CHEM 221 section 52

LECTURE #02 Thurs., Jan.10, 2008

ASSIGNED READINGS:

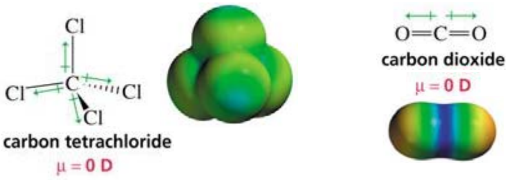
TODAY'S CLASS: not in same order as text

1.15	Molecular dipole moments
1.21	Review of Lewis acid-base theory
1.16	Review of Brønsted-Lowry acids & bases
1.17	Organic acids & bases: pK_a & pH
1.18	Effect of structure on pK_a
1.19	Introduction to delocalized electrons & resonance
7.2-7.5	Understanding & drawing resonance structures
7.9	How delocalized electrons affect pK_a

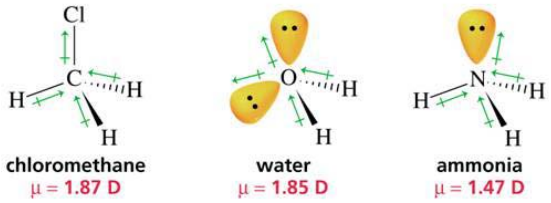
NEXT CLASS: Ch.2

1.15 Review: Dipole Moment of Molecules

The vector sum of magnitude and direction of individual bond dipole determines overall dipole moment of a molecule



Net: NONPOLAR
due to symmetric arrangement of bond dipoles



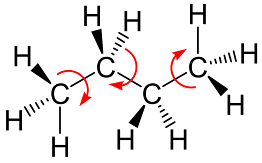
Net: POLAR
due to element of asymmetry in arrangement of bond dipoles

Judging polarity of organic molecules

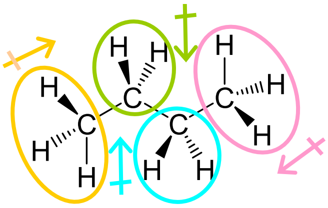
1. Consider lone pairs as contributing δ^- character
2. Treat C-H bonds as if they were totally nonpolar
   (even though $\Delta\chi = 0.4$ and D = 0.4)

WHY?

- Molecules are flexible:
  - → Free rotation occurs about single bonds
  - → Exist in many different "conformations"



THUS: on average…
small regional dipoles caused by C-H bonds end up canceling out over whole molecule !



Identify the polar *vs.* nonpolar character of…

(label δ^+/δ^- in **net polar regions** of molecules only)

Draw intuitively helpful structures, with polarity:

$(CH_3)_3CCH(OH)CH_3$

$CH_3N(CH_3)_2$

$CH_3(CH_2)_{14}COOH$

1.21 The Lewis concept of acids & bases

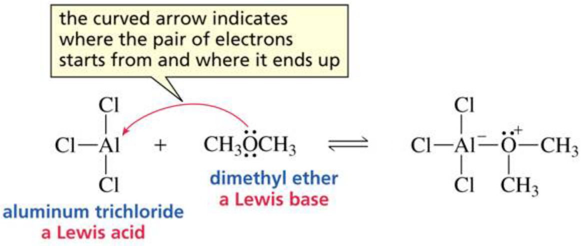
- A general, MECHANISTIC, way of thinking
- Explains H^+ transfer reactions (Brønsted-Lowry theory) & ***many others***

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

A LEWIS ACID = an electron pair acceptor
"need two from you"
} **anything with 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!

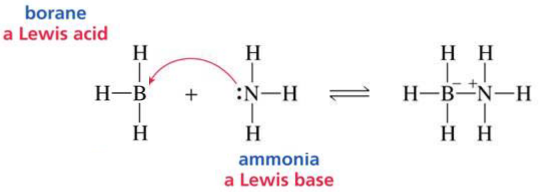


$$AlCl_3 + CH_3OCH_3 \rightleftharpoons Cl_3\overset{-}{Al}-\overset{+}{O}(CH_3)CH_3$$

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

VERY REACTIVE (open valence), pyrophoric in damp air

QUITE STABLE



$$BH_3 + :NH_3 \rightleftharpoons H_3\overset{-}{B}-\overset{+}{N}H_3$$

Note: the ammonia will also now behave very differently!
(*i.e.*, no longer a base...)

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)...

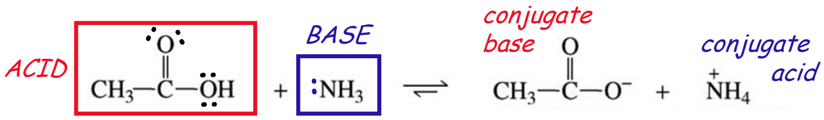
1.16-1.17: Brønsted–Lowry Acids and Bases

Acids donate a proton

Which is the most acidic H?
- the most δ^+ H *(…in a polar bond)* in the molecule

Bases accept a proton

- Use a pair of e^-s *(e.g., lone pair)* to form a covalent to bond to the δ^+-H



$CH_3COOH + :NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$

- Reactions between acids & bases are INSTANTANEOUS
  - base removes the most acidic H^+ from the acid molecule
  - equilibrium is reached in less than a second
  - if no rxn occurs: base wasn't strong enough → eqm lies to left (*i.e.,* acid's conjugate base was stronger!)

