

CHEM 221 section 01

slide 5 now fixed..

LECTURE #05

Tues., Sept.20, 2005

ASSIGNED READINGS:

TODAY'S CLASS:

- 1.20 Effect of pH on structure of organic compounds
- 1.21 Lewis acids & bases
& resonance structures...

NEXT CLASS: Ch.2: 2.1 - 2.9

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

(1)

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 σ -framework stays the same:
atoms do not move, & their σ -bonds don't change.
2. Only π -electrons and lone-pair electrons move.
3. The total number of e⁻s in the molecule does not change.
4. The numbers of paired e⁻s and unpaired e⁻s do not change.
5. The total charge on the molecule does not change.

Remember why the e⁻s move:

being delocalized via overlapping p-orbitals

(2)

Rules for Drawing Resonance Contributors: Part 2

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

1. Move π e⁻s 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

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 (π -type) overlap is energetically favourable
- Thus: atom can actually change to sp^2 -hybridization
 - the e⁻ repulsion that normally forces it to go sp^3 will be compensated for by the stabilization provided by the π overlap

(3)

Draw resonance structures (if appropriate!)



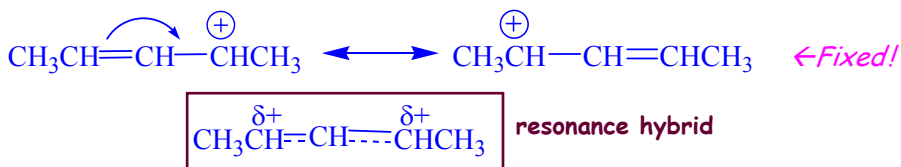
If the atom carrying lone pair were to **rehybridize** so it had an unhybridized p-orbital, could delocalization then occur?

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

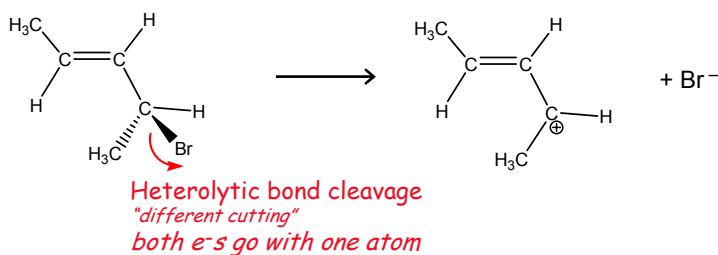
So: which of these will be the stronger base?

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

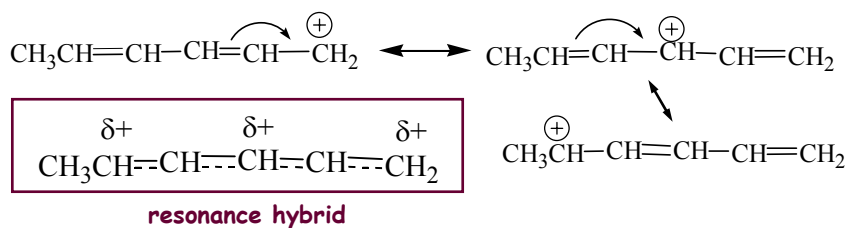


Aside: where could a carbocation like this come from?



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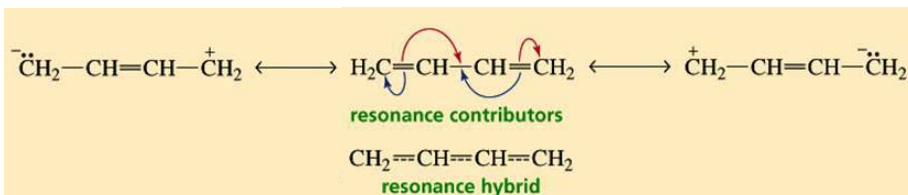
Resonance contributors are obtained by moving π electrons toward a positive charge:



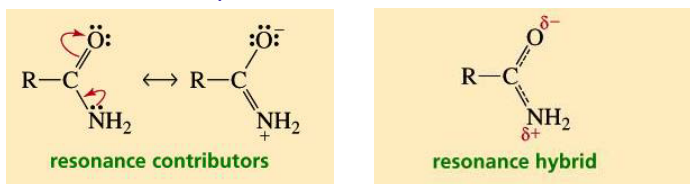
More resonance contributors \Rightarrow more stable hybrid

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

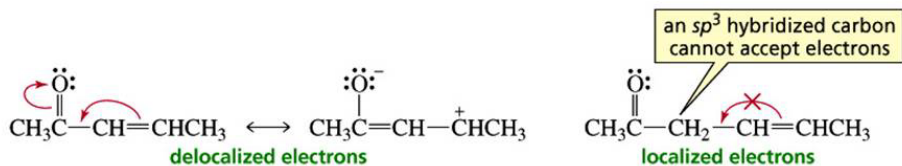


Resonance contributors also obtained by moving lone pair e -s toward a π -bond (an sp^2 -atom):



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



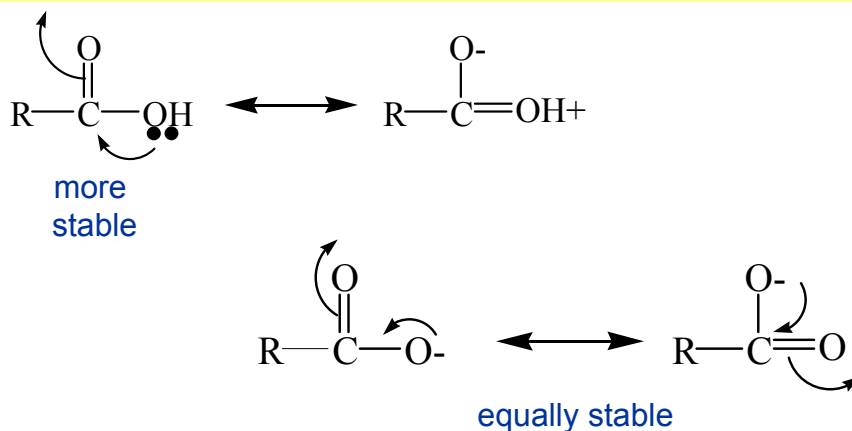
(8)

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...

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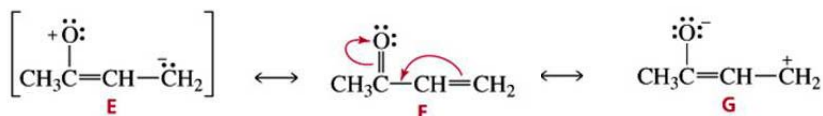
Resonance contributors with separated charges are less stable



**The more stable a resonance structure is,
the more it contributes to the resonance hybrid**

(10)

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



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

- 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

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

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

What would the resonance hybrid be like?

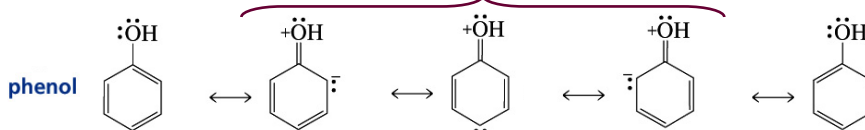
(11)

Explaining the properties of phenol ($\text{p}K_a = 10$)

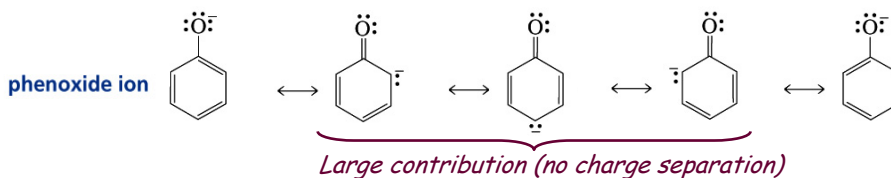
Remember: most alcohols have $\text{p}K_a \sim 15$ (do not act as acids in water)
but phenol loses H^+ when dissolved in water!

Phenol is not very basic: lone pair on O, but also somewhat delocalized ("brought into the ring" via resonance)

Small but significant contribution (charge separation)

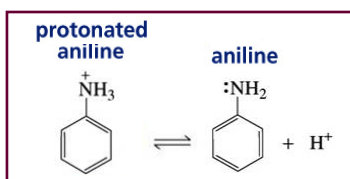


Phenol is quite acidic: conjugate base is highly resonance stabilized

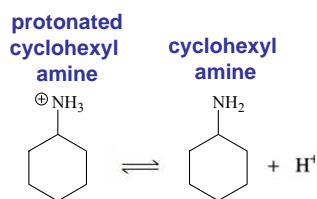


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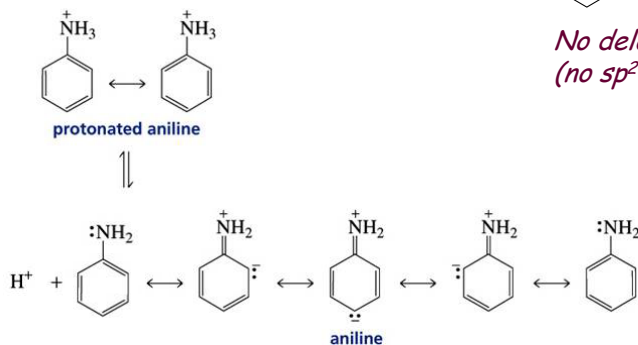
Which is more acidic?



OR

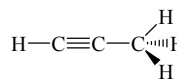
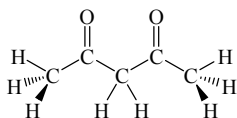


No delocalization
(no sp^2 C's \Rightarrow no p orbitals)



(13)

Identify the most acidic hydrogen in...

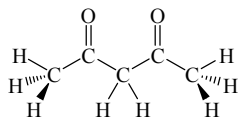


From Chem206: polyprotic acids

- the most acidic H on each molecule is lost before any molecule loses its next-acidic H
- THUS: if we add "1 equivalent" of base, only the most acidic H is lost

(14)

Find a strong enough base to deprotonate...



Back inside cover of Bruice:

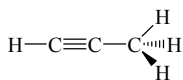
Approximate pK_a Values See Appendix II for more detailed information.

protonated carbonyl groups	$\begin{matrix} +OH \\ \\ RCOH \end{matrix}$	} < 0	α -carbon (aldehyde)	$\begin{matrix} O \\ \\ RCHCH \end{matrix}$	} -20
protonated alcohols	$\begin{matrix} + \\ ROH \\ H \end{matrix}$		α -carbon (ketone)	$\begin{matrix} O \\ \\ RCHCR \end{matrix}$	
protonated water	$\begin{matrix} + \\ HOH \\ H \end{matrix}$		α -carbon (ester)	$\begin{matrix} O \\ \\ RCHCOR \end{matrix}$	-25
carboxylic acids	$\begin{matrix} O \\ \\ RCOH \end{matrix}$	} -5	α -carbon (amide)	$\begin{matrix} O \\ \\ RCHCN(CH_3)_2 \end{matrix}$	-30
protonated aniline	$\begin{matrix} + \\ ArNH_3 \end{matrix}$		amines	RNH_2	-40
protonated amines	$\begin{matrix} + \\ RNH_3 \end{matrix}$	} -10	alkanes	RCH_3	-50
phenol	$ArOH$				
alcohols	ROH	} -15			
water	H_2O				

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Find a strong enough base to deprotonate...

(See Appendix II)



Compound	pK_a	Compound	pK_a	Compound	pK_a
	8.0		10.7		17
H_2NNH_3	8.1	$(CH_3)_3NH_2$	10.7	$(CH_3)_3COH$	18
CH_3COOH	8.2		11.1	CH_3CCH_3	20
$CH_3CH_2NO_2$	8.6	$CH_3CH_2NH_3$	11.0	$CH_3COCH_2CH_3$	24.5
$CH_3CCH_2CCH_3$	8.9		11.3	$HC\equiv CH$	25
$HC\equiv N$	9.1	HPO_4^{2-}	12.3	$CH_3C\equiv N$	25
	9.3	CF_3CH_2OH	12.4	$CH_3CN(CH_3)_2$	30
	9.4	$CH_3CH_2OCCH_2COCH_2CH_3$	13.3	NH_3	36
NH_4^+	9.4	$HC\equiv CCH_2OH$	13.5		36
$HOCH_2CH_2NH_3^+$	9.5	H_2NCH_2	13.7		40
$H_3N^+CH_2CO^-$	9.8	$CH_3NCH_2CH_2OH$	13.9		41
	10.0		14.4		43
$CH_3-C_6H_4-OH$	10.2	CH_3OH	15.5	$CH_2=CHCH_3$	43
$HC_3O_2^-$	10.2	H_2O	15.7	$CH_2=CH_2$	44
CH_3NO_2	10.2	CH_3CH_2OH	16.0		46
$H_2N-C_6H_4-OH$	10.3	CH_3CNH_2	16	CH_4	50
CH_3CH_2SH	10.5		16.0	CH_3CH_3	50
$(CH_3)_3NH$	10.6		-17		
$CH_3CCH_2COCH_2CH_3$	10.7				
$CH_3NH_3^+$	10.7				

Also common:
 H_2 $pK_a = 35$
 conj. base = H^-
 used as NaH

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1.21 The Lewis concept of acids & bases

- A more general, MECHANISTIC, way of thinking
- Explains H^+ transfer reactions (Brønsted-Lowry theory) & *many others*

A LEWIS BASE = an electron pair donor } anything with
 "have pair, will share" } a lone pair!

A LEWIS ACID = an electron pair acceptor } anything with
 "need two from you" } attraction for e^- s
 (open valence, cationic, or δ^+)

AND WHEN THEY REACT:

Lewis base shares its lone pair of e^- s with Lewis acid

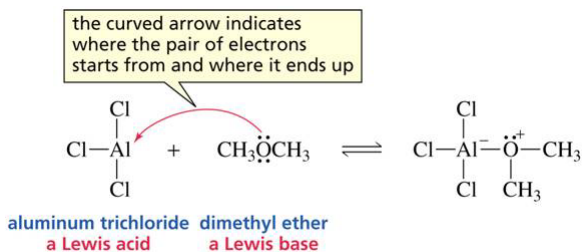
→ A new covalent bond is formed

→ Sometimes called a "coordinate covalent bond"

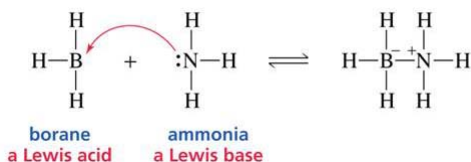
to denote that the pair of e^- s were both provided by the same atom

IMPORTANT: Lewis acid-base (δ^+ - δ^-) interactions
 let you predict the outcome of nearly all reactions!

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Note: the ether will have totally different reactivity as a Lewis adduct!



Note: the ammonia will also now behave very differently!

Organic chemists often use Lewis acids to react with e^- -rich centres
 → distorts the molecule's polarity
 → can enhance or entirely change the molecule's reactivity
 → see more soon (Ch.4)...

(18)

ASSIGNED READINGS

BEFORE NEXT LECTURE:

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

Practice: predicting relative acidity/basicity