistribution (change in configuration)
is the origin of chemical change (reactivity)

Curved Arrow Notation

1. Graphical way to depict changes in electron configuration during a reaction.
2. Show how electron configurations can be rearranged to generate an alternative bonding representation of the same structure (resonance)



Arrows must be very precise on problem sets and exams!
Electrons must move from “source” to “sink”

Describing Resonance with Curved Arrows

Mechanics

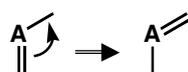
1. Nonbonding pair to adjacent bond (vertex-to-edge transfer)



2. Bonding pair to an adjacent atom (edge-to-vertex transfer)



3. Bonding pair to an adjacent bond (vertex-edge-vertex transfer)



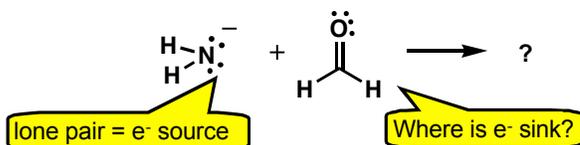
Notice that the sigma network does not change and the placement of atoms remains the same.

Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

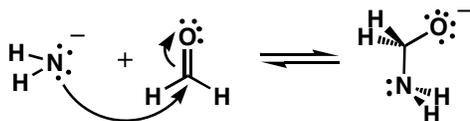
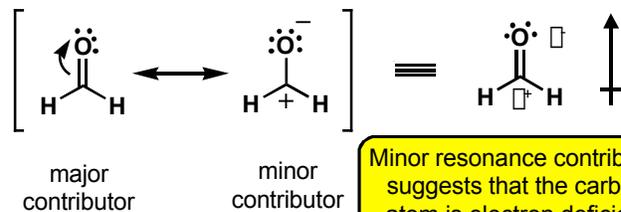
Rules for Resonance Structures

- Resonance forms are imaginary
- They differ only in the placement of pi or nonbonding electrons, atom placement is the same
(Electron movement takes place in the pi system, not sigma system)
- Must be valid Lewis structures and obey the rules of valency
- Difference resonance forms don't have to be energetically equivalent
(Lower energy resonance structures contribute most to overall structure of molecule)
- The resonance hybrid (weighted average) is more stable than any individual resonance form
- Use a double-headed arrow between structures and brackets around them, keep track of lone pairs and formal charges

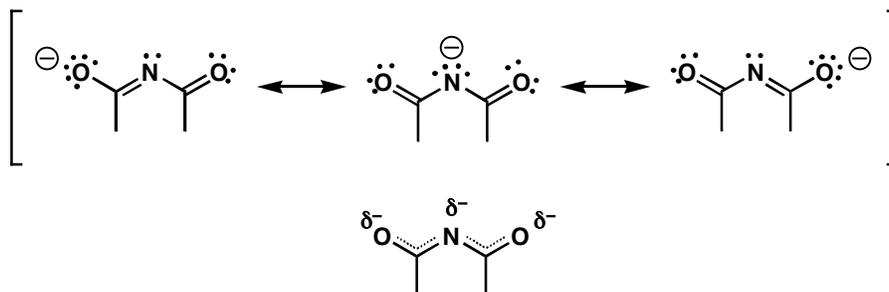
Using Resonance to Predict Site of Reactivity



Look at resonance contributors:
e⁻ flow from pi bond to electronegative oxygen



Relative Energies of Resonance Contributors



Resonance hybrid: *weighted average* of resonance contributors

Which structure contributes more in resonance hybrid?

In other words: which structure is more **STABLE**
(has lower potential **ENERGY**)

Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign. Used with permission. Adapted by Kimberly Berkowski.

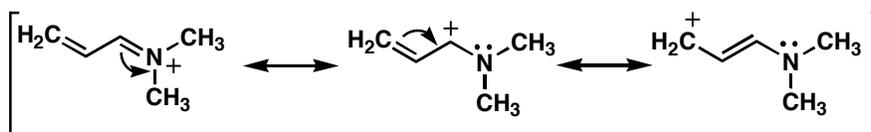
Predicting Energies of Resonance Structures

Which structure counts more in resonance hybrid?