Measuring acid strength: K_a & pK_a

$HA + H_2O \rightleftharpoons A^- + H_3O^+$ *where HA = any acid, & A^- = its conj. base*

Acid dissociation constant = $K_a = \dfrac{[A^-][H_3O^+]}{[HA]}$

$$\boxed{pK_a = -\log(K_a)}$$

IMPORTANT:

- **pH** describes a **solution** *(how much H_3O^+ is present?)*
- **pK_a** describes a **compound** *(how good is it at losing an H^+?)*

Chemists use pK_a in two ways:

1.) To see inherent acidity of compound *i.e.,* **strength**:

Lower pK_a ⇨ stronger acid **(weaker conj.B)**
Higher pK_a ⇨ weaker acid **(stronger conj.B)**

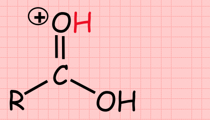
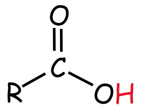
2.) To identify protonation state of a compound in solution, *i.e.,* **speciation**:

A compound will exist primarily in its:
acidic form at a pH < its pK_a
basic form at a pH > its pK_a

The stronger an acid is, the weaker its conjugate base.

Acidity & basicity: depend on STRUCTURE

Table 1.8: Approximate pK_a values (see text's back cover for more)

STRONG ACIDS	MODERATELY STRONG…	← WEAK ACIDS →		…EXTREMELY WEAK
pK_a < 0	pK_a ~ 5	pK_a ~ 10	pK_a ~ 15	pK_a >> 15
$H_3O^{\oplus}$ protonated water			H_2O water	**TO USE CONJ. BASE OF THESE:**
$R\overset{\oplus}{O}H_2$ a protonated alcohol			ROH an alcohol	**"DRY" SOLVENT REQUIRED**
 a protonated carboxylic acid	 a carboxylic acid	$R\overset{\oplus}{N}H_3$ a protonated amine		RNH_2 an amine RCH_3 an alkane

Note: "R" is short for any unidentified carbon-based group
e.g., CH_3, CH_3CH_2, *etc…*

Acidity & basicity: depend on STRUCTURE

- The stronger the base, the weaker is its conjugate acid
  (if it's so good at bonding to H^+, then it's harder for it to let go…)
- A base deprotonates an acid by forming a covalent bond to H^+ 1s orbital
  - BOTH e^-s for the bond come from B:
  - Thus: a base will be *stronger* if it REALLY *needs to share* its e^-s
    a base will be weaker if it is quite stable carrying its e^-s

What factors decrease basicity? *(more stable ⇨ less basic)*

1.) Diminished electron density
- lone pair on large atom
- due to inductive effects (e^--withdrawing groups)
- due to resonance (delocalization of electrons)

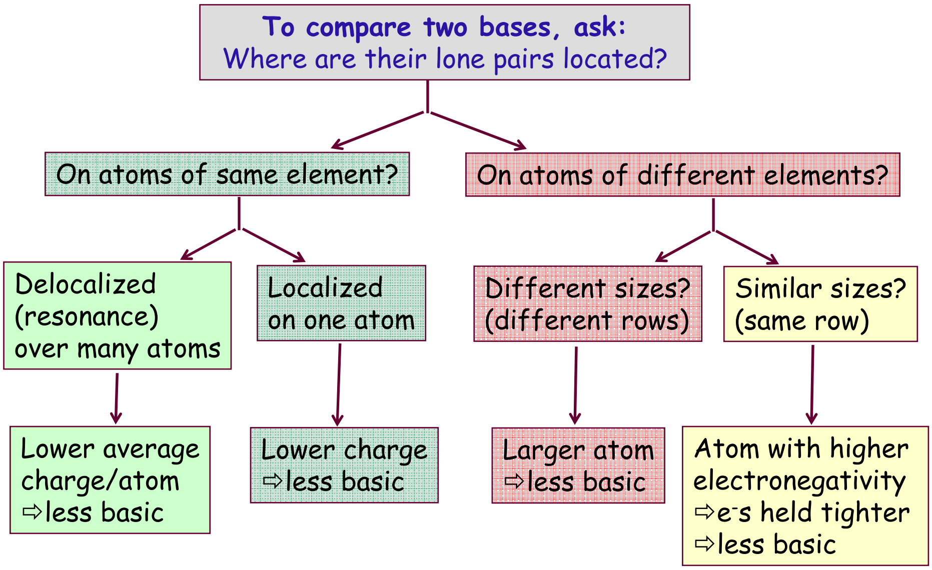
Lone pairs on smaller atoms are more basic…

To compare lone pairs on same type of atom, consider these.

