Today

Sections 2.1, 2.3, 2.12
Acids and Bases

Next Class

Sections 2.6 - 2.9
How structure affects acidity and basicity

In aqueous solutions, the solution is considered **acidic** if the concentration of **H^+** is **greater than** the concentration of **OH^-**. At 25 °C, this occurs when the pH is less than 7.

In every day language, we might say that the solution is an acid. More precisely, there is an **acid in the solution that is causing the solution to be acidic**.

We will call molecules or ions **acids or bases based on how they react** (or could do).

There are **many molecules** that can **act as a base** in some circumstances **or an acid** in other circumstances.

acid because it made

$HCl \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$

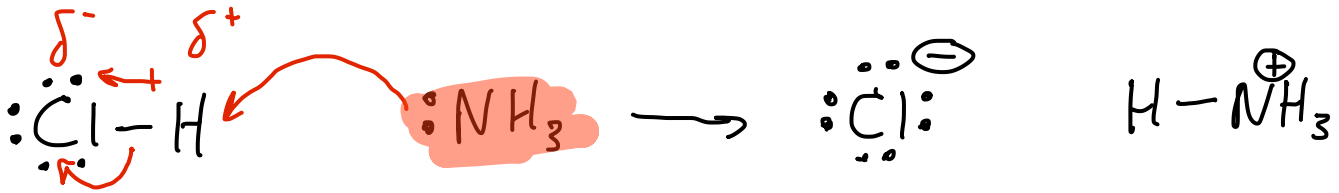
$NaOH \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$

an Arrhenius base because it dissociated in Na^+ + OH^-

$HCl \rightarrow H^{\oplus} + Cl^{\ominus}$

↑ donates/releases H^+ acid

$HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$ NH_4^+ Cl^-



accepts a proton

$^3H^+ e^-$ $^2H^+ e^-$ $^1H^+ e^-$

this is just a proton

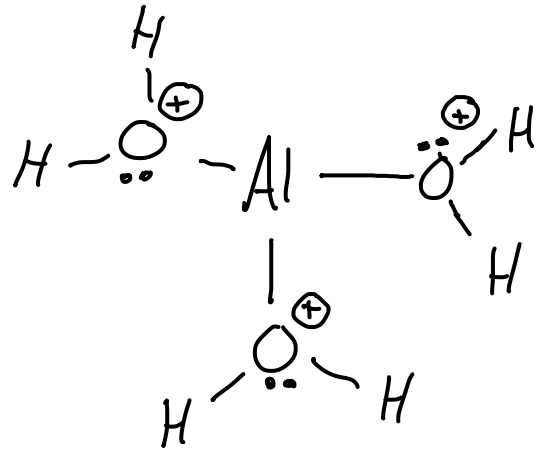
$AlCl_3 \xrightarrow{H_2O}$ 

water is the Lewis base. It is donating a pair of e^-'s to Al^{3+}

$$AlCl_3 + 3H_2\ddot{O}: \longrightarrow \left[Al(OH_2)_3\right]^{3+} + 3\,Cl^-$$

Al^{3+} is an acid

it is an e^- pair acceptor



$Al(OH)_3$

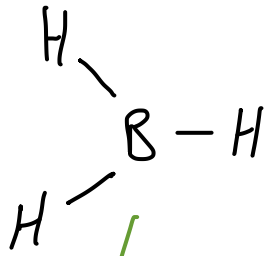
$3H^+ + 3Cl^-$

+2 & +3 metals

H^+ can H^+ donate e^-'s? NO, H^+ has no e^-'s to donate

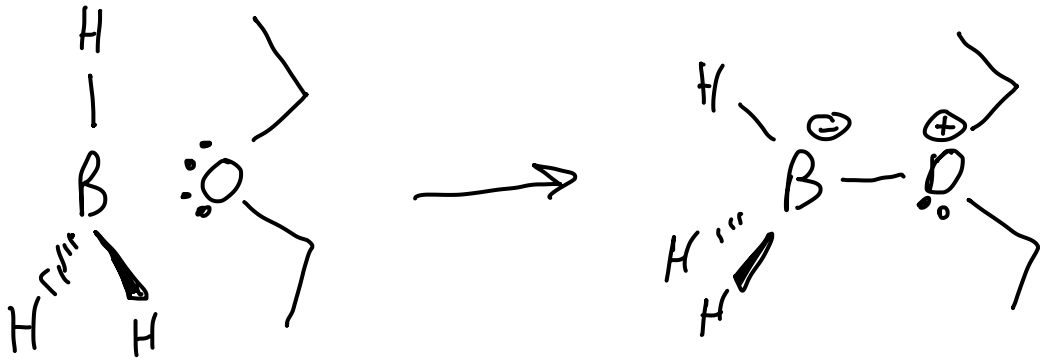
H^+ can only accept e^-'s

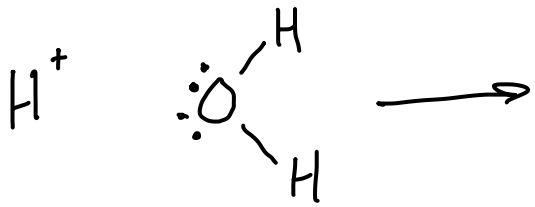
BH_3



6 e⁻'s in B's valence shell

room for 2 more





when I add a H^+ to a base I get the . . .

conjugate acid of H_2O

Lewis acid

Lewis base

K_a and pK_a

equilibrium constant

[ ] conc in $\frac{mol}{L}$

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$HA(aq) \longrightarrow H^+(aq) + A^-(aq)$

$K = \frac{[products]}{[reactants]}$

reaction goes to the right

$pK_a = -6$

$K = \frac{1000000}{1}$

$K = 10^6$

reaction stays or left

$pK_a = 6$

$K = \frac{1}{1000000}$

$K = 10^{-6}$

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow pK_a = pH + \log\frac{[HA]}{[A^-]}$ or

