# Organic Chemistry Prep Workshop – Day 4

## Acids and Bases

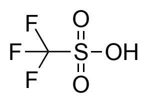
- **Arrhenius Acid – acids that dissociate to give $H^+$**
- **Arrhenius Base – acids that dissociate to give $HO^-$**
- **Bronsted-Lowry Acid – Proton ($H^+$) donors**
- **Bronsted-Lowry Base – Proton ($H^+$) acceptors**

## Common Strong Acids

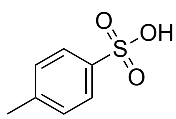
**Inorganic**

**HCl**
**HBr**
**HI**
**$H_2SO_4$**
**$HClO_4$**
**$HClO_3$**
**$HNO_3$**

**Organic**




Triflic Acid




p-Toluenesulfonic Acid

## Common Strong Bases

**Group IA Metal Hydroxides**

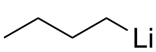
**LiOH, NaOH, KOH**

**Heavier Group IIA Metal Hydroxides**

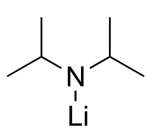
**$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$,**

**Strong Organic Bases**

**M-C Compounds**




**M-N Compounds**




## Writing Acid/Base Reactions

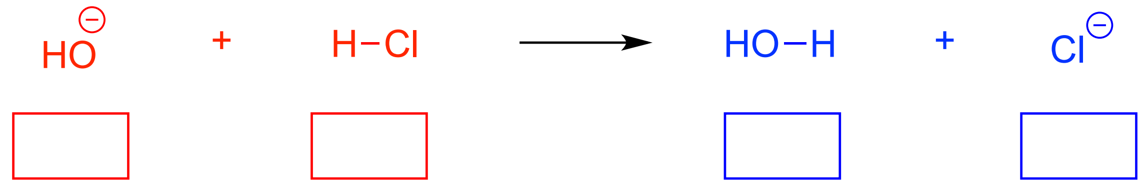
**In an acid base reaction, a Bronsted Lowry acid donates a proton to a Bronsted Lowry base.**

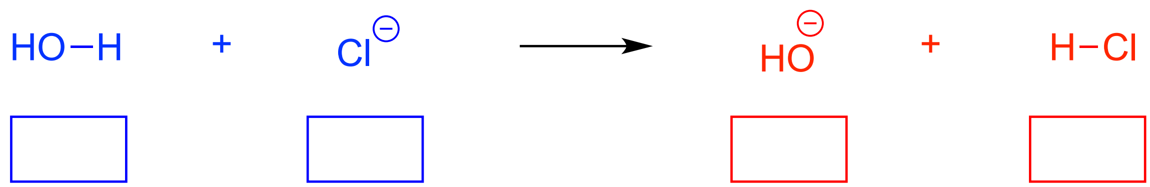
$$HO^{\ominus} + H{-}Cl \longrightarrow HO{-}H + Cl^{\ominus}$$

**Acid = Proton Donor**
**Base = Proton Acceptor**
**Conjugate Acid = The product that has accepted the proton**
**Conjugate Base = The product that has lost the proton**

**Another way to look at it...**

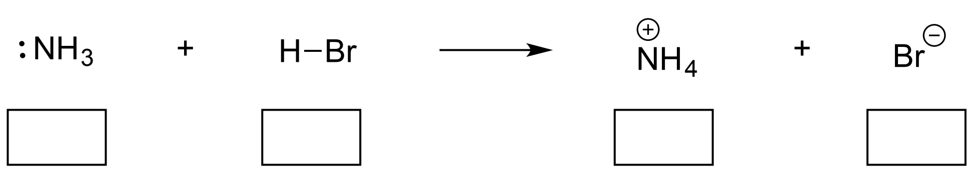
- **Conjugate acid = the acid on the right side**
- **Conjugate base = the base on the right side**

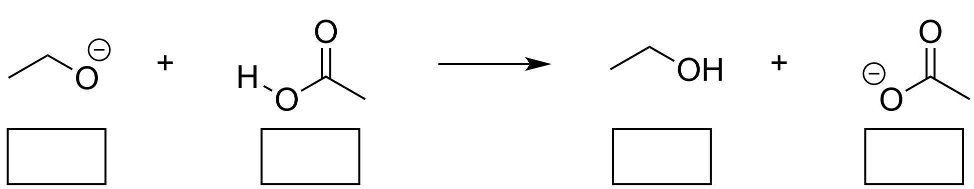




| **You Try 4-1** | | |
|---|---|---|
| **Write the conjugate base for each of the following** | | |
| $H_2PO_4^-$ | $CH_3OH_2^+$ | $CH_3CH_2OH$ |
| **Write the conjugate acid for each of the following** | | |
| $H_2S$ | $CH_3O^-$ | $H_2PO_4^-$ |

| **You Try 4-2** |
|---|
| **For each reaction below, label the acid, base, conjugate acid, and conjugate base** |

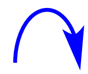


