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

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

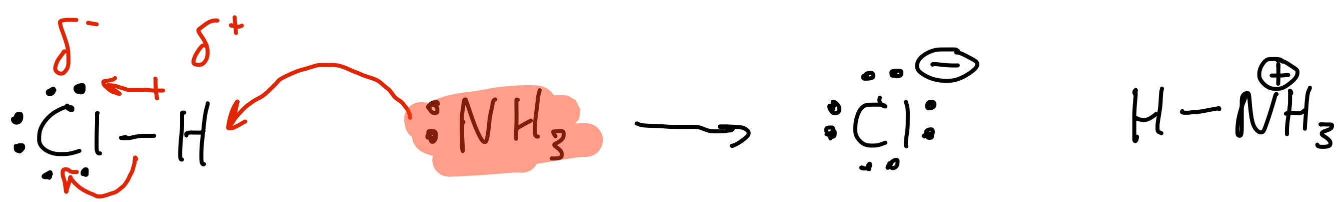
$$NaOH \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

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

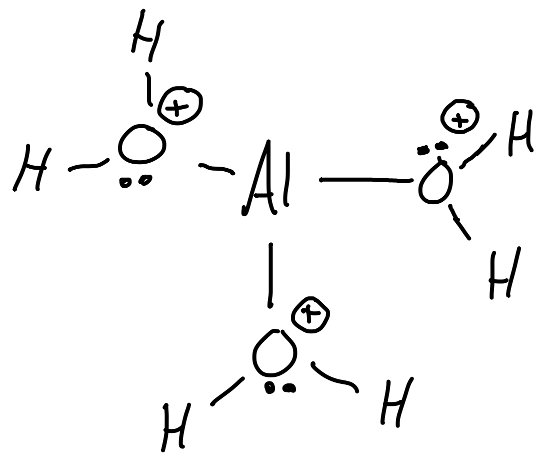
$AlCl_3 \xrightarrow{H_2O}$ 

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

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

Al^{3+} is an acid

it is an e^- pair acceptor



$\rightarrow Al(OH)_3$

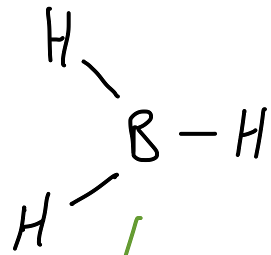
$3H^+ + 3Cl^-$

+2 & +3 metals

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

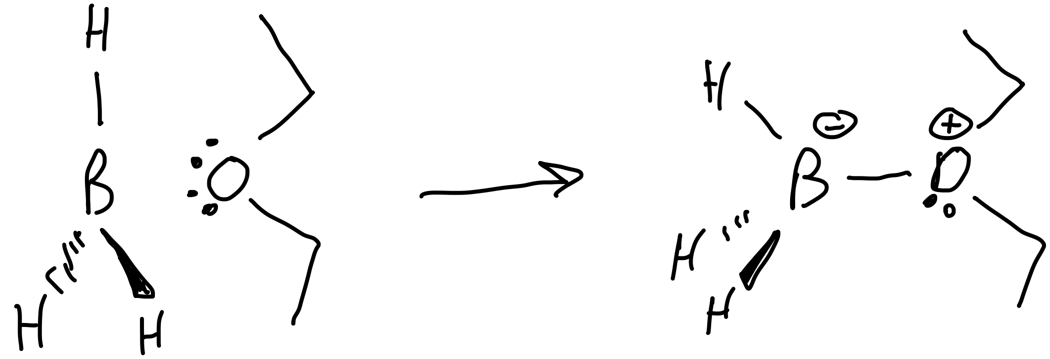
H^+ can only accept e^-'s

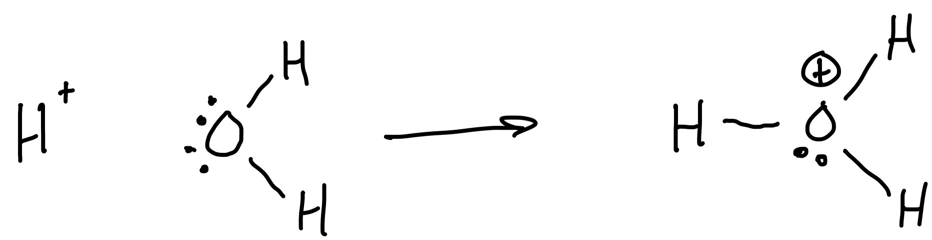
BH_3



$6e^-$'s in B's valence shell

room for 2 more





Lewis acid

Lewis base

when I add a H^+ to a base I get the ... conjugate acid of H_2O

K_a and pK_a

Section 2.6

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

↑ equilibrium constant

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

$pK_a = 6$

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

$pK_a = -6$

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

reaction goes to the right

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

$$K = 10^6$$

reaction stays on left

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

$$K = 10^{-6}$$

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

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

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

$$pK_a = -\log[K_a]$$

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

$$= -[-6] = 6$$

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

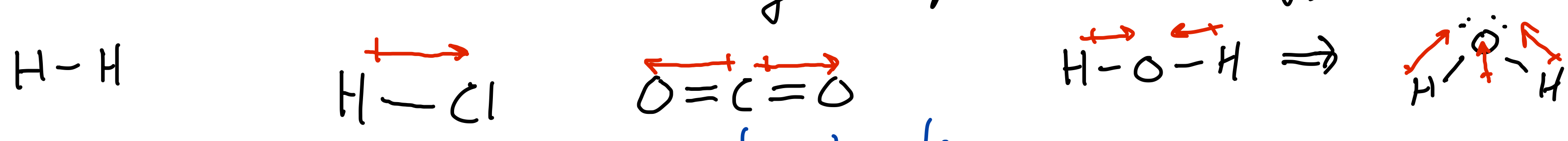
Organic lecture on Friday, September 30 is canceled.