$pK_a = pH - \log\frac{[A^-]}{[HA]}$ or

$pH = pK_a + \log\frac{[A^-]}{[HA]}$

$pK_a = -\log[K_a]$

$= -\log[10^{-6}]$

$= -[-6] = 6$

pK_a is *backwards*

Today

Sections 2.6 - 2.9
How structure affects acidity and basicity

Next Class

Finish acids and bases

Sections 3.1-3.3
Nomenclature of Alkanes and Cylcoalkanes

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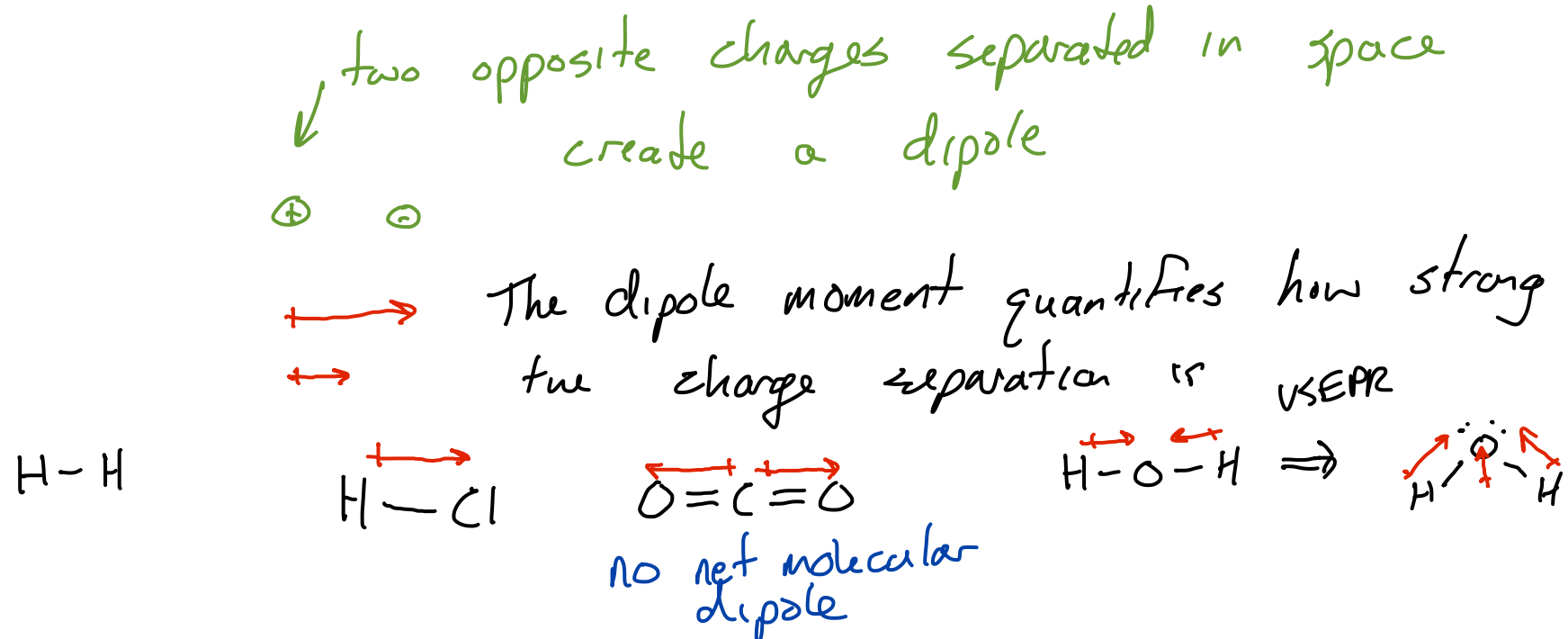
Test on Chap 1 and 2 on October 7 is one week from Friday.



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pK_a is *backwards*

Same Shell More Positive Nucleus

weakest

CH_4

NH_3

H_2O

strongest HF

the lower the pka
the better the molecule
is at releasing H^+

$K_a = 10^{-50}$

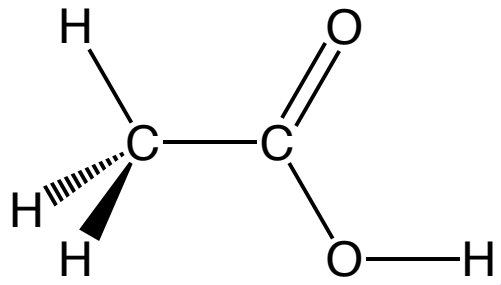
$K_a = 10^{-3.18}$

.001 ~ .01

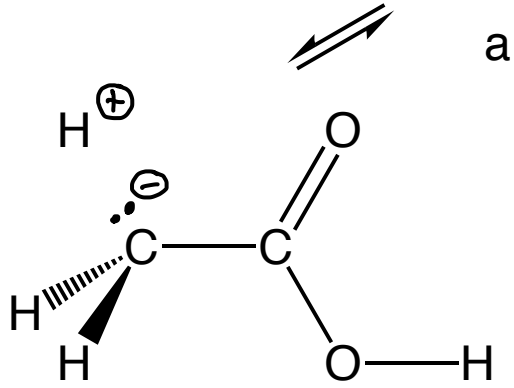
pK_a's CH_4, ~50 NH_3, ~36 H_2O, 15.6 HF, 3.18

Which is the acidic H^+ in acetic acid ($HC_2H_3O_2$)?

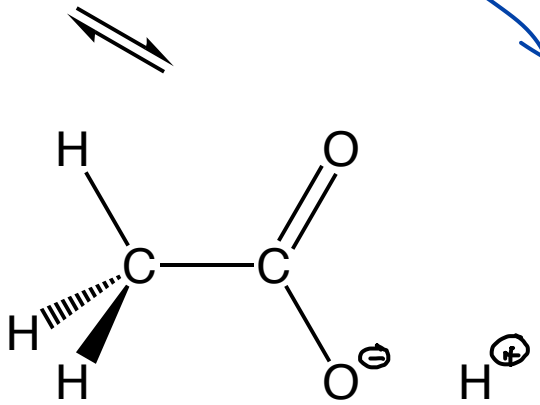
the lower in E the conj base is, the easier it is to release an H^+



a.k.a. CH_3CO_2H



?



Which atom is better a supporting/stabilizing a ⊖?

