

CHEM 109A

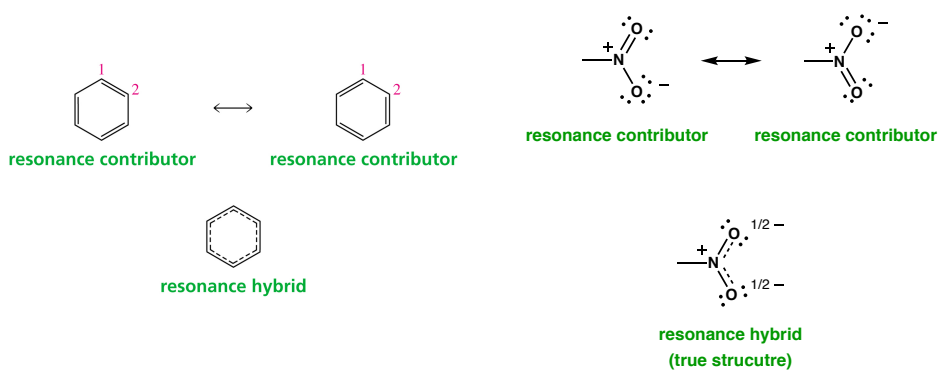
Organic Chemistry

<https://labs.chem.ucsb.edu/zakarian/armen/courses.html>

Chapter 8

Delocalized Electrons: The Resonance Effect
Aromaticity: Benzene

Resonance Contributors and the Resonance Hybrid



The Greater the Number of Relatively Stable Resonance Contributors and the More Nearly Equivalent Their Structures, the Greater the Resonance Energy (a.k.a. delocalization energy)

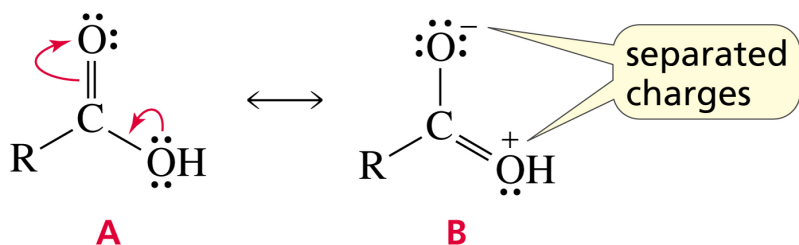
Rules for Drawing Resonance Contributors

1. Only **electrons move**. Atoms never move.
2. Only **π electrons** (electrons in π bonds) and **lone-pair electrons** can move. (Sigma (σ) electrons never move.
3. The total **number of electrons** in the molecule **does not change**.
4. Electrons always move to an **sp^2 or sp** atom; **sp^3** atoms cannot accept electrons.

Features that decrease the “stability” of resonance contributors [relative to each other], and therefore their contributions

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 on an electronegative atom.
4. **Separated charges**.

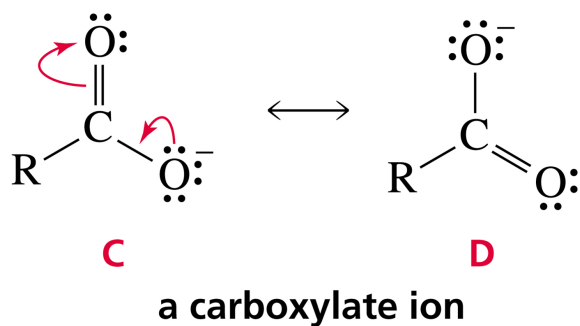
A Has a Greater Predicted Stability Than B



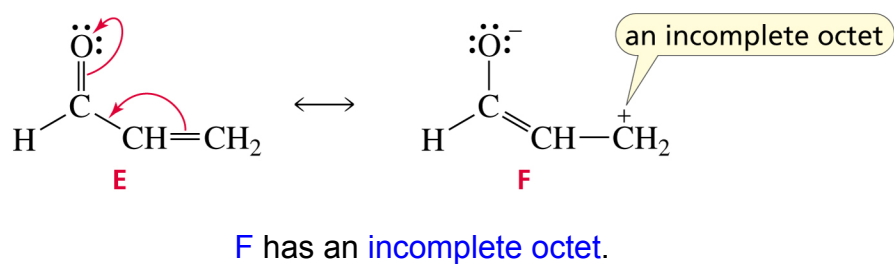
a carboxylic acid

B has **separated charges**.