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

two opposite charges separated in space create a dipole

The dipole moment quantifies how strong the charge separation is

VSEPR



no net molecular dipole

K_a and pK_a

↑ equilibrium constant

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

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

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

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

$pK_a = -6$

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

pK_a is *backwards*

Same Shell More Positive Nucleus

weakest

CH_4

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

NH_3

H_2O

strongest HF

$K_a = 10^{-50}$

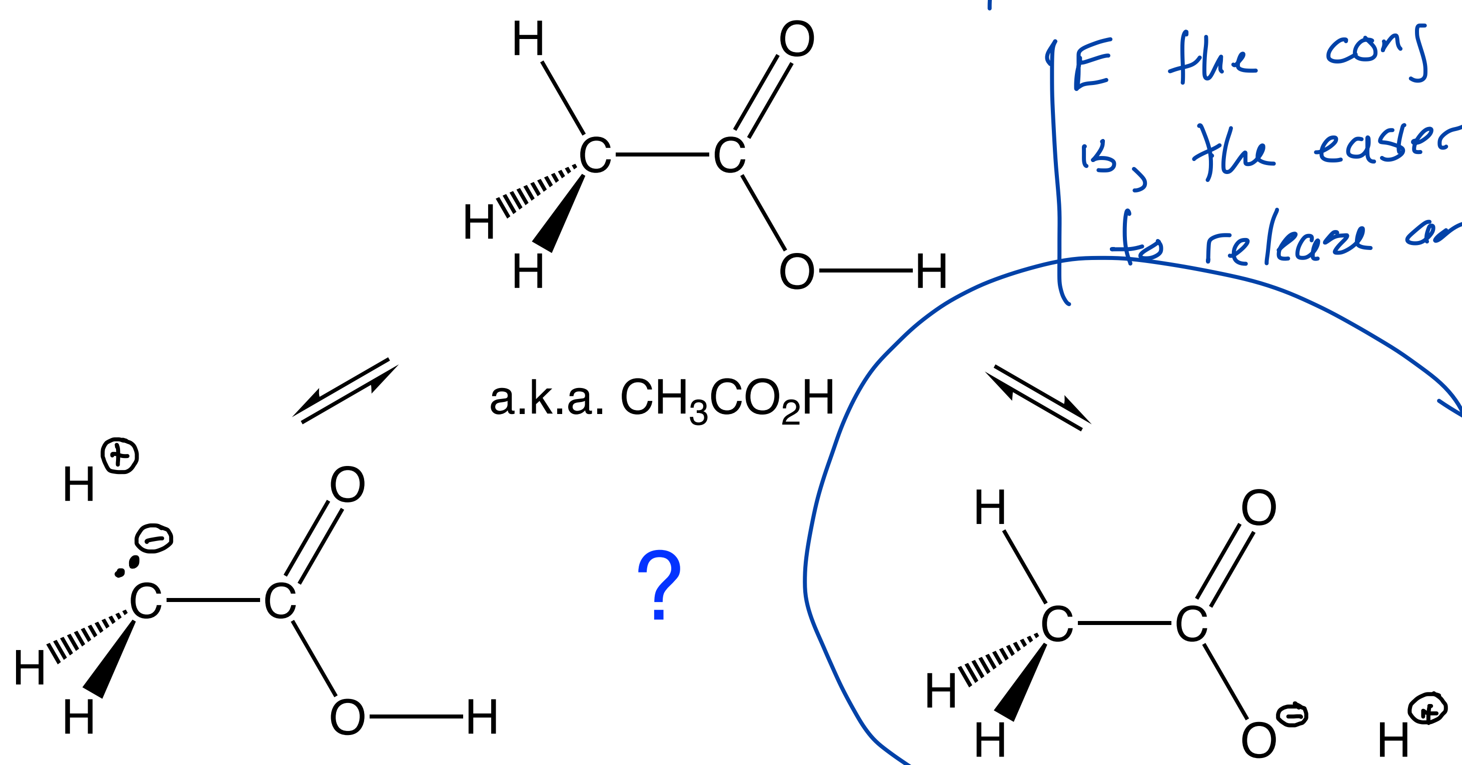
$K_a = 10^{-3.18}$

.001 ~ .01

pKa'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^+



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

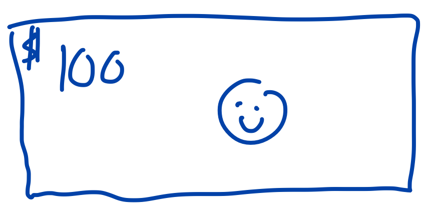
The one that leaves the more/most stable base behind

Stabilization of a Base or Conjugate Base Summary

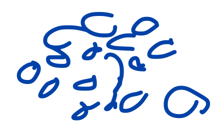
Get electrons near a positive charge

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

Five ways to stabilize the electrons on the conjugate base

Section 2.6 – 2.9

Same Shell More Positive Nucleus

these atoms that bear the $\ominus$ 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^{+}