Which one is better at attracting e⁻'s? O?

more eneg. The ⊖ on O is more stable because e⁻ are near a +8 nucleus. ⊖ on C would be less stable 'cuz near a 6+ nucleus

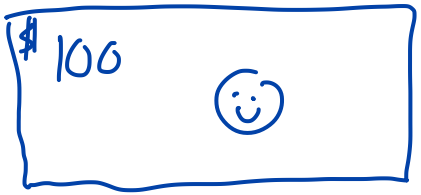
The one that leaves the more/most stable base behind

Stabilization of a Base or Conjugate Base Summary

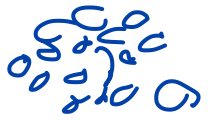
Get electrons near a positive charge

e⁻ on conjugate base are stabilized by being attracted to a ⊕ charge

Spread electrons out over a larger volume



concentrated charge attractive



10,000¢ diffuse charge

Same Shell More Positive Nucleus

these atoms that bear the ⊖ are all similar sizes

weakest

$CH_4 \rightarrow H_3C^{\ominus} + H^{\oplus}$ 6+

$NH_3 \rightarrow H^{\oplus} + H_2N^{\ominus}$ 7+

$H_2O \rightarrow H^{\oplus} + HO^{\ominus}$ 8+

strongest

$HF \rightarrow H^{\oplus} + F^{\ominus}$ 9+ nucleus

pK_a's CH_4, ~50 NH_3, ~36 H_2O, 15.6 HF, 3.18

Same Column Larger Valence Shell

strongest

HI → $H^{\oplus}$ $I^{\ominus}$ n = 5

HBr → $H^{\oplus}$ $Br^{\ominus}$ n = 4

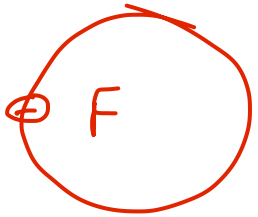
HCl → $H^{\oplus}$ $Cl^{\ominus}$ n = 3

HF ⇌ $H^{\oplus}$ $F^{\ominus}$ n = 2

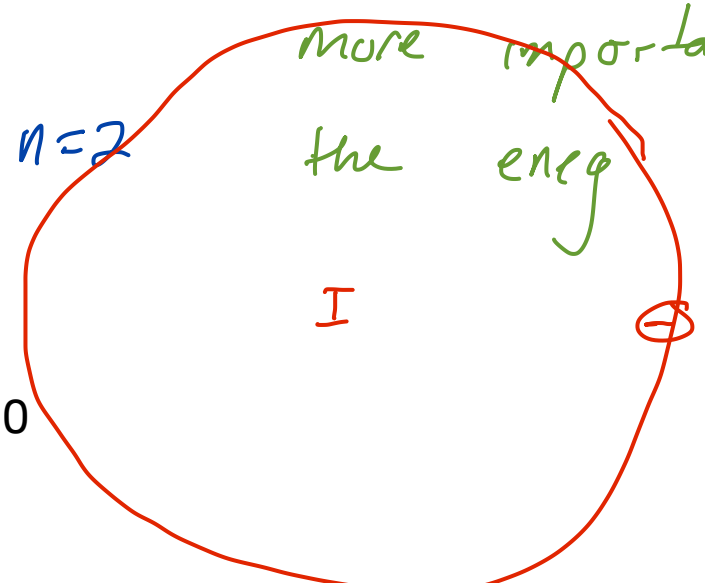
weakest

e^- are spread out in large n=5 orbital

When changing shells the increasing size of the atom becomes more important than the energ



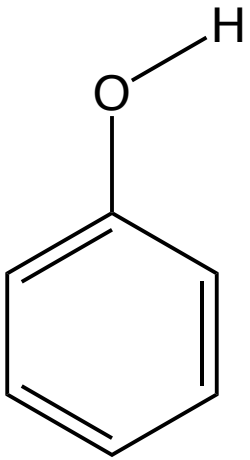
H^+



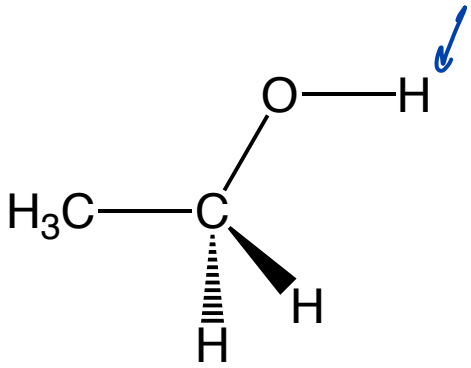
pK_a's HF, 3.18 HCl, -7 HBr, -9 HI, -10

Resonance

middle

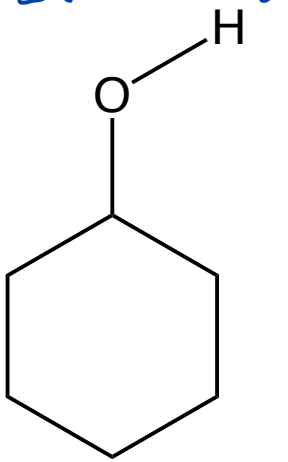


phenol



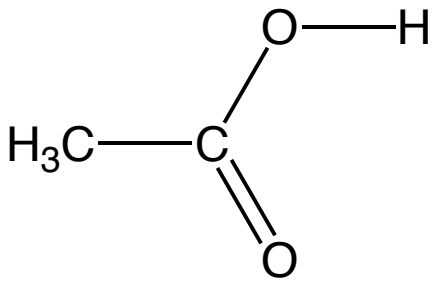
ethanol

weakest



cyclohexanol

strongest



acetic acid

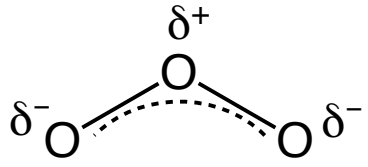
pK_a's cyclohexanol, 16.0 phenol, 10.0 ethanol 16.0 acetic acid 4.74

10^{-16} 10^{-10} 10^{-16} $10^{-4.74}$

Wait, what, resonance?

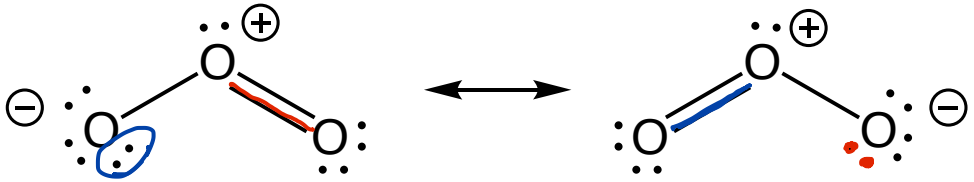
It is a fix for valance bond theory to accommodate extended π systems seen in MO theory

MO Theory matches reality



O to O bonds are the same length,
and, surprisingly, the molecule is slightly polar

Electron delocalization using resonance contributors

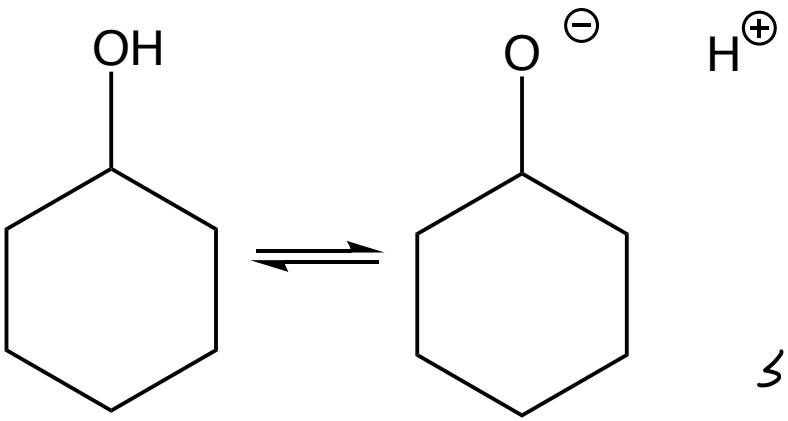


To draw resonance contributors we switch the positions of the lp e⁻'s + the π bond