Resonance hybrid: *weighted* average of resonance contributors

In other words: which structure is more **STABLE** with a lower **ENERGY**

- Filled octets for second row elements (C, N, O, F)
possible for **C only** to be electron deficient ($6 e^-$)
- Minimum # of formal charges and maximum number of bonds
- Negative charge on most electronegative atom ($C < N < O$)
- Minimize charge separation, keep formal charges close together

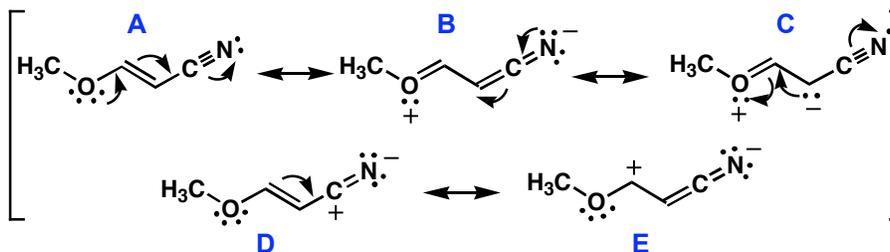


Major
Follows guidelines

Minor
Violates i

Minor
Violates i

Predicting Relative Energies



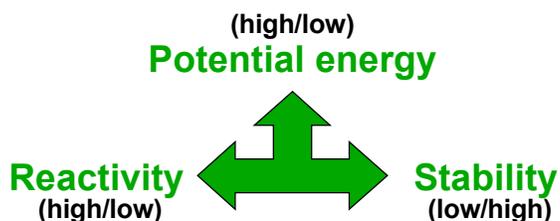
- A: follows all guidelines
 B: violates ii (2 formal charges)
 C: violates ii (2 formal charges) and iii (negative charge on C)
 D: violates i ($6 e^-$ on C) and ii (2 formal charges)
 E: violates i ($6 e^-$ on C), ii (2 formal charges), and iv (more charge separation than D)

Relative energy: $A \ll B < C \ll D < E$

Relative contribution to resonance hybrid: $A > B > C > D > E$

Structure and Energy

Goal: Determine relative **energy** of a compound by analyzing it's **structure**

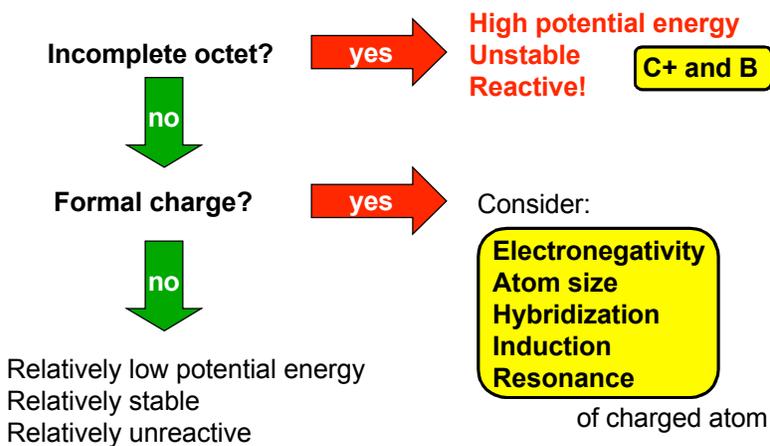


Analyzing the energy of a structure allows you to:

- Determine relative energies of resonance contributors
- Determine which reaction will proceed faster
- Determine position of equilibrium

Courtesy of Jeffrey S. Moore, Department of Chemistry, University of Illinois at Urbana-Champaign.
Used with permission. Adapted by Kimberly Berkowski.