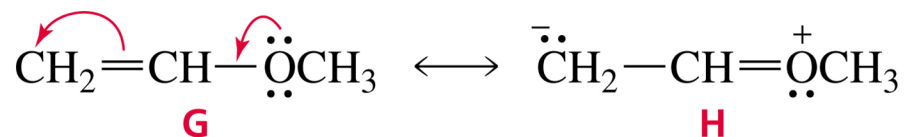
C and D Have an Equal Predicted Stability



E Has a Greater Predicted Stability Than F

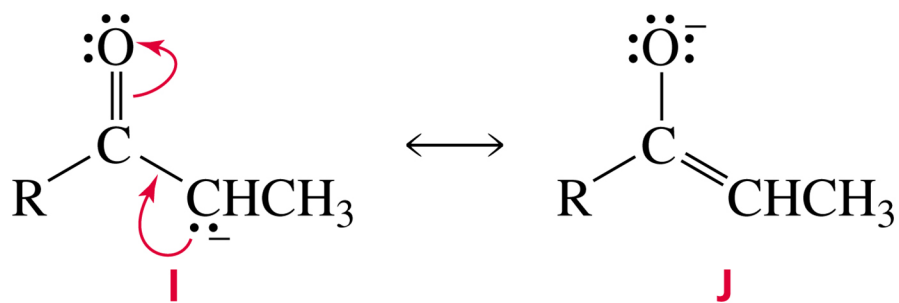


G Has a Greater Predicted Stability Than **H**



H has a positive charge on an electronegative atom.

J Has a Greater Predicted Stability Than **I**



J has a negative charge on oxygen, whereas **I** has negative charge on carbon.

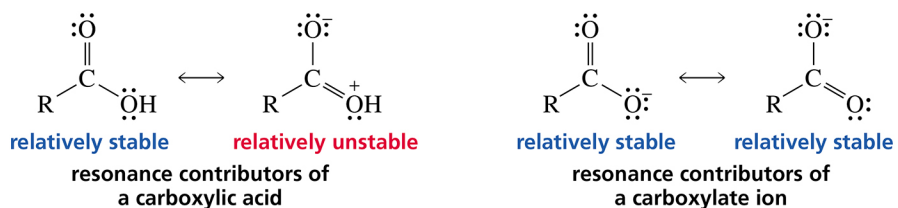
Delocalization Energy

The **delocalization energy** is the **extra stability** a compound has as a result of having **delocalized electrons**.

Electron delocalization is also called **resonance**.
Therefore,
delocalization energy is also called **resonance energy**.

The **resonance hybrid** is **more stable** than any of its resonance contributors is predicted to be.

The Greater the Number of Relatively Stable Resonance Contributors, the Greater the Delocalization Energy



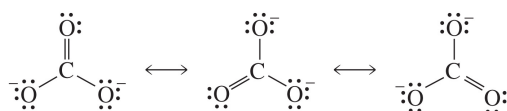
The delocalization energy is **greater** for the **carboxylate ion** than for the **carboxylic acid**.

The Greater the Number of Relatively Stable Resonance Contributors and the More Nearly Equivalent Their Structures, the Greater the Resonance Energy

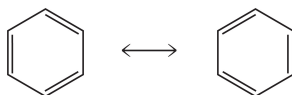
little delocalization energy: **one relatively stable** resonance contributor



significant delocalization energy: **three relatively stable** resonance contributors



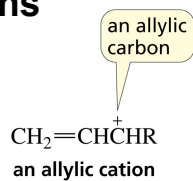
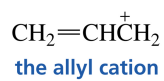
significant delocalization energy: **two equivalent** resonance contributors



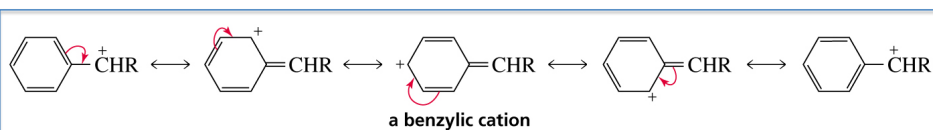
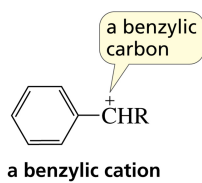
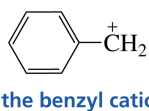
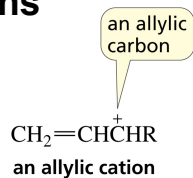
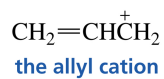
Summary

- 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 the delocalization energy**.
- The more **nearly equivalent** the resonance contributors, the **greater the delocalization energy**.