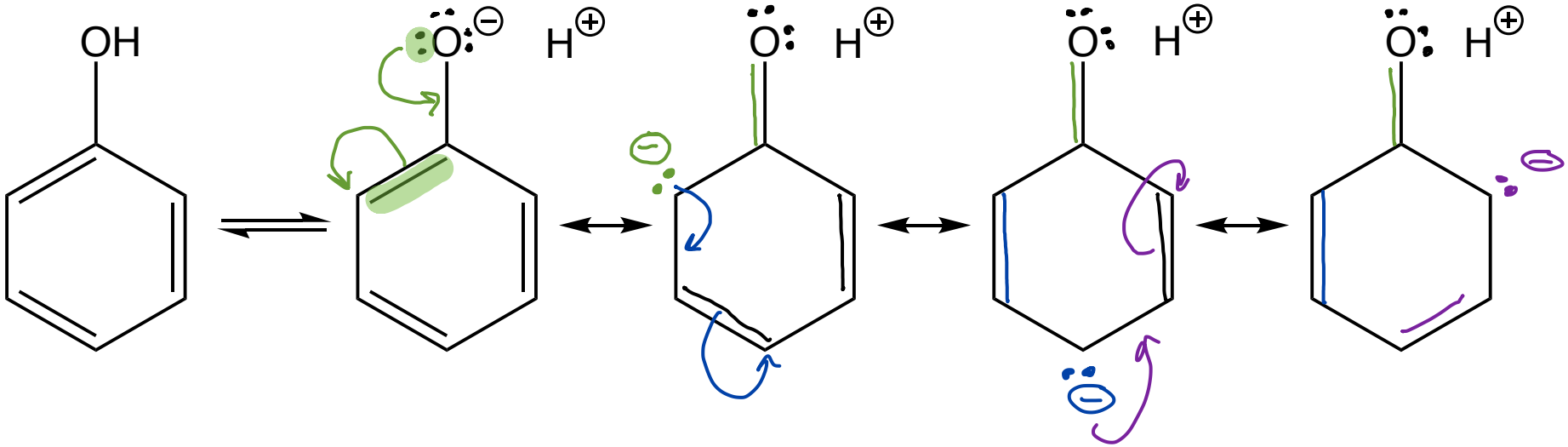
When there are lone-pair e⁻'s adjacent to a π bond or more than two p orbitals in a row, we must consider drawing resonance contributors to have a better understanding of the structure, properties, and reactivity of a molecule

Resonance

is stabilized by O's +8 nucleus



stabilized by O's 8+ nucleus & three other 2 nuclei



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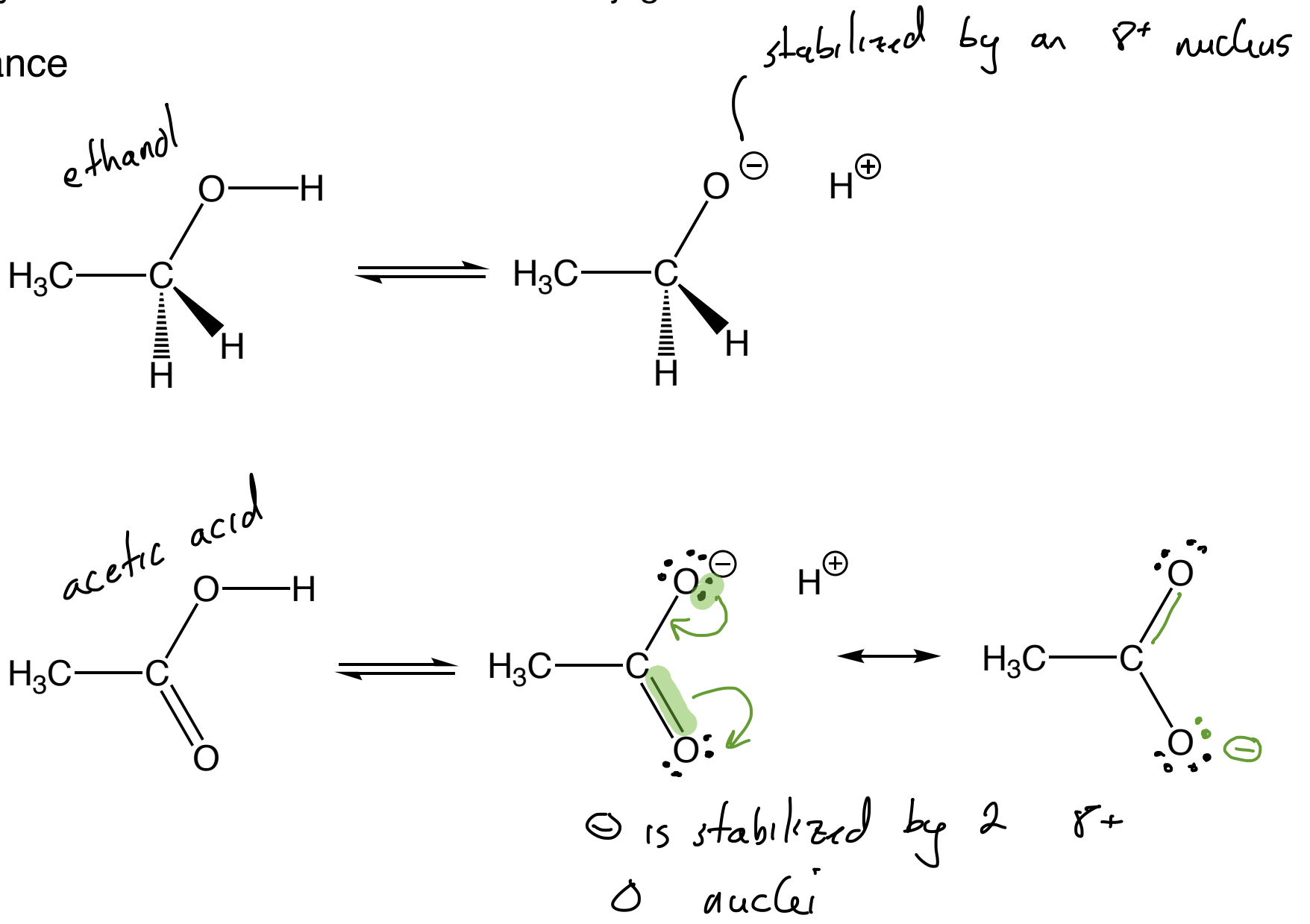