Determining Molecule Stability from Structure

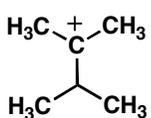


Most important parameters in determining stability:

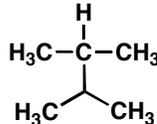
1. Incomplete octet
2. Formal charge

Examples of Most Important Parameters

Incomplete octet

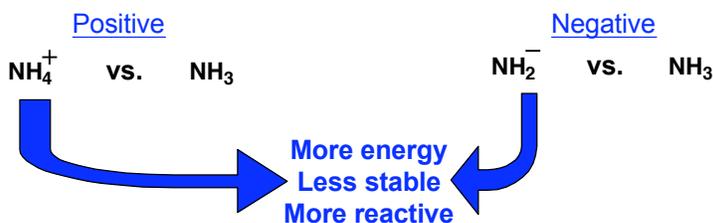


High potential energy
Unstable
Reactive!



Low potential energy
Stable
Unreactive

Charged vs. Noncharged



Stability of Molecules with Formal Charges

1. Electronegativity
2. Atom size
3. Hybridization
4. Induction
5. Resonance

Must consider the effect of each parameter for both **positive** and **negative** charged atoms

Meaningful comparison = only 1 factor varied

1. Electronegativity

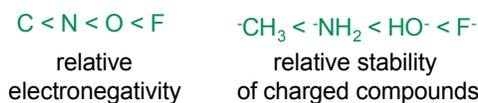
Criteria: atoms in **same row** and have same **# of electron pair domains**

(Atoms in same row are relatively the same size)

For Negative Charges:

The more electronegative the atom, the better it can hold a negative charge

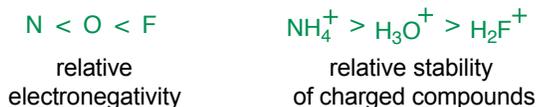
Electronegativity increases stability (lowers energy)



For Positive Charges:

The more electronegative the atom, the worse it can hold a positive charge

Electronegativity decreases stability (raises energy)



2. Atom Size

Criteria: atoms in **same column** and have same **# of electron pair domains**

(Atoms in same column significantly different size)

For Negative Charges:

The larger the atom, the greater the stability

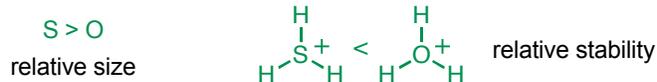
Surplus of electrons, electrons repel each other
larger atoms allow this charge to spread out (lowering the charge density)



For Positive Charges:

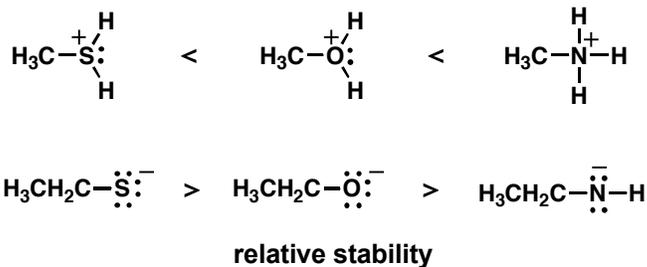
The smaller the atom, the greater the stability

Surplus of protons in the nucleus
Smaller atoms allow the valence electrons to be held more tightly to the (+) nucleus



Example: N vs O vs S

When comparing atoms of different size, size matters more than electronegativity



Nitrogen is most effective at stabilizing a positive charge and least effective at stabilizing a negative charge

Sulfur is most effective at stabilizing a negative charge and least effective at stabilizing a positive charge

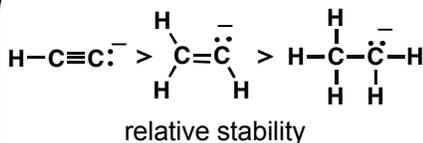
3. Hybridization



The more s character

the closer the electrons are held to the (+) nucleus
the more electron withdrawing the orbital

For Negative Charges:

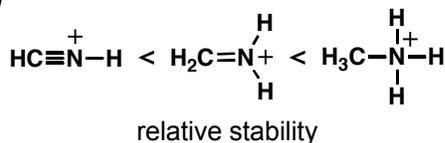


(-) stabilized by greater s character

1. the electrons are held closer to the (+) nucleus (more stable)
2. more electron withdrawing

Energy is decreased!