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

strongest

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

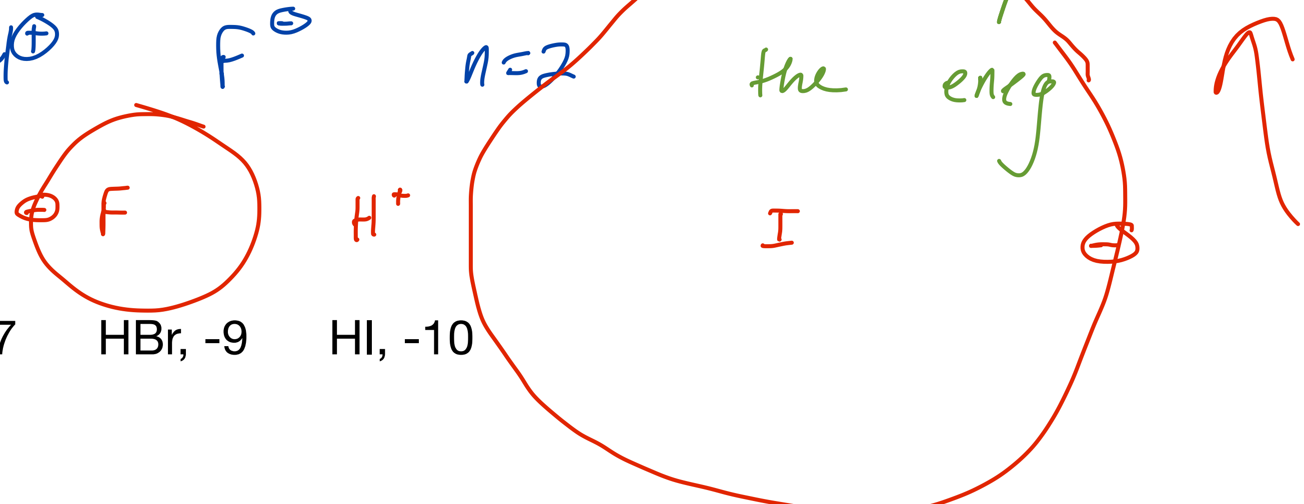
HCl → $H^{\oplus}$ $Cl^{\ominus}$ n=3

HF ⇌ $H^{\oplus}$ $F^{\ominus}$ n=2

weakest

$\bar{e}$ are spread out in large n=5 orbital

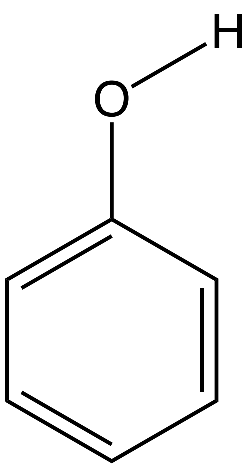
when changing shells the increasing size of the atom becomes more important than the eneg



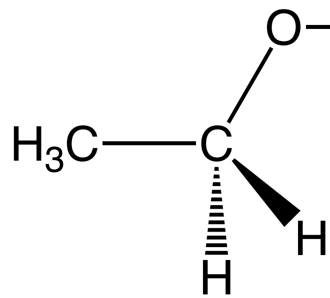
pK$_a$'s HF, 3.18 HCl, -7 HBr, -9 HI, -10

Resonance

middle

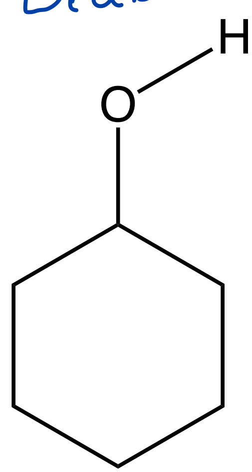


phenol



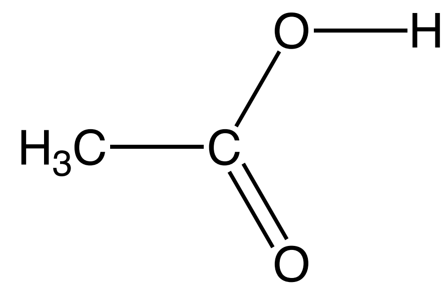
ethanol

weakest



cyclohexanol

strongest



acetic acid

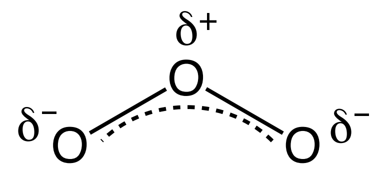
pK_a's cyclohexanol, 16.0 phenol, 10.0 ethanol 16.0 acetic acid 4.74

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

Wait, what, resonance?

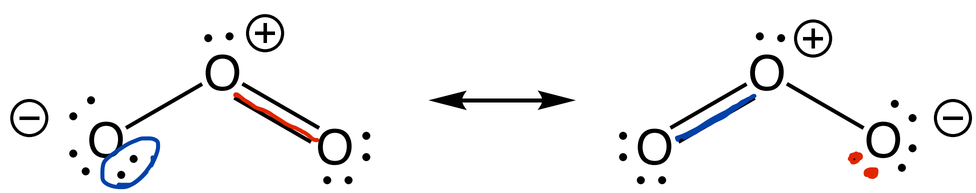
It is a fix for valance bond theory to accommodate extended π systems seen in MO theory