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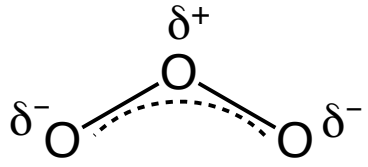

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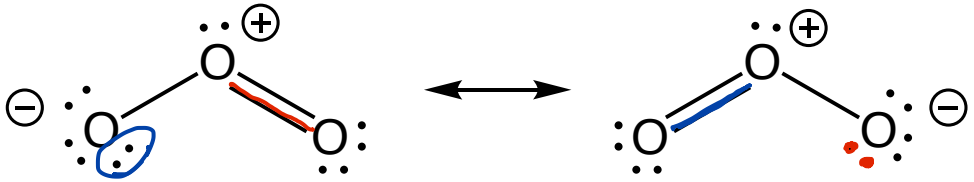

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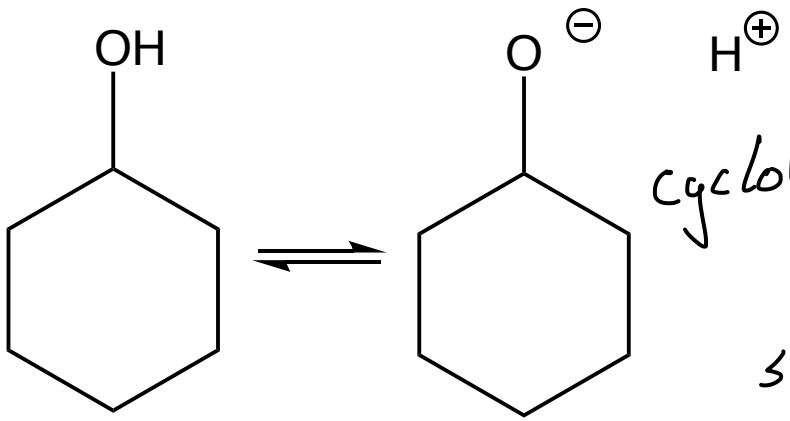
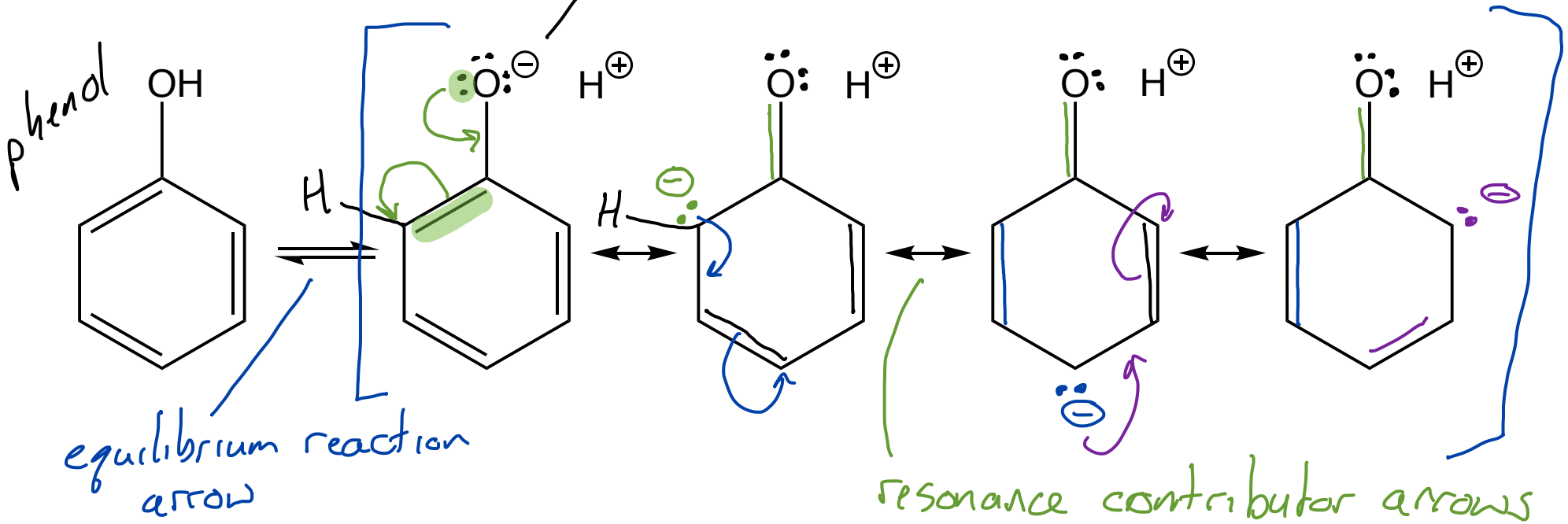
Resonance