For Positive Charges:



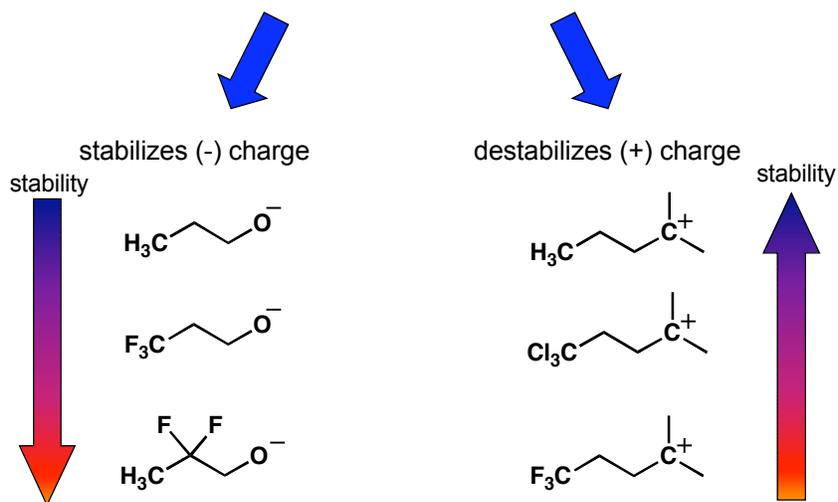
(+) destabilized by greater s character

1. the electrons are held closer to the (+) nucleus - less accessible for bonding to an atom
2. more electron withdrawing

Energy is increased!

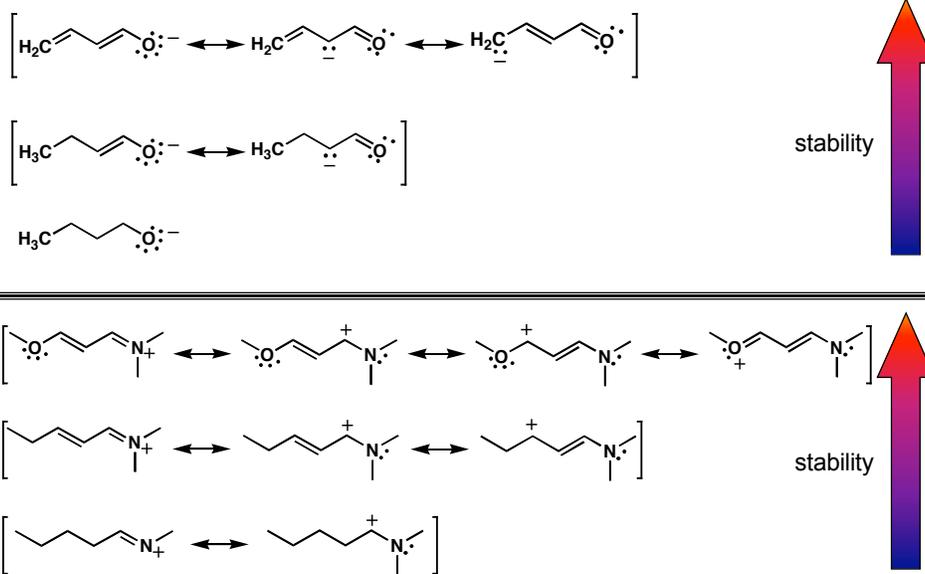
4. Inductive Effects - Electron Withdrawing

electronegative atoms draw electron density towards them through the **sigma bond network**



5. Resonance

The more the charge is spread out (delocalized), the more stable the structure

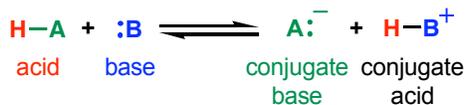


Acidity of Organic Molecules

Brønsted-Lowry

Acid - donates a hydrogen ion (H⁺)