MO Theory matches reality



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

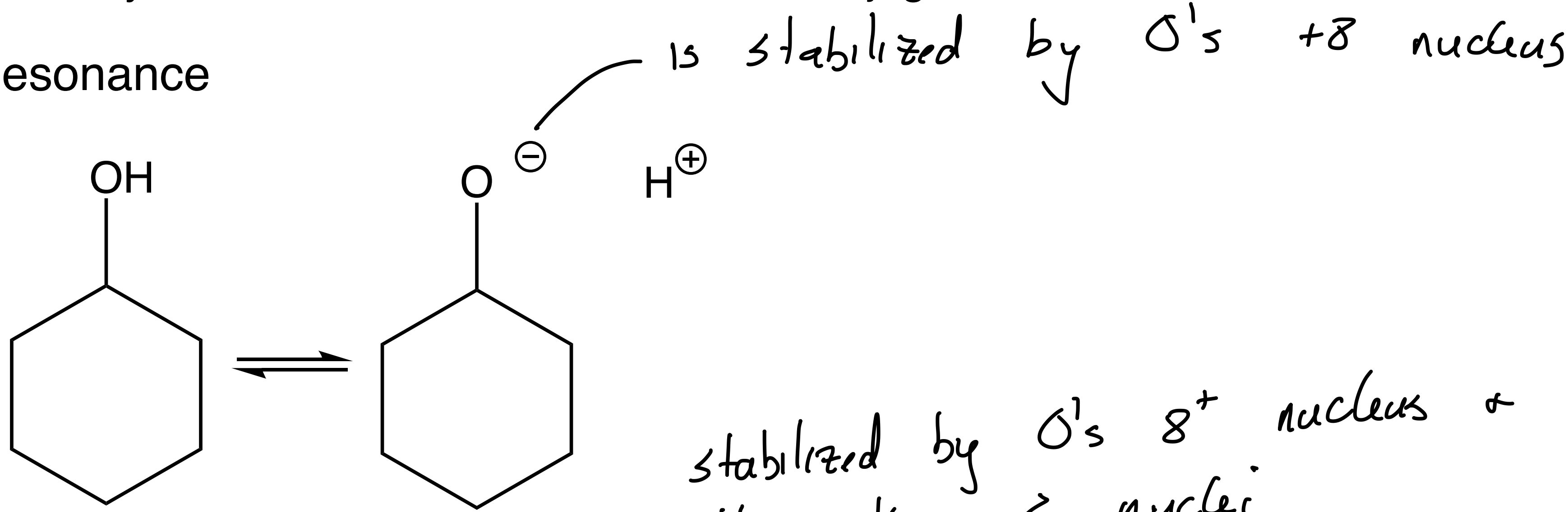
Electron delocalization using resonance contributors