is stabilized by O's +δ nucleus



cyclohexanol

stabilized by O's δ+ nucleus & three other 2 nuclei

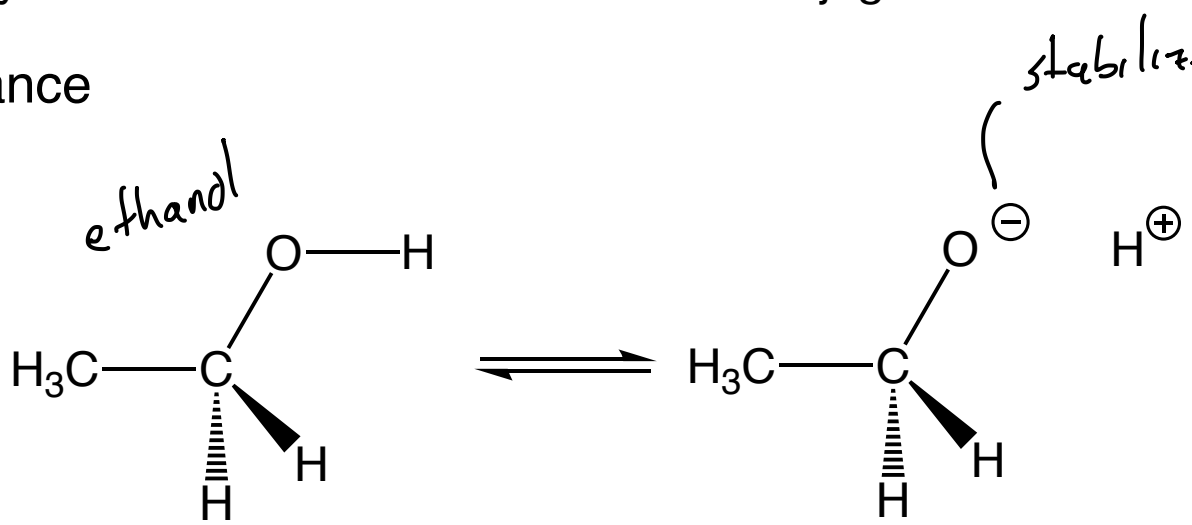


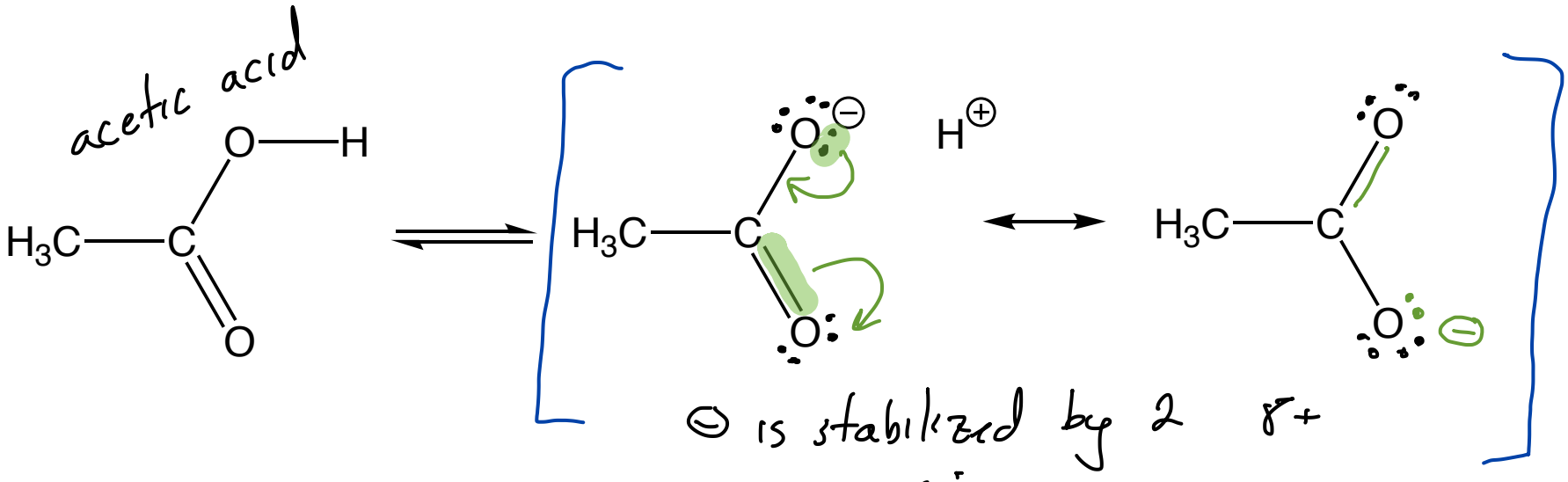
equilibrium reaction arrow

resonance contributor arrows

pKa's cyclohexanol, 16.0 phenol, 10.0 ethanol 16.0 acetic acid 4.74

Resonance





⊖ is stabilized by 2 δ+ O nuclei

Spreading out e⁻'s by resonance stabilizes them so it is easier for CH_3CO_2H to release H^+

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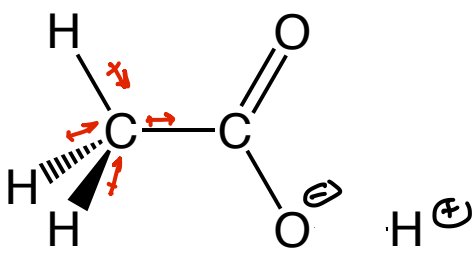
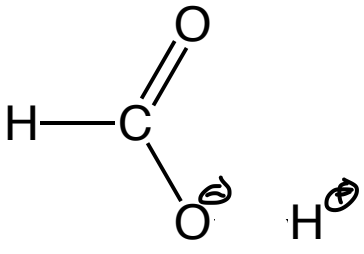
Inductive Effect



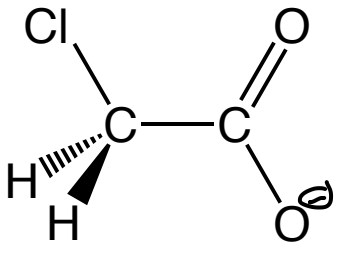
4.76

(4)

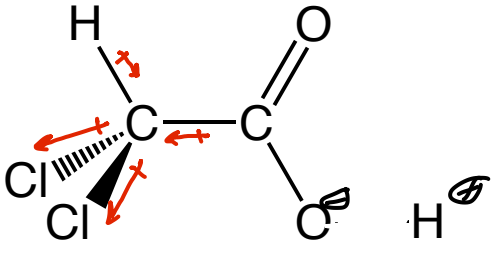
e⁻ pushed toward O atoms... higher E



3.75



2.87

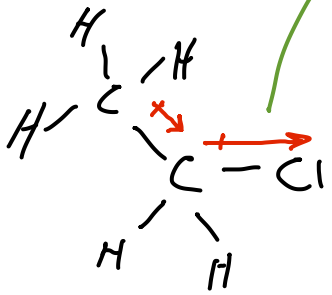


1.25

(1)

e⁻ are drawn away from the O by the inductive effect

e⁻'s are stabilized by spreading them out by making the C more ⊕



First dipole induces a second dipole but the effects drops of by the 3rd bond

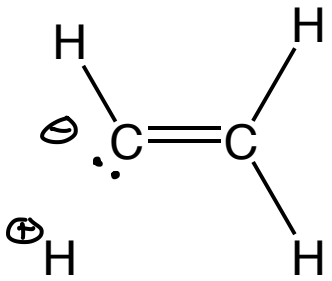
pK$_a$'s acetic, 4.76 formic, 3.75 chloroacetic, 2.87 dichloroacetic, 1.25

Greater s character

strongest

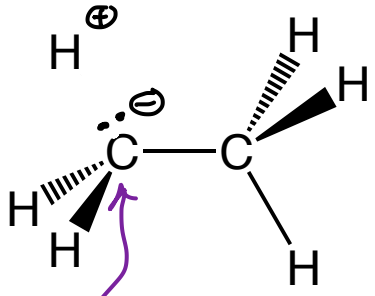
sp

s 50% p 50%



sp^2

s 33% p 67%



weakest

what is the hybridization?