2.) Diminished ability to <u>share</u> electrons
- lone pair on highly electronegative atom

Consider this when lone pairs are on atoms of similar size (<u>same row</u>).

Comparing basicity: more stable e⁻s = less basic



To compare two bases, ask:
Where are their lone pairs located?

On atoms of same element?

- Delocalized (resonance) over many atoms
  - Lower average charge/atom ⇨less basic
- Localized on one atom
  - Lower charge ⇨less basic

On atoms of different elements?

- Different sizes? (different rows)
  - Larger atom ⇨less basic
- Similar sizes? (same row)
  - Atom with higher electronegativity ⇨e⁻s held tighter ⇨less basic

The conjugate base's -ve charge is due to a LONE PAIR of e⁻s!
Will the 2e⁻s easily come together to attack the H⁺ again?

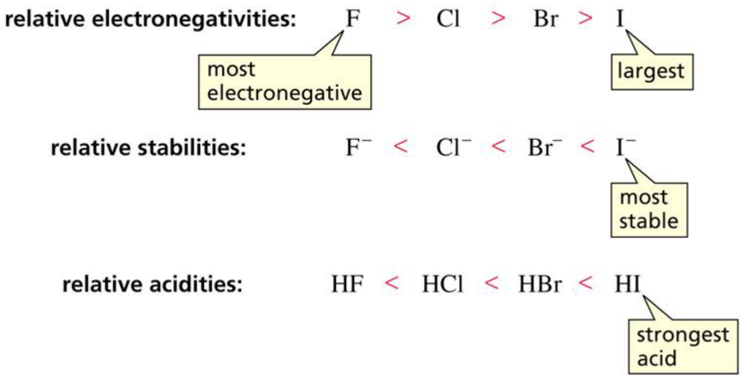
When comparing / predicting acid strengths:

1.) consider their conjugate bases

2.) compare atom carrying lone pair (= atom with bond to H in acid)

1st: consider SIZE

- When atoms are very different in size,
  the stronger acid will have its proton attached to the largest atom



relative electronegativities: F > Cl > Br > I

most electronegative

largest

relative stabilities: $F^- < Cl^- < Br^- < I^-$

most stable

relative acidities: HF < HCl < HBr < HI

strongest acid

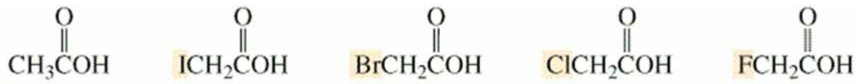
When comparing / predicting acid strengths:
1.) consider their conjugate bases
2.) compare atom carrying lone pair (= atom with bond to H in acid)
  1st: consider SIZE
  2nd: if sizes similar → compare ELECTRONEGATIVITY

- When atoms are similar in size, the stronger acid will have its H^+ attached to the more electronegative atom

CH_3OH	CH_3NH_2
methanol	**methylamine**
pK_a = 15.5	**pK_a = 40**

When comparing / predicting acid strengths:
1.) consider their conjugate bases
2.) compare atom carrying lone pair (= atom with bond to H in acid)
  1st: consider SIZE
  2nd: if sizes similar → compare ELECTRONEGATIVITY
  3rd: if same element → compare rest of molecule (EWGs)

- **Inductive electron withdrawal** increases the acidity of an acid *(by stabilizing the conjugate base)*



$CH_3\overset{\overset{O}{\|}}{C}OH$ **pK_a = 4.76**

$ICH_2\overset{\overset{O}{\|}}{C}OH$ **pK_a = 3.15**

$BrCH_2\overset{\overset{O}{\|}}{C}OH$ **pK_a = 2.86**

$ClCH_2\overset{\overset{O}{\|}}{C}OH$ **pK_a = 2.81**

$FCH_2\overset{\overset{O}{\|}}{C}OH$ **pK_a = 2.66**

When comparing / predicting acid strengths:

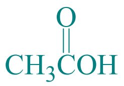
1.) consider their conjugate bases

2.) compare atom carrying lone pair (= atom with bond to H in acid)

- 1st: consider SIZE
- 2nd: if sizes similar → compare ELECTRONEGATIVITY
- 3rd: if same element → compare rest of molecule (EWGs)
- 4th: → compare degree of resonance stabilization

Acetic acid's conjugate base is stabilized by **resonance**

⇨ e- pair is delocalized over many atoms



$CH_3\overset{O}{\overset{\|}{C}}OH$

$pK_a = 4.76$

acetic acid

CH_3CH_2OH

$pK_a = 15.9$

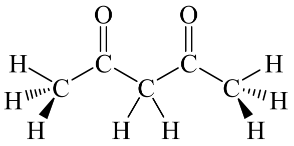
ethanol

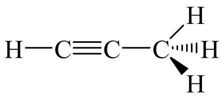
Ethanol's conjugate base is NOT…

Draw structures for these 2 conjugate bases:

What does acetate REALLY look like?

