Ch 6 Resonance and Stability of Molecules

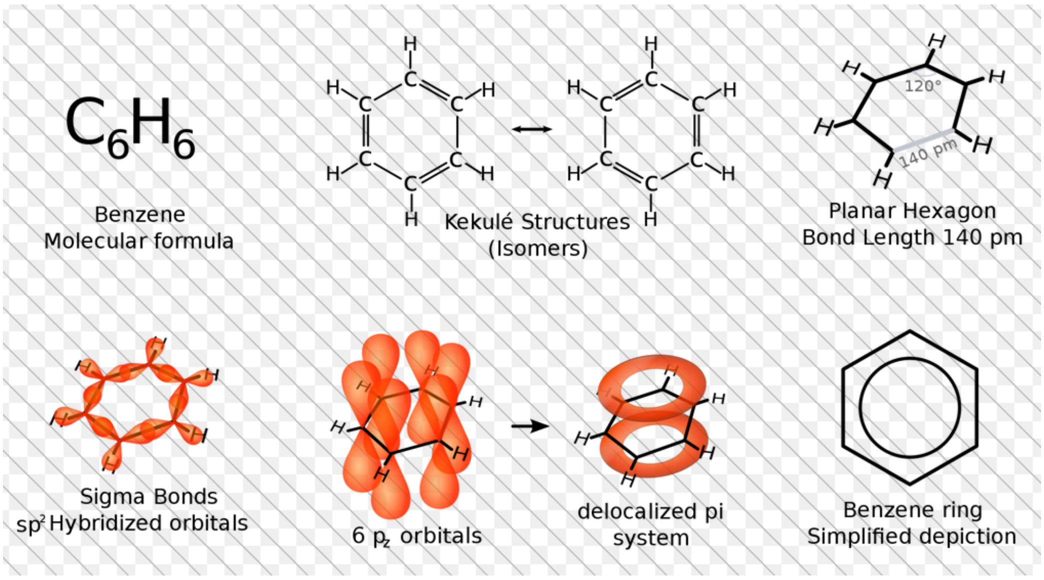
Localized Electrons - electrons that are restricted to a particular region

Delocalized Electrons - electrons that DO NOT belong to a particular atom or bond and ARE SHARED BY 3 OR ATOMS

Resonance - Having a structure "somewhere in between" the two shown structures (use of ⟷)

Benzene - All C in benzene are sp2 hybridized, each C having a p orbital that points vertical to benzene ring

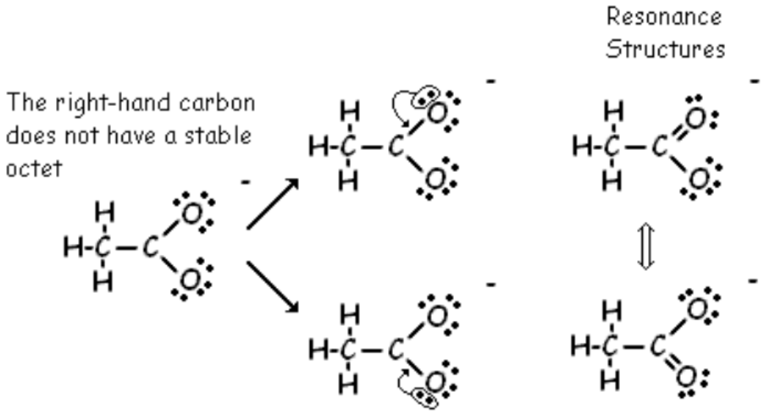
- This vertical "p orbital ring" forms a 2nd cloud of e- above and below the planar sp2 bonds



Resonance Contributors: approximate structure with localized electrons.

Resonance Hybrid: actual structure with delocalized electrons.

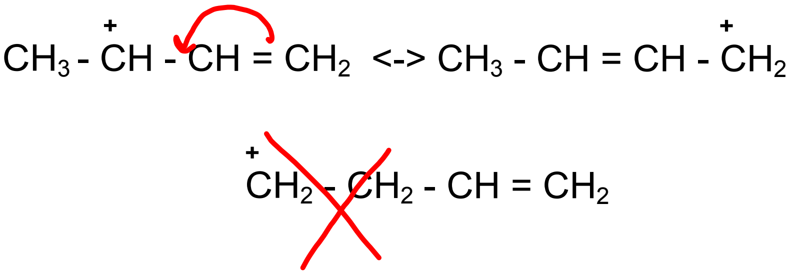
ex. Acetate ion



Rules for Resonance Forms:

1) Individual resonance forms are imaginary, not real
    - the real molecule, radical, or ion is like a hybrid of all of them
    - they are connected by a double-headed arrow (not equilibrium)

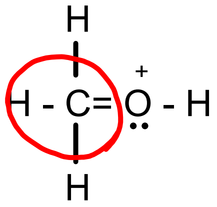
2) Resonance forms differ only in the placement of their pi or nonbonding electrons. Atoms are fixed and cannot move



$$CH_3-\overset{+}{C}H-CH=CH_2 <-> CH_3-CH=CH-\overset{+}{C}H_2$$

$$\xcancel{\overset{+}{C}H_2-CH_2}-CH=CH_2$$

3) Resonance forms obey normal rules of valency - the octet rule still applies to main group atoms.



$$H - \overset{H}{\underset{H}{C}} = \overset{+}{\underset{\cdot\cdot}{O}} - H$$

4) All resonance structures for a given molecule or ion must contain the same number of unpaired electrons (radical)

$CH_2 = CH\dot{C}H_2$

5) All atoms that are a part of the delocalized system must lie in a plane or be nearly planar

6) The energy of the actual molecule is lower than the energy that might be estimated for any contributing structure

$$CH_2 = CH - \overset{+}{C}H_2 \quad \leftrightarrow \quad \overset{+}{C}H_2 - CH = CH_2$$

The actual allyl cation is more stable than either resonance structure taken separately. The 2 structures resemble primary carbocations and yet the allyl cation is more stable (has lower energy) than a secondary carbocation.

7) The resonance hybrid is more stable than any individual resonance form

8) Equivalent resonance structures make equal contributions to the hybrid, and systems described by them have a large resonance stabilization.

9) Some resonance forms may contribute more to the overall hybrid than others. As a rule the more stable resonance structures will contribute more to the hybrid than unstable ones.
  a) the more covalent bonds a structure has, the more stable it is
  b) Charge separation decreases stability

$$CH_2 = CH - Cl \quad \text{<->} \quad \overset{-}{C}H_2 - CH = \overset{+}{Cl}$$

10) In general, the greater the number of resonance structures, the greater the degree of delocalization and the more stable the molecule or ion.

11) Each of the resonance forms must have the same net charge.

Common Mistakes:

1) Forgetting charges

2) Breaking the octet rule

3) Moving single bonds

4) Not following the electron flow

Extra Resonance Notes:

- resonance forms do not jump back and forth
- the molecule has 1 unchanging structure that is a resonance hybrid of the forms and has characteristics of all
- resonance makes a species more stable by delocalizing the electrons
- delocalization reduces electron - electron repulsion
- If a molecule has its p orbitals in different planes, those e- cannot undergo resonance distribution

cyclooctatetraene - has p orbitals that ARE NOT in the same plane

Draw resonance forms for the following:

1) Acetone + base --> acetone anion (CH_2COCH_3) (2)

2) 2,4 - pentanedione + base --> $CH_3COCHCOCH_3$ (3)

3) $CH_3OPO_3^{-2}$ (3)

5) NO_3^{-1} (3)

6) benzoate ion (4)

STABILITY:

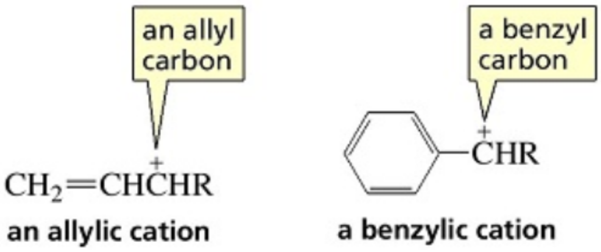
1) Isolated double bond vs conjugated double bond

C = C - C - C = C C = C - C= C -

localized delocalized

2) allylic cation - 2 forms

benzylic cation - 5 forms C_6H_5CHR



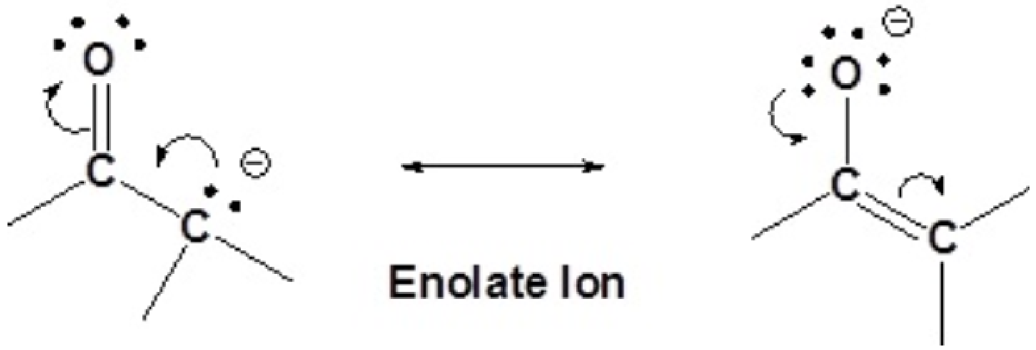
an allylic cation a benzylic cation

Primary allylic & benzylic cations have delocalized electrons and are more stable than primary carbocations with localized electrons - they are about the same as secondary carbocations