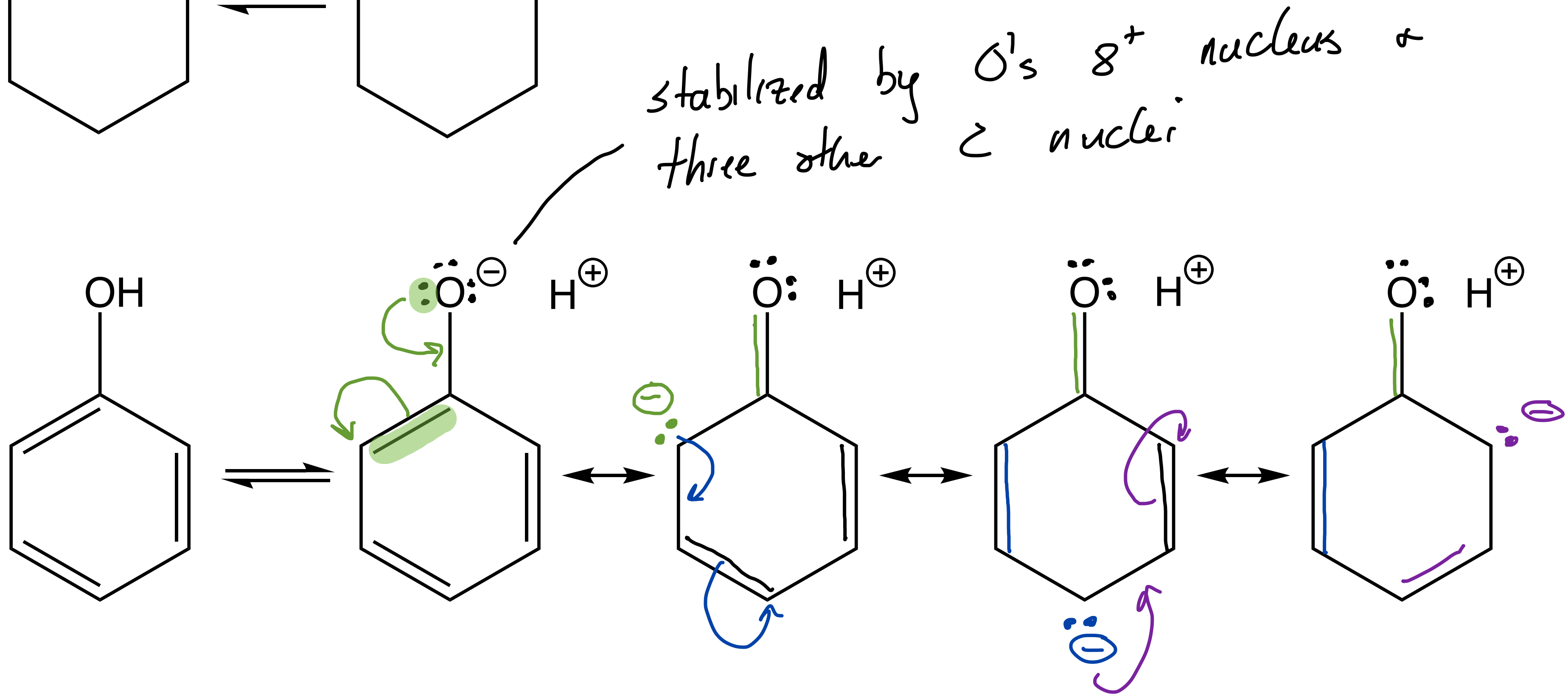


To draw resonance contributors we switch the positions of the lp e⁻'s + the π bond