4 directions,

4 HO's needed

cross $s \times p_x \times p_y \times p_z$

to get 4 sp^3

s 25% p 75%

more s like character gets e^-'s close to nucleus so e^-'s more stable

approximate pK_a's ethane (C_2H_6) 50, ethene (C_2H_4) 44, ethyne (C_2H_2) 25

Stabilization of a Base or Conjugate Base Summary

Get electrons near a positive charge

same row p-table more ⊕ nucleus stabilizes e⁻'s

increase s character of hybrid orbitals

Spread electrons out over a larger volume

increasing the size of the atom n=3 vs n=2

spreading out e⁻ by e⁻ delocalization (resonance)

use the inductive effect to move charge around in a molecule

Base Strength: Concentrated, High Energy Electrons...

increased ⊖ charge

NaOH Na^+ + $:\ddot{O}H^-$

$NaOCH_3$ Na^+ $:\ddot{O}-CH_3$

$NaSCH_3$ Na^+ $:\ddot{S}-CH_3$

bigger, e^- more stable

$H_3C-\ddot{O}H$ $H-O-H$

$H_3C-\ddot{N}H_2$ H_3N

e^- here see +7
which is lower than +8
these e^-'s are less stable

$NaOCH_3$ Na^+ $:\ddot{O}CH_3^-$

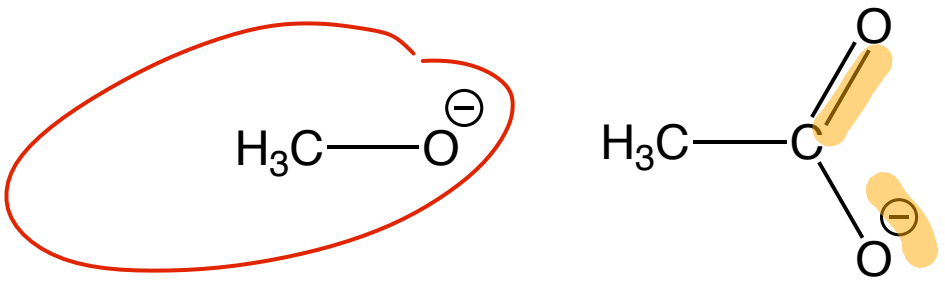
$HOCH_3$ $H-\ddot{O}-CH_3$

$H-\ddot{O}-H$

H_3C-ONa $H_3C-\ddot{O}:^-$ Na^+

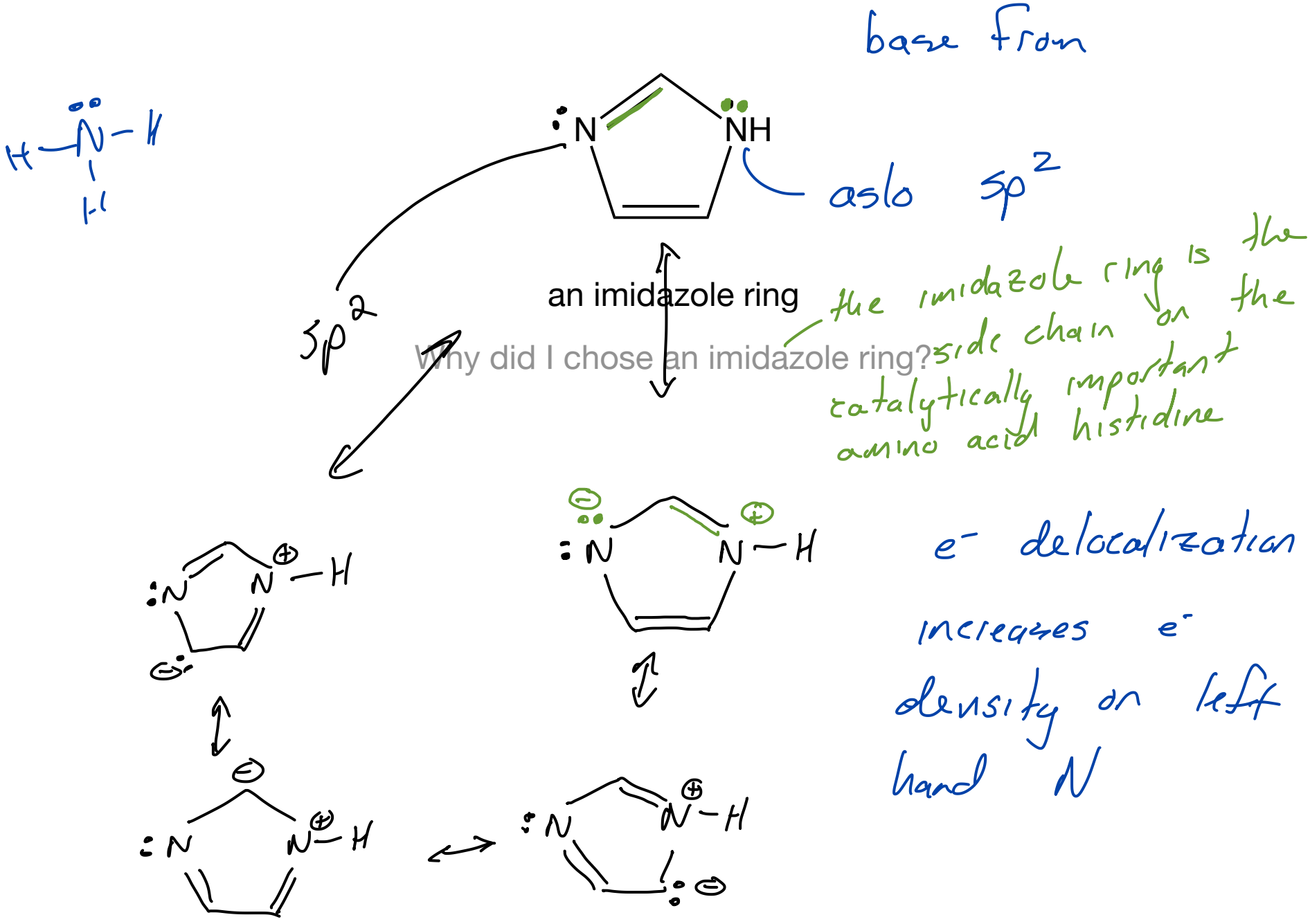
H_3C-NH_2 $H_3C-\ddot{N}H_2$

Base Strength: Concentrated, High Energy Electrons...