Things that DO NOT make a resonance structure stable:

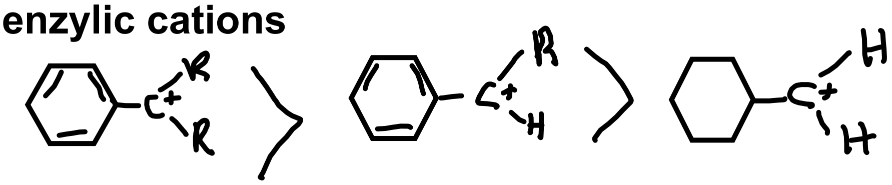
1) The more electronegative atom bearing a (+) charge
2) a + and - charge all in the same molecule

Which of the following pairs is more stable?



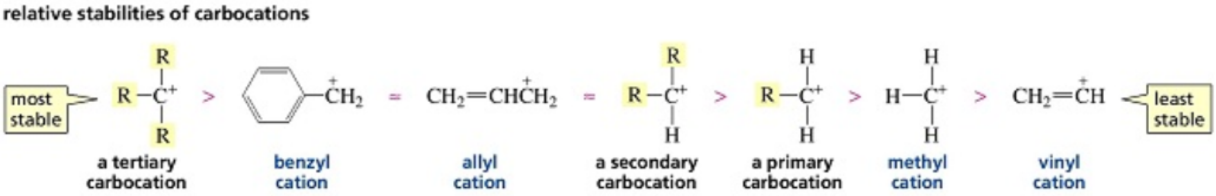
Order of stability:

Benzylic cations



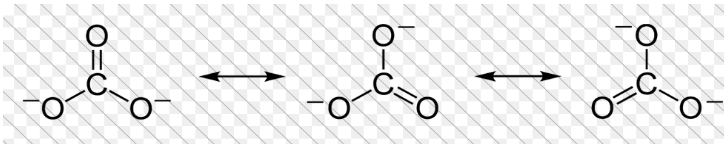
Allylic cations

$CH_2 = CH - \overset{+}{C}RR'$ > $CH_2 = CH\overset{+}{C}HR$ > $CH_2 = CH\overset{+}{C}H_2$



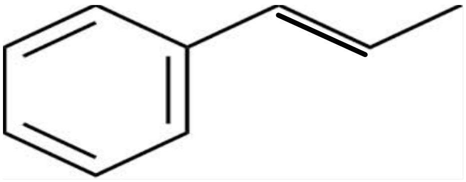
Delocalization Energy

1) The Greater the number of relatively stable resonance contributors, the greater the delocalization energy



Chp. 7: p182-185: Delocalization and affect on reaction products

1) $C_6H_5CH{=}CHCH_3$ + HBr -->



2) Isolated dienes:

$CH_2=CHCH_2CH=CH_2$ + excess HBr -->

$CH_2=CHCH_2C=C(CH_3)_2$ + HCl -->

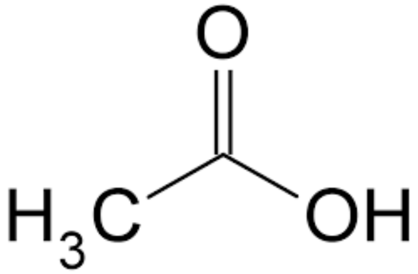
Reactions of Conjugated Dienes:

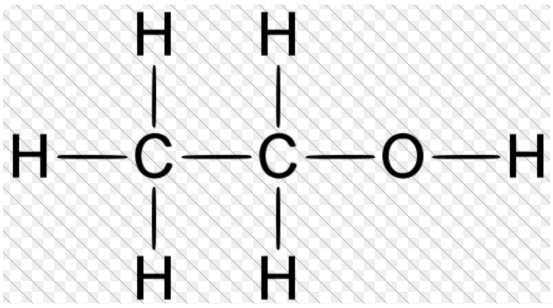
CH_2=CH-CH=CH_2 + HBr -->

Delocalized electrons can affect pKa

Remember - the lower the pKa = stronger acid

Compare acetic acid and ethanol





pKa = 4.76

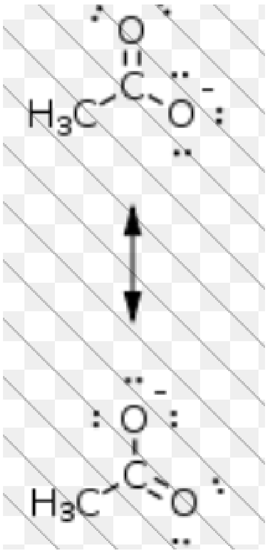
pKa = 15.9

Why the difference?

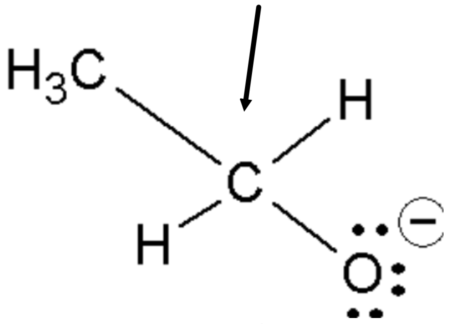
Remember - greater delocalization energy = more stable

Also Remember - a strong acid has a weak conjugate base. This CB is stable for the acid to be strong!!

Look to the right, see whey acetic acid is stronger than ethanol, who has its CB shown below.

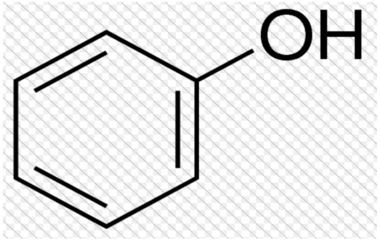


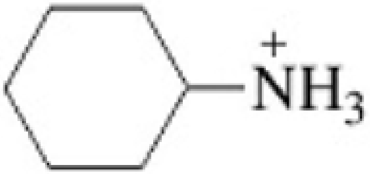
Acetic acids CB

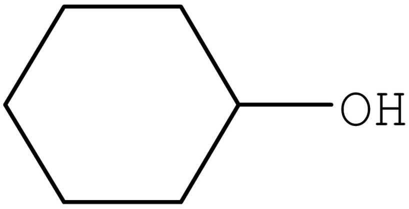


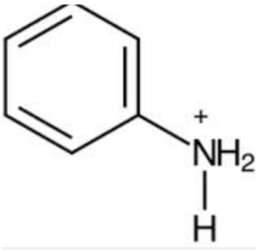
Ethanol CB

Predict which of the following would be a strong acid:

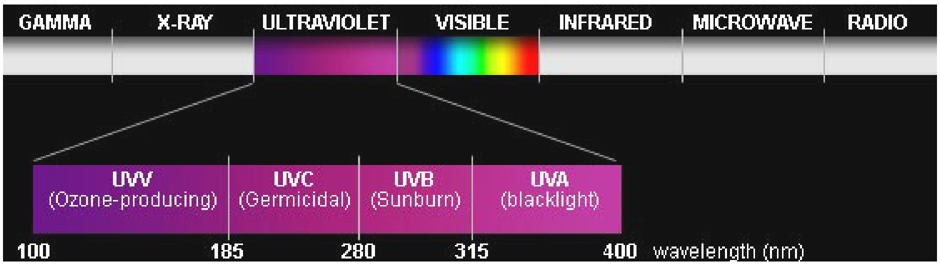








Ultraviolet and visible spectroscopy



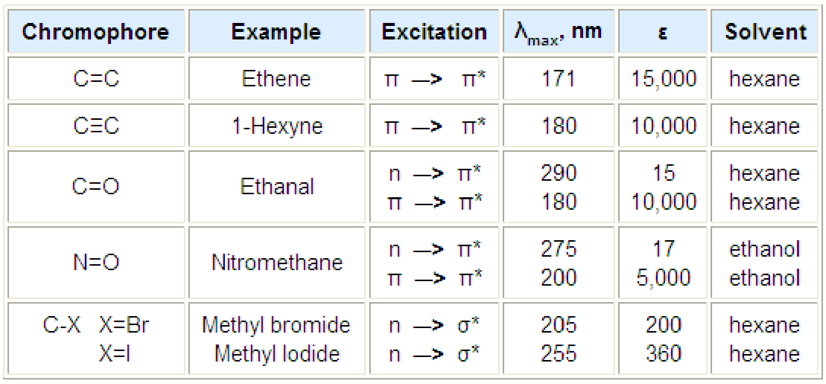
1) UV/Vis Spectroscopy gives info about compounds =