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



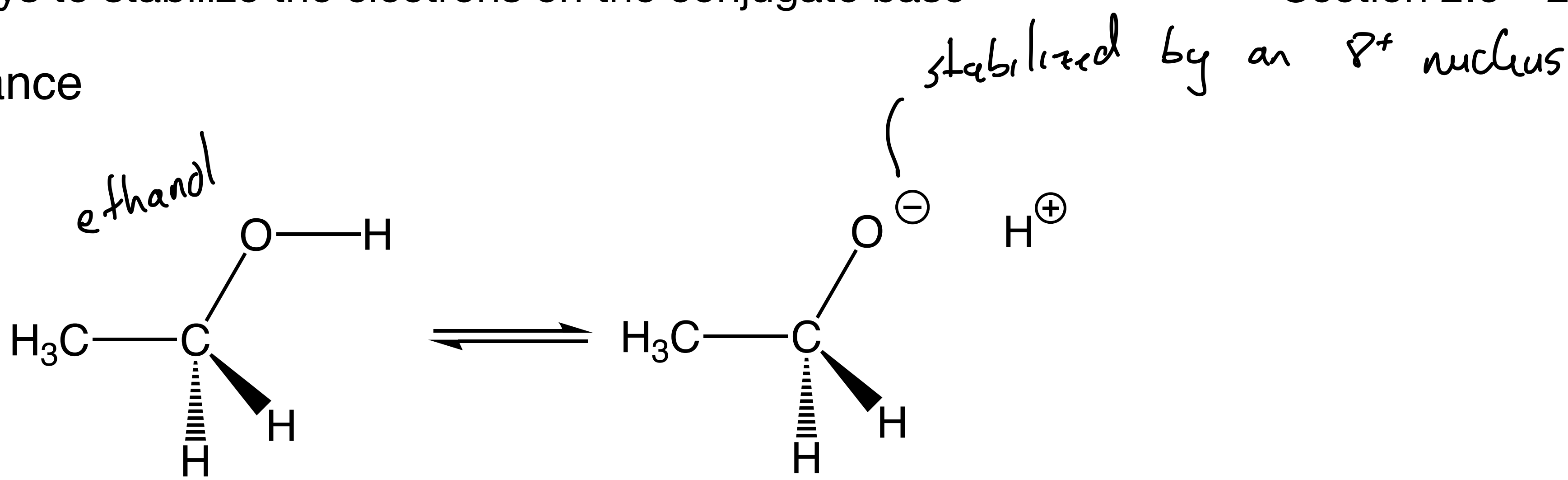


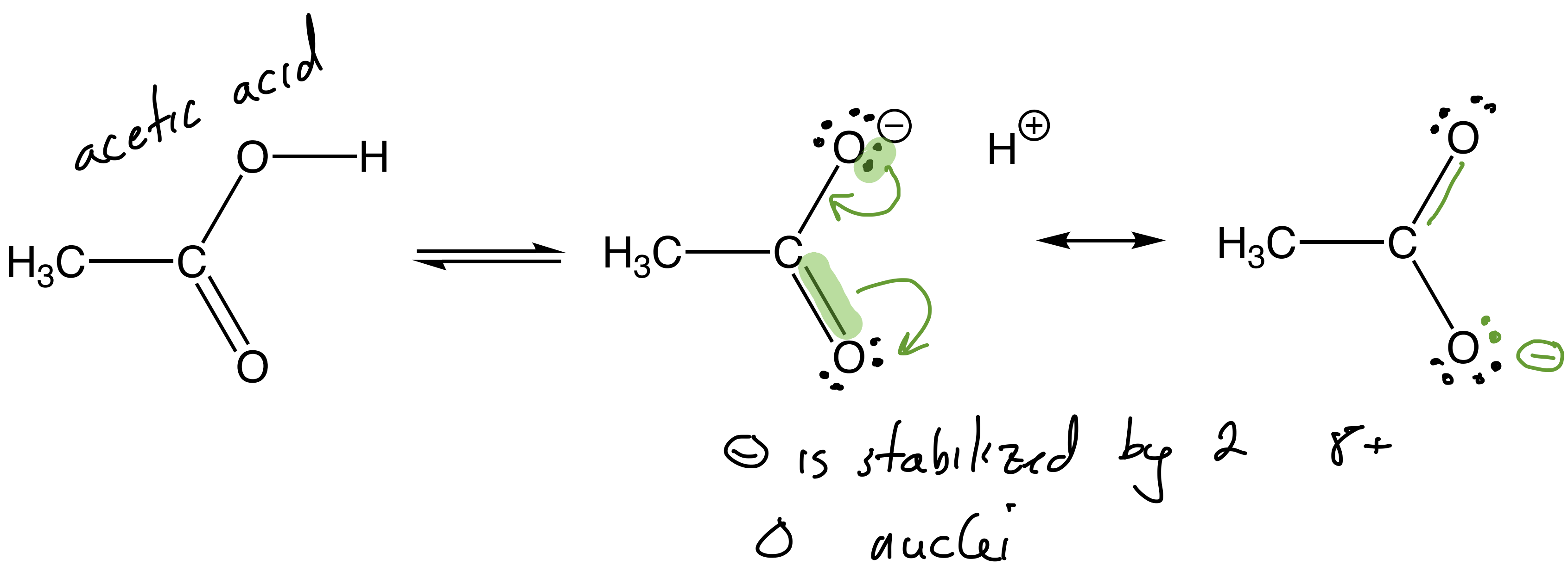
pK_a's cyclohexanol, 16.0 phenol, 10.0 ethanol 16.0 acetic acid 4.74