Identify the most acidic hydrogen in…





Polyprotic acids (review Chem 206…)

- the most acidic H on <u>each</u> 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

Predicting if an acid-base rxn will occur…

To efficiently deprotonate another molecule: the attacking base (B:) must be **stronger than** the other molecule's conjugate base…

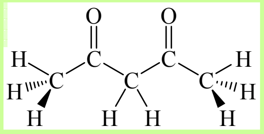
How to analyze a potential A/B reaction:

1. Identify which is more basic (BASE) & which is more acidic (ACID)
2. Identify the corresponding conjugate species
3. Compare strengths of the 2 bases: BASE, & ACID's conj. base
   - look up pK_a's of the acids ⇨ think about conj. bases
   - the stronger base = better at accepting H^+
   - at equilibrium: stronger base preferentially carries the H^+

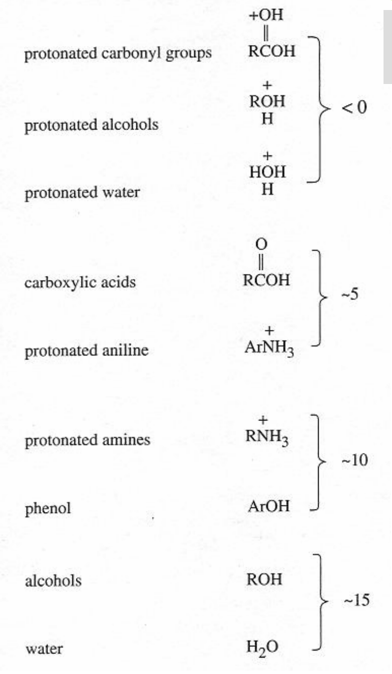
ACID		BASE				
CH_3CH_2OH	+	CH_3NH_2	$\rightleftharpoons$	$CH_3CH_2O^-$	+	$CH_3\overset{+}{N}H_3$
$pK_a = 15.9$ weaker acid		weaker base		stronger base		$pK_a = 10.7$ stronger acid

Convention: organic chemists use pK_a data (not pK_b)
∴ to discuss base strength, must infer from pK_a of conj.acid

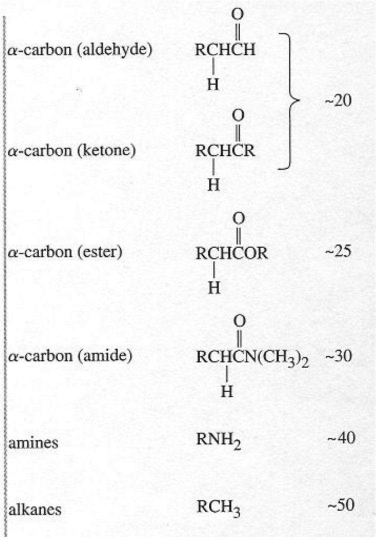
Find a strong enough base to deprotonate:



Learn pK_a values (back of Bruice)



protonated carbonyl groups	$\mathrm{R\overset{\overset{+OH}{\|}}{C}OH}$	< 0
protonated alcohols	$\mathrm{R\underset{H}{\overset{+}{O}}H}$	
protonated water	$\mathrm{H\underset{H}{\overset{+}{O}}H}$	
carboxylic acids	$\mathrm{R\overset{\overset{O}{\|}}{C}OH}$	~5
protonated aniline	$\mathrm{Ar\overset{+}{N}H_3}$	
protonated amines	$\mathrm{R\overset{+}{N}H_3}$	~10
phenol	ArOH	
alcohols	ROH	~15
water	H_2O	

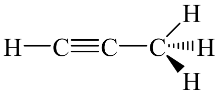


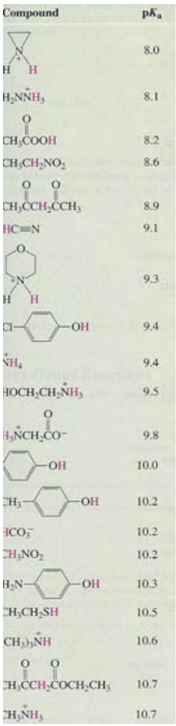
α-carbon (aldehyde)	$\mathrm{R\underset{H}{\underset{\|}{C}}H\overset{\overset{O}{\|}}{C}H}$	~20
α-carbon (ketone)	$\mathrm{R\underset{H}{\underset{\|}{C}}H\overset{\overset{O}{\|}}{C}R}$	
α-carbon (ester)	$\mathrm{R\underset{H}{\underset{\|}{C}}H\overset{\overset{O}{\|}}{C}OR}$	~25
α-carbon (amide)	$\mathrm{R\underset{H}{\underset{\|}{C}}H\overset{\overset{O}{\|}}{C}N(CH_3)_2}$	~30
amines	RNH_2	~40
alkanes	RCH_3	~50

See Appendix II for more detailed information.