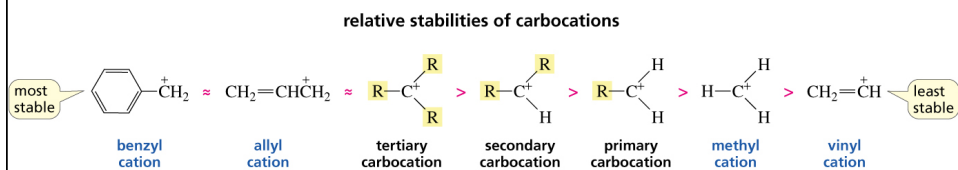
Allylic and Benzylic Cations



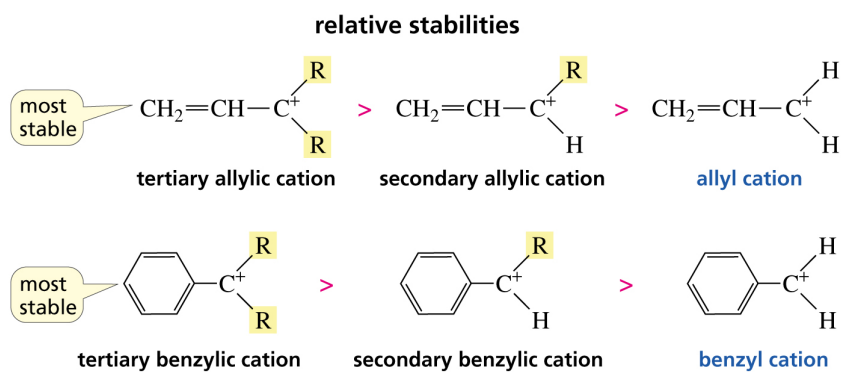
Allylic and Benzylic Cations



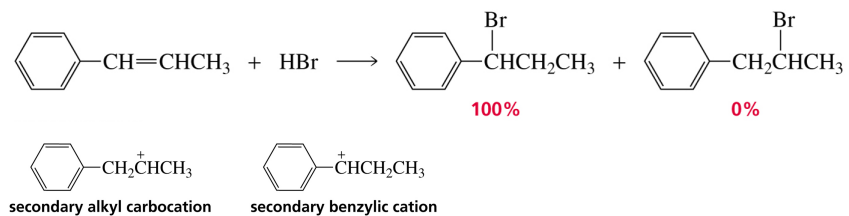
Relative Stabilities of Carbocations



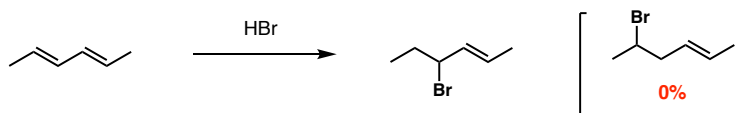
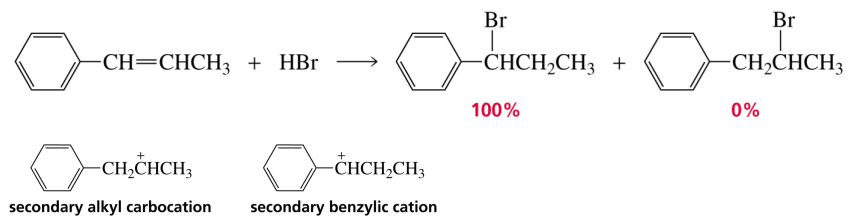
Relative Stabilities of Carbocations



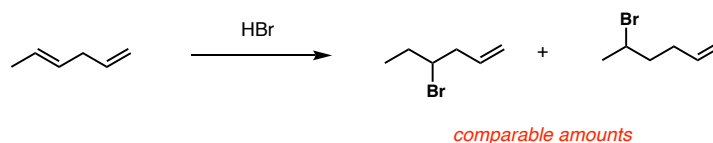
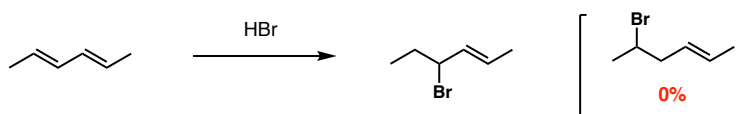
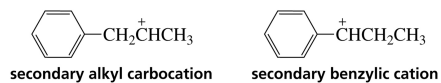
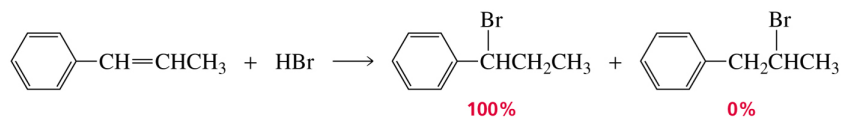
Electron Delocalization Can Affect the Product of a Reaction