Five ways to stabilize the electrons on the conjugate base

Section 2.6 – 2.9

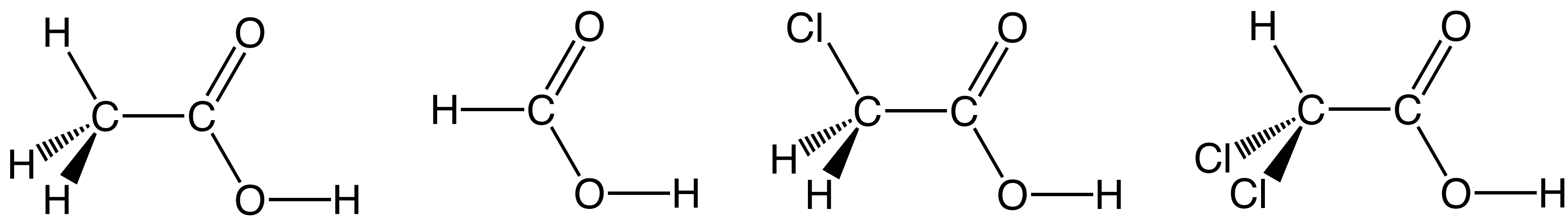
Resonance





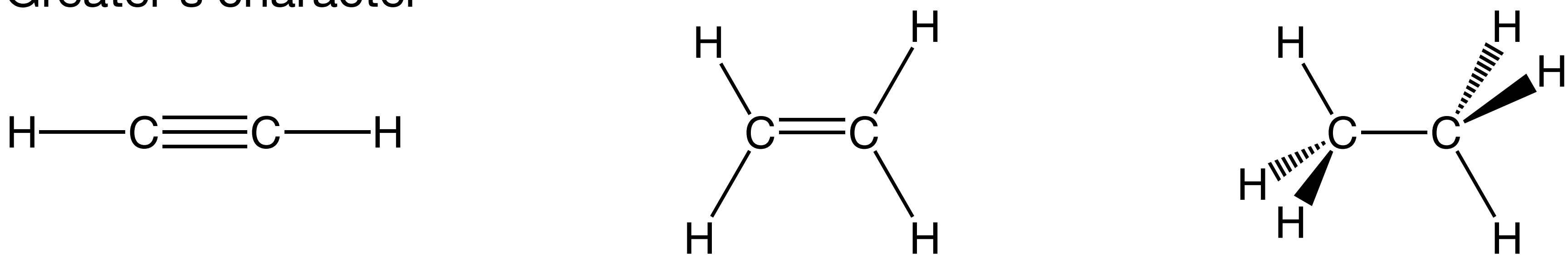
pK_a's   cyclohexanol, 16.0   phenol, 10.0   ethanol 16.0   acetic acid 4.74

Inductive Effect



pK_a's acetic, 4.76 formic, 3.75 chloroacetic, 2.87 dichloroacetic, 1.25

Greater s character