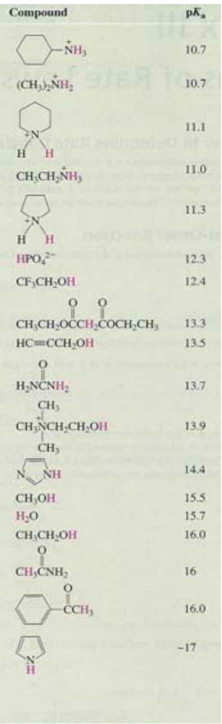
Find a strong enough base to deprotonate…

(See Appendix II)

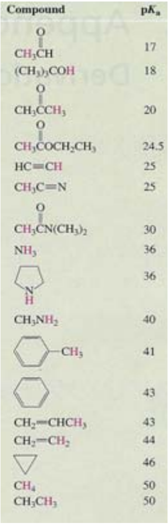




Compound	pK_a
$\overset{+}{N}$ H H	8.0
$H_2N\overset{+}{N}H_3$	8.1
$CH_3\overset{O}{\overset{\|}{C}}OOH$	8.2
$CH_3CH_2NO_2$	8.6
$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	8.9
$HC\equiv N$	9.1
O $^+$N H H	9.3
Cl— —OH	9.4
$\overset{+}{N}H_4$	9.4
$HOCH_2CH_2\overset{+}{N}H_3$	9.5
$H_3\overset{+}{N}CH_2\overset{O}{\overset{\|}{C}}O^-$	9.8
—OH	10.0
CH_3— —OH	10.2
HCO_3^-	10.2
CH_3NO_2	10.2
H_2N— —OH	10.3
CH_3CH_2SH	10.5
$(CH_3)_3\overset{+}{N}H$	10.6
$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$	10.7
$CH_3\overset{+}{N}H_3$	10.7



Compound	pK_a
—$\overset{+}{N}H_3$	10.7
$(CH_3)_2\overset{+}{N}H_2$	10.7
$^+$N H H	11.1
$CH_3CH_2\overset{+}{N}H_3$	11.0
$^+$N H H	11.3
HPO_4^{2-}	12.3
CF_3CH_2OH	12.4
$CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$	13.3
$HC\equiv CCH_2OH$	13.5
$H_2N\overset{O}{\overset{\|}{C}}NH_2$	13.7
$CH_3\overset{+}{N}(CH_3)(CH_3)CH_2CH_2OH$	13.9
N NH	14.4
CH_3OH	15.5
H_2O	15.7
CH_3CH_2OH	16.0
$CH_3\overset{O}{\overset{\|}{C}}NH_2$	16
—$\overset{O}{\overset{\|}{C}}CH_3$	16.0
N H	~17



Compound	pK_a
$CH_3\overset{O}{\overset{\|}{C}}H$	17
$(CH_3)_3COH$	18
$CH_3\overset{O}{\overset{\|}{C}}CH_3$	20
$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$	24.5
$HC\equiv CH$	25
$CH_3C\equiv N$	25
$CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2$	30
NH_3	36
N H	36
CH_3NH_2	40
—CH_3	41
	43
$CH_2=CHCH_3$	43
$CH_2=CH_2$	44
	46
CH_4	50
CH_3CH_3	50

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

Resonance-stabilized anions = rather weak bases.

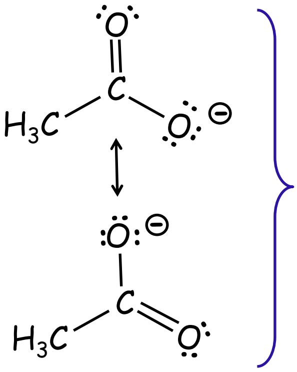
Why? What does resonance "do", anyway?

Understanding resonance (7.2-7.5)

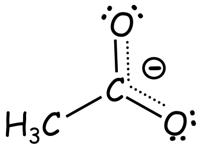
Resonance contributors are imaginary, but the resonance hybrid is **real**

unicorn
resonance contributor

dragon
resonance contributor



Drawn with
localized electrons



rhinoceros
resonance hybrid

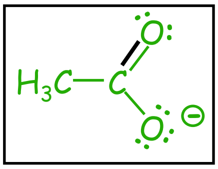
In reality = a hybrid

- The π-bonding e$^-$s & the lone pair are **delocalized** between the C & both O's

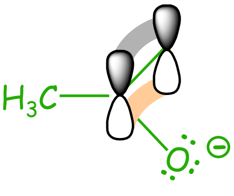
Each ⋯⋯ line = 2 e$^-$s here

WHAT IS GOING ON?

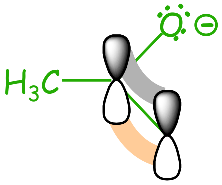
Resonance requires an "extended π-system"



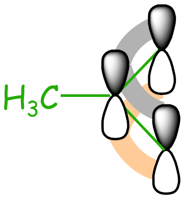
Picture the
π-bond:



& the other
option:

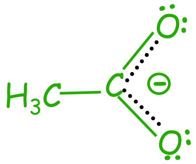


Both overlaps
occur!