2) If a compound absorbs UV light = UV spectrum obtained

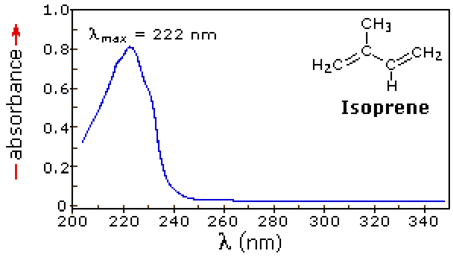
   If a compound absorbs Vis light = Visible spectrum obtained

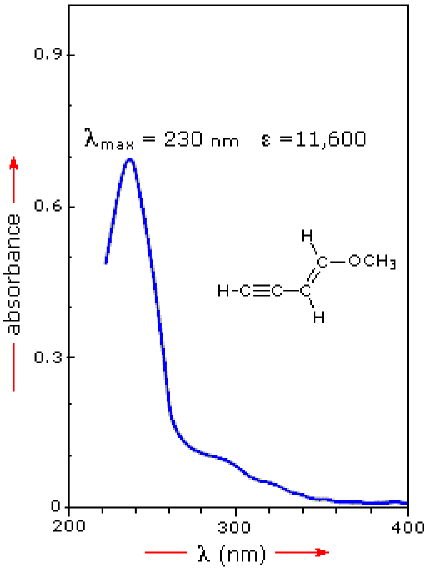
3) UV = 180 nm - 400 nm

   Visible = 400 - 780 nm



Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	π —> π*	171	15,000	hexane
C≡C	1-Hexyne	π —> π*	180	10,000	hexane
C=O	Ethanal	n —> π* π —> π*	290 180	15 10,000	hexane hexane
N=O	Nitromethane	n —> π* π —> π*	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	n —> σ* n —> σ*	205 255	200 360	hexane hexane



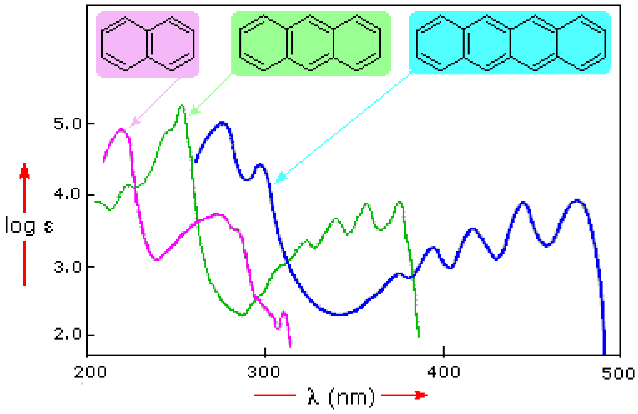


1) The λ max increases as # of conjugated = increases in a molecule

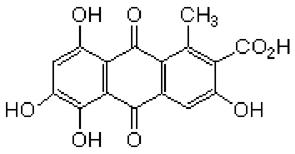
2) If a molecule has ENOUGH = bonds, it will absorb visible light and be colored

Ex: Beta-carotene (orange)

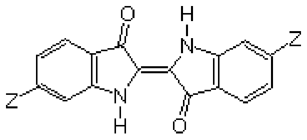
Lycopene (red)



Some Natural Organic Pigments

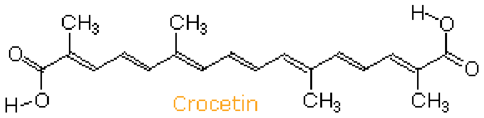


Kermesic Acid
(Carminic Acid)
from the insect *Coccus cacti*

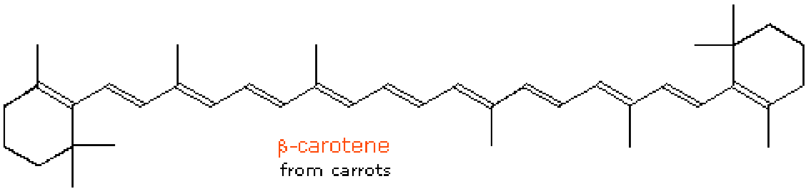


Z=H
Indigo
from *Isatis tinctoria* (woad)

Z=Br
Punicin or Tyrian Purple
from mollusks of the genus *Murex*



Crocetin
from saffron



β-carotene
from carrots