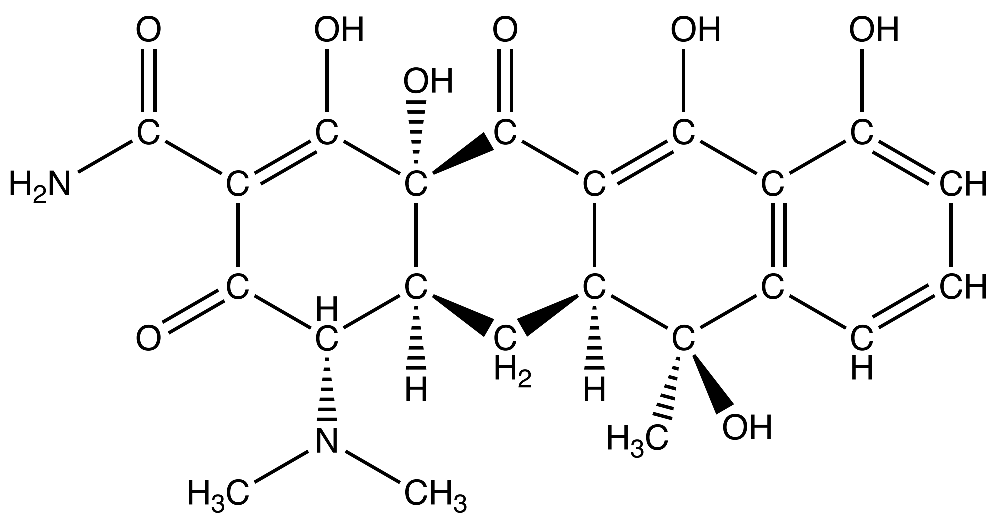
approximate pK_a's ethane (C_2H_6) 50, ethene (C_2H_4) 44, ethyne (C_2H_2) 25

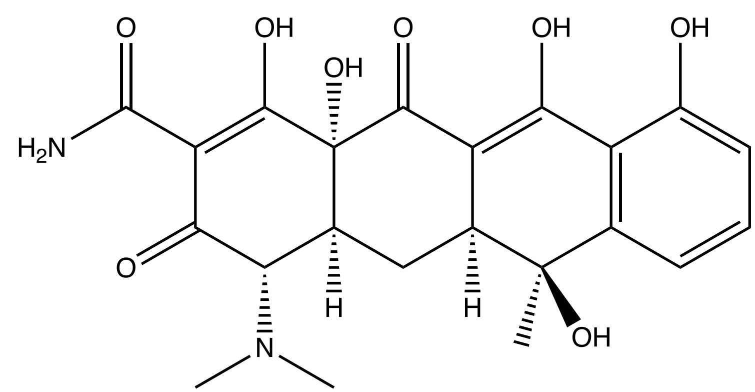
Stabilization of a Base or Conjugate Base Summary

Get electrons near a positive charge

Spread electrons out over a larger volume

Base Strength and Water Solubility





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