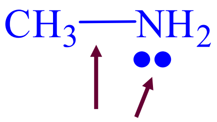
An extended π-system
= 3 or more adjacent atoms with aligned p-orbitals
Atoms must be:
- sp^2 or sp hybridized *(need unhybridized p-orbitals)*
- directly σ-bonded to each other

Result: a very stable, *delocalized* π-bond
- parallel p-orbitals WILL overlap *(E-favourable)*
- e$^-$s become spread over several atoms
- more stable than a 2-atom π-bond

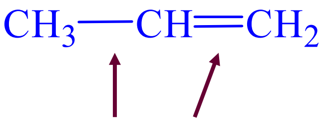


= resonance hybrid

Localized Versus Delocalized Electrons

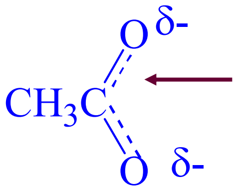


localized
electrons



localized
electrons

Do not have
an extended
array of
adjacent
p-orbitals



delocalized
electrons

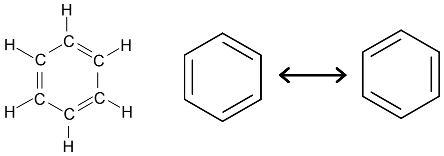
p-orbitals on 3 atoms in a row are
able to align parallel
→ overlap occurs over multiple atoms
→ makes a bonding M.O.

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

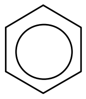
1. **Lone pair on atom next to a π-bond**
2. **Alternating double & single bonds in a structure**

Benzene: the prototypical example of resonance

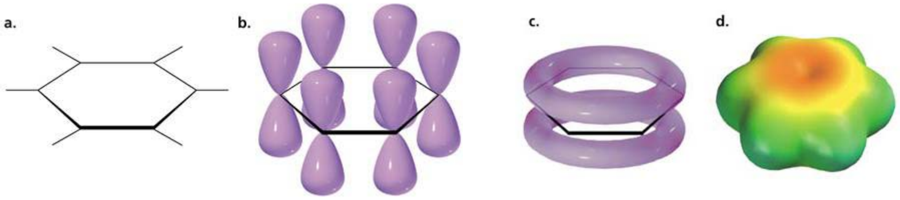
Lewis
structures:
localized
views



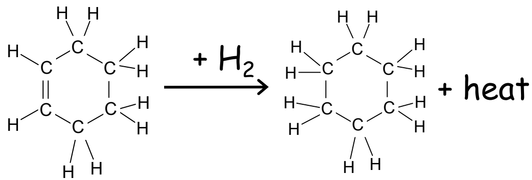
Common
drawing:
Delocalized
= simplified view
of resonance hybrid



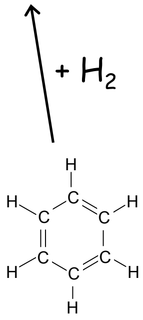
- A planar molecule with "alternating" single & double bonds
- All carbon atoms are sp^2 hybridized ⇨ all p-orbitals actually overlap!
- From experiment: all 6 C-C bond distances are same
  between single & double bond (B.O. = 1.5)
- The 6 p-electrons are delocalized: each p-electron shared by every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



How much stabilization does resonance provide?



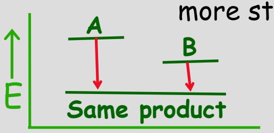
Observed ΔH_{rxn} for 6-C ring with 1 localized C=C bond:
⇨ ΔH_{rxn} = -120 kJ/mol



Expected ΔH_{rxn} for 6-C ring with 3 **localized** C=C bonds:
x 3 ⇨ **ΔH_{rxn} = -359 kJ/mol**

Measured ΔH_{rxn} for benzene (3 **delocalized** C=C bonds):
⇨ **ΔH_{rxn} = -208 kJ/mol**

Experimental evidence: heat of reaction with H_2
- Compounds with C=C bonds react exothermically with H_2
- Less heat ⇨ reactant was more stable



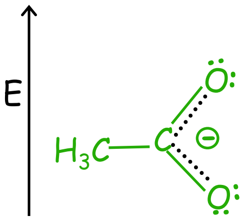
Difference in E between localized *vs.* delocalized = *resonance energy*
- larger resonance E ⇨ greater stabilization due to delocalization

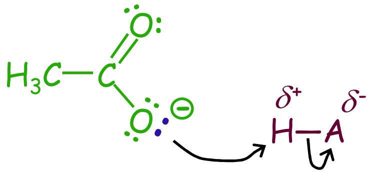
Chemical significance of resonance:
1) Resonance-stabilized anions = rather weak bases. Why?

See 7.10

Remember the mechanism of deprotonation:
- a base attacks a δ^+ H using its lone pair
- to form a bond: pair of e^-s must localize between two atoms
- a delocalized lone pair must be "rounded up" into one orbital first!