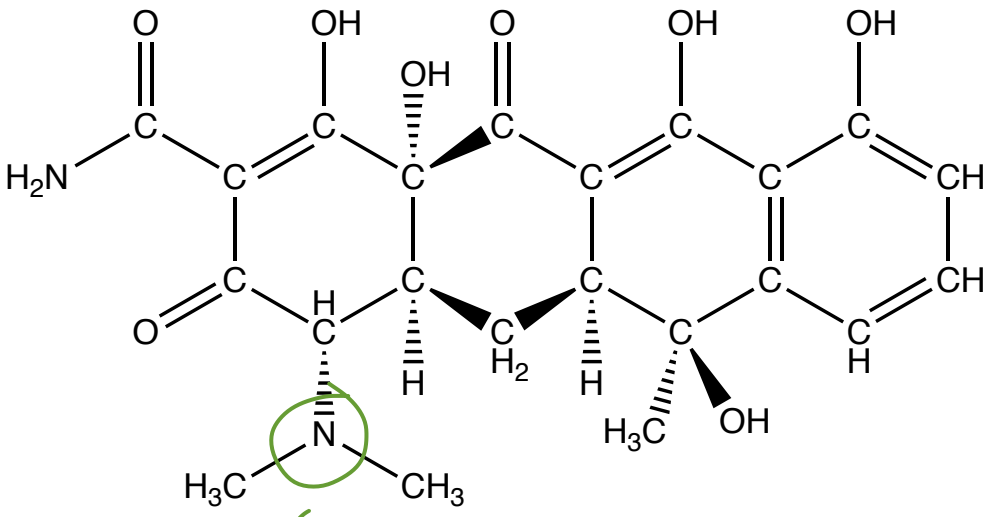


e⁻ concentrated on 1 O vs e⁻ spread out over 2 O's

Base Strength: Concentrated, High Energy Electrons...

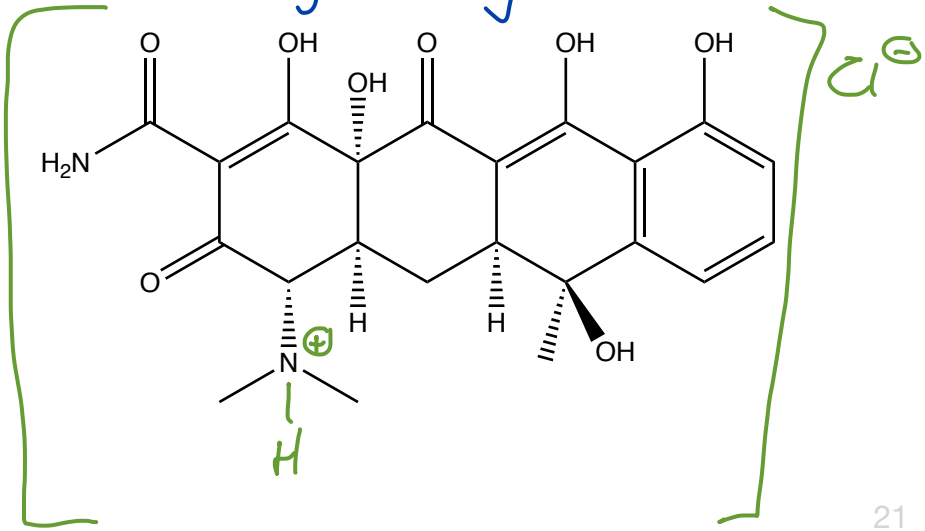


Base Strength and Water Solubility

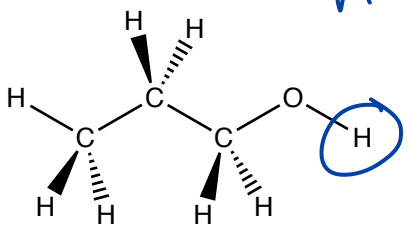


me, me, me!
protonate me!

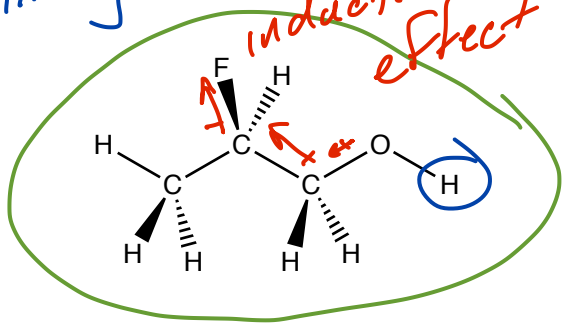
tetracycline hydrochloride
the drug is made more H_2O soluble by making it more polar



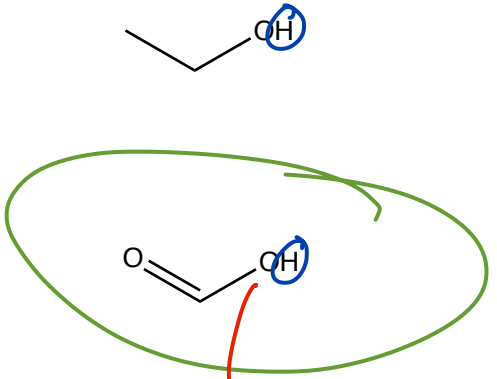
Practice: For each molecule, which proton is the most likely to be lost and for each pair, which is the stronger acid



most likely

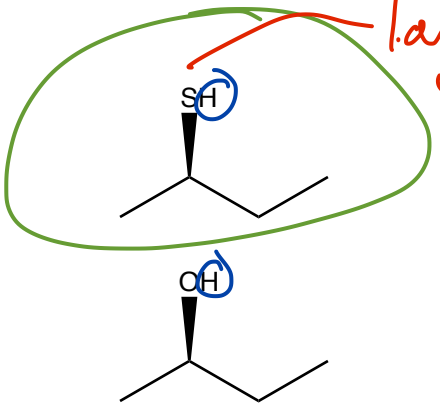


inductive effect

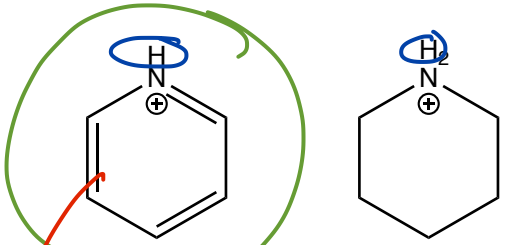


resonance e^- adjacent to π bond

more acidic



larger atom can support the negative charge better



e^-'s on N will be in an sp^2 hybrid instead of sp^3 and will be lower in E