Base - accepts H⁺



Lewis

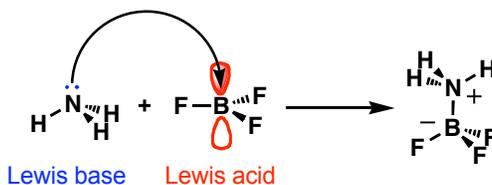
Acid - accepts an electron pair to form a bond

(must have empty or easily vacated orbital, or polar bond to a hydrogen)

Base - donates an electron pair to form a bond (must have lone pairs to donate)

Lewis acid is an "electrophile"
it seeks electrons

Lewis base is a "nucleophile"
it seeks a nucleus



Lewis Acids and Bases

Lewis Acid

Accepts electron pair

if H⁺ is doing
the accepting

"acid"

if atom other
than H⁺ is doing
the accepting

"electrophile"

Lewis Base

Donates electron pair

If donates electron
pair to H⁺

"base"

If donates
electron pair
to atom other
than H⁺

"nucleophile"

"nucleophilic site" - has electron density to donate

"electrophilic site" - wants more electron density

Acid Strength

ability to donate H⁺
the stronger the acid, the better able to donate a proton



Can act as either acid or base

$$K_{eq} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

Dilute solution -
[H₂O] ~55.6 M
(constant)

acidity constant

$$K_a = K_{eq}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

pH when half of the acid molecules are dissociated

$$\text{p}K_a = -\log K_a$$

Stronger Acid

equilibrium toward right

larger K_a

smaller $\text{p}K_a$

weaker (more stable) conjugate base

Weaker Acid

equilibrium toward left

smaller K_a

larger $\text{p}K_a$

stronger (less stable) conjugate base

Why should we care so much about $\text{p}K_a$?

acid-base reactions comprise a major set of reactions in organic chemistry

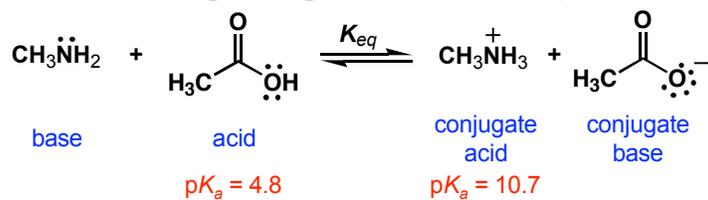
“The key to understanding organic chemical reactions is knowledge of acids and bases.”

-Richard F. Daley

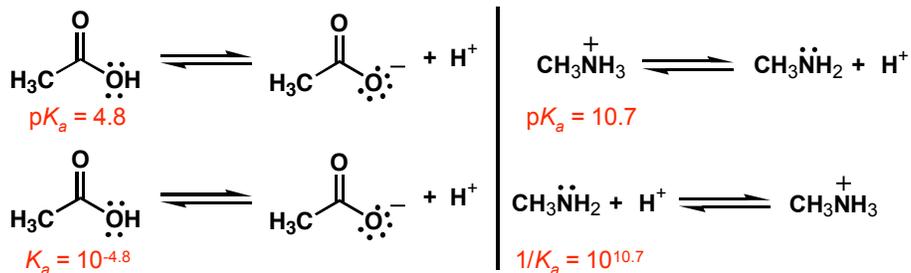
Learn $\text{p}K_a$ values on **general $\text{p}K_a$ handout** (understand relative values)
Understand $\text{p}K_a$ values on **specific $\text{p}K_a$ handout** (for your reference)

By knowing a few specific values, you can compare the structure of the compound with a known $\text{p}K_a$ to predict $\text{p}K_a$ of an unknown compound

Determining Magnitude of Equilibrium



H⁺ will always go from the stronger acid to the stronger base



$$K_{eq} = K_a \times 1/K_a = 10^{5.9}$$