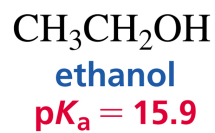
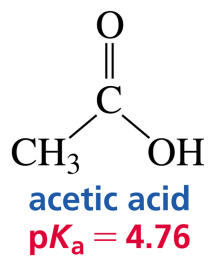
Electron Delocalization Can Affect the Product of a Reaction



Electron Delocalization Can Affect the Product of a Reaction

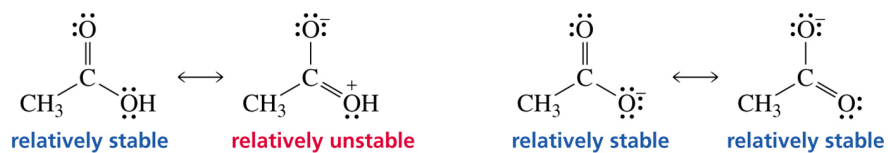


Delocalized Electrons Affect pK_a Values

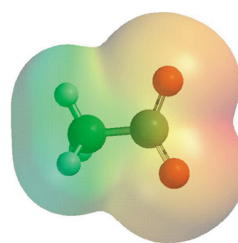


A carboxylic acid is a stronger acid than an alcohol because of inductive electron withdrawal and electron delocalization.

Proton Loss Is Accompanied by an Increase in Delocalization Energy

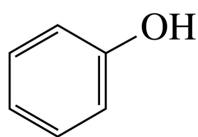


The negative charge is
shared by two oxygens.

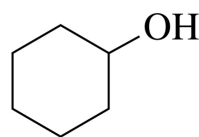


acetate ion

Phenol versus Cyclohexanol

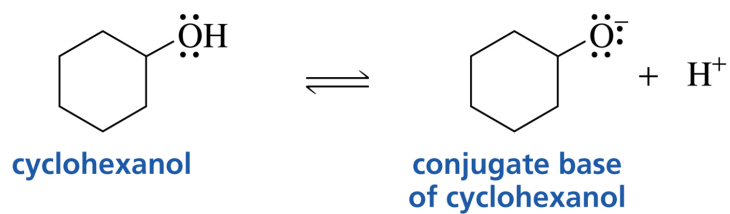


phenol
 $pK_a = 10$

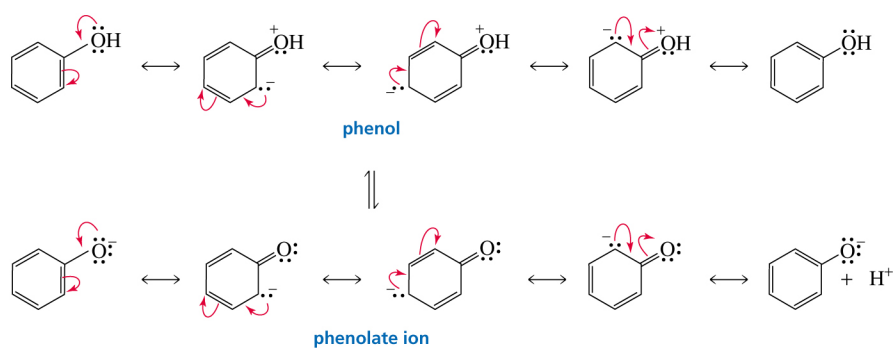


cyclohexanol
 $pK_a = 16$

No Electron Delocalization

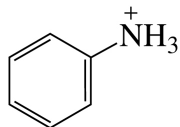


Why Phenol is More Acidic

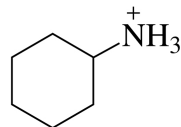


The conjugate base has greater delocalization energy than the acid.

Protonated Aniline *versus* Protonated Cyclohexylamine

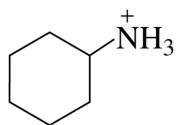


protonated aniline
 $pK_a = 4.60$

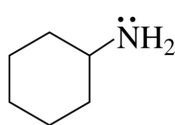


protonated cyclohexylamine
 $pK_a = 11.2$

No Delocalized Electrons



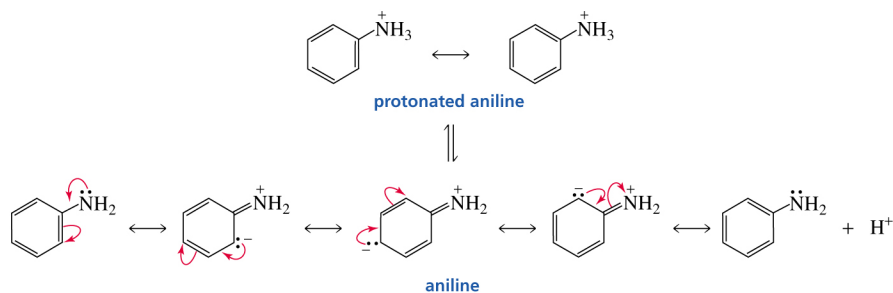
protonated
cyclohexylamine



cyclohexylamine



Why Protonated Aniline is More Acidic



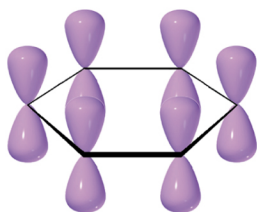
The conjugate base has greater delocalization energy than the acid.

Important!

Two new terms have been added to the Table 2.1 in Chapter 2.

Table 8.2 Approximate pK_a Values			
$pK_a < 0$	$pK_a \approx 5$	$pK_a \approx 10$	$pK_a \approx 15$
ROH^+ H	$\text{R}-\text{C}(=\text{O})-\text{OH}$	RNH_3^+	ROH
$\text{R}-\text{C}(=\text{OH}^+)-\text{OH}$	$\text{C}_6\text{H}_5\text{NH}_3^+$	$\text{C}_6\text{H}_5\text{OH}$	H_2O
H_3O^+			

Criteria for a Compound to Be Aromatic

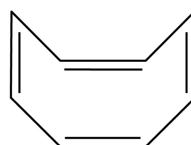
benzene's p orbitalsbenzene's π cloudbenzene has
3 pairs of π
electrons

- It must have an uninterrupted cloud of π electrons.
(cyclic, planar, and every ring atom must have a p orbital)
- The π cloud must have an odd number of pairs of π electrons;
that is **$4n+2$ electrons** (2, 6, 10 etc...)

Examples of Compounds That Are Not Aromatic



cyclobutadiene

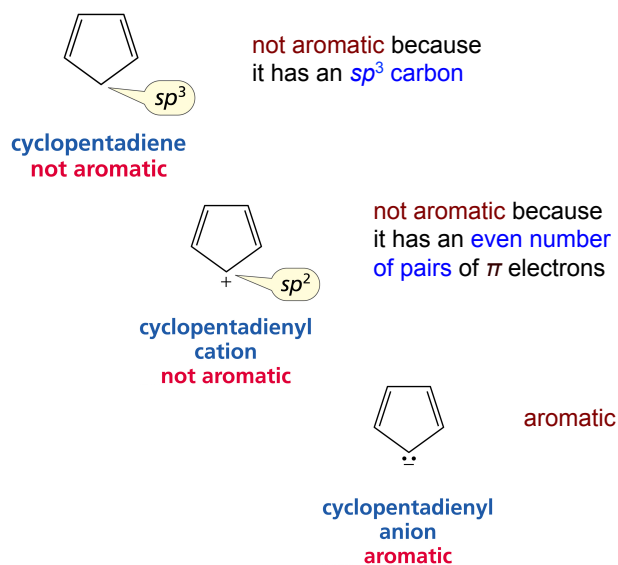


cyclooctatetraene

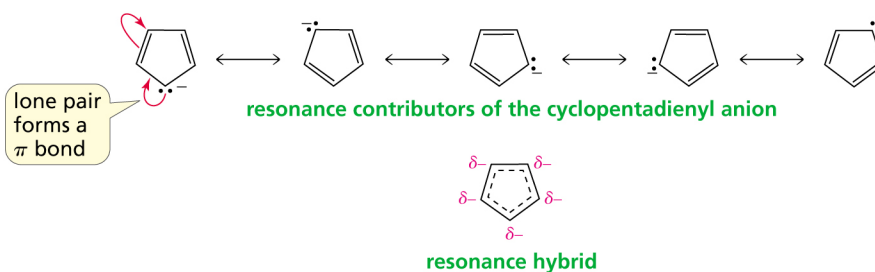
Cyclobutadiene has an even number of pairs of π electrons.

Cyclooctatetraene has an even number of pairs of π electrons,
and it is not planar.

Nonaromatic and Aromatic Compounds



How Do We Know That Cyclopentadiene's Lone-Pair Electrons Are π Electrons?



If a lone pair can be used to form a π bond in a resonance contributor, the lone-pair electrons are π electrons.