- In terms of energetics: delocalized e^-s are stabilized
  → lower in energy than if localized
  → less driving force for reaction





More stable = less reactive.

Rules for Drawing Resonance Contributors: Part 1

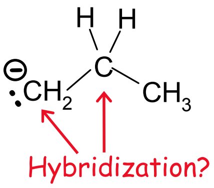
1. The molecule's σ-framework stays the same:
   atoms do not move, & their σ-bonds don't change.
2. Only π-electrons and lone-pair electrons move.
3. The total number of e^-s in the molecule does not change.
4. The numbers of paired e^-s and unpaired e^-s do not change.
5. The total charge on the molecule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

Remember why the e^-s move:
being delocalized via overlapping p-orbitals

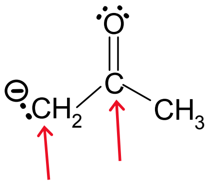
Larger # resonance structures (resonance contributors)
⇨ more extensive delocalization ⇨ greater stabilization

(27)

Draw resonance structures (if appropriate!)



vs.



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

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

(28) Which of these will be the stronger base?

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?

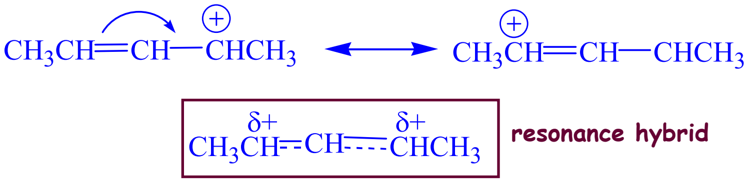
- **e⁻s move towards an atom with a p-orbital** ⇨ sp or sp^2-hyb.

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

---

Resonance contributors can be obtained by moving π e⁻s toward an open-valence atom: *e.g.*, C+ (an sp^2-atom!)

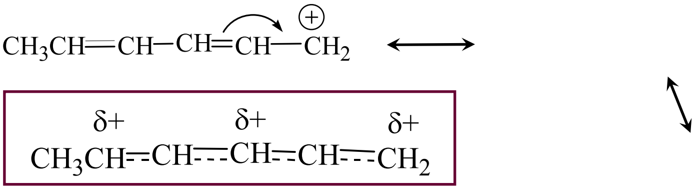


$$CH_3CH{=}CH{-}\overset{+}{C}HCH_3 \longleftrightarrow CH_3\overset{+}{C}H{=}CH{-}CHCH_3$$

$$\boxed{CH_3\overset{\delta+}{C}H{=}CH{-}\overset{\delta+}{C}HCH_3}$$

resonance hybrid

Similarly…



$$CH_3CH{=}CH{-}CH{=}CH{-}\overset{+}{C}H_2 \longleftrightarrow$$

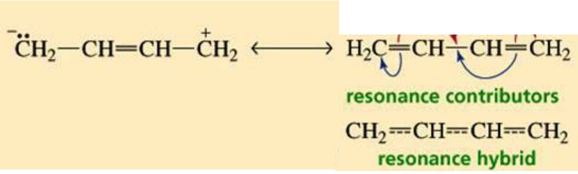
$$\boxed{CH_3\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}H{=}CH{=}\overset{\delta+}{C}H_2}$$

resonance hybrid

More resonance contributors ⇨ more stable resonance hybrid

Resonance contributors can also be obtained by…

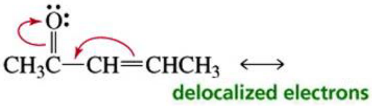
….moving π–electrons toward a π-bond (an sp^2 atom!):

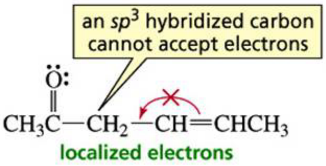


…moving lone pair e^-s toward a π-bond (an sp^2-atom):

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

(heteroatoms can rehybridize)





Do all resonance structures contribute equally?

How do we know how many contributors to draw?

- **draw as many as the preceeding "rules" allow**

Will they all contribute the same to the resonance hybrid?

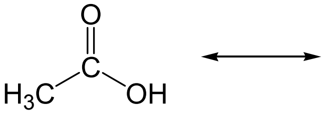
- **more stable ⇨ contribute more**

Features that decrease the stability (= importance) of a contributing resonance structure:

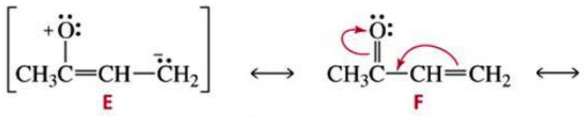
1. An atom with an incomplete octet ("open shell")
2. Formal charge & polarity mismatched
   a) A negative charge on the more electropositive atom
   b) A positive charge on the more electronegative atom
3. Charge separation

Draw another contributor:

Which is more stable, and why?



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

resonance contributor obtained by moving π electrons toward 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

- 1 open-shell atom
- charge separation
- -ve charge on more electroneg. atom

→ Moderately stable

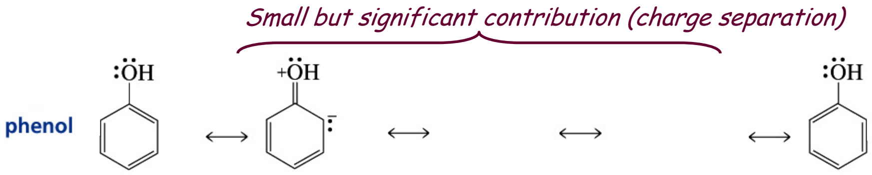
→ Contributes somewhat to hybrid

What would the resonance hybrid be like?

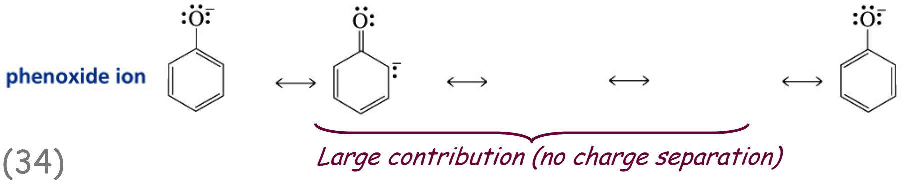
Explaining the properties of phenol (pK_a = 10)

Remember: most alcohols have pK_a ~15 *(do not act as acids in water)*
but phenol loses H^+ when dissolved in water!

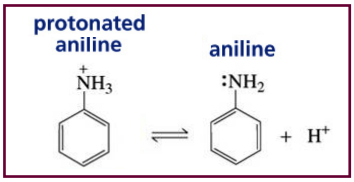
Phenol is not very basic: lone pair on O, but also somewhat delocalized ("brought into the ring" via resonance)



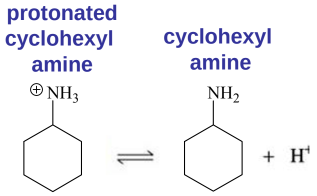
Phenol is quite acidic: conjugate base is highly resonance stabilized



Which is more acidic? Why?



OR



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

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Ch.1

Ch.7: 7.2-7.5, 7.10

Practice: Lewis structures, resonance structures

Acids & bases

- conjugate pairs
- pH, pK_a, pK_b (concepts!)
- reactions of acids & bases
- effect of structure on acidity

Why consider conj.base stability, and not HX bond "weakness"?

- For A/B rxns: thermal E >> $\Delta G^{\ddagger}$s for fwd & reverse ⇨ **always reach EQM**
- Thus: $K = e^{-\Delta G_{rxn}/RT}$ Dominant product = most thermo. stable product

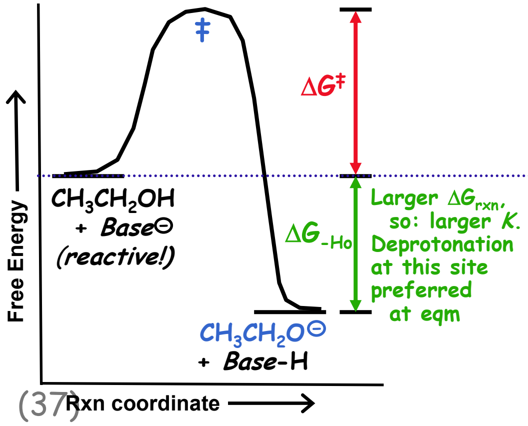
Example: Ethanol's most acidic H is the hydroxyl hydrogen. WHY?

If base removes the O-H:

- breaks OH bond (BDE ≈ 463 kJ/mol)
  - → but, not homolytic cleavage!
- Base-H bond forms (stronger)
- lone pair left on O (more stable than on Base)

If base removes a C-H:

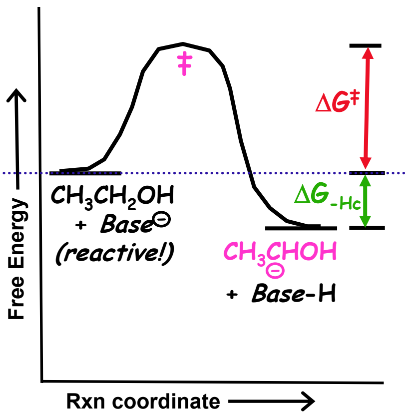
- breaks CH bond (BDE ≈ 346 kJ/mol)
- Base-H bond forms (stronger)
- lone pair left on C (not as stable as O)
- rxn less favourable…



CH_3CH_2OH + *Base*⊖ *(reactive!)*

$CH_3CH_2O^{\ominus}$ + *Base*-H

Larger ΔG_{rxn}, so: larger *K*. Deprotonation at this site preferred at eqm



CH_3CH_2OH + *Base*⊖ *(reactive!)*

$CH_3\underset{\ominus}{C}HOH$ + *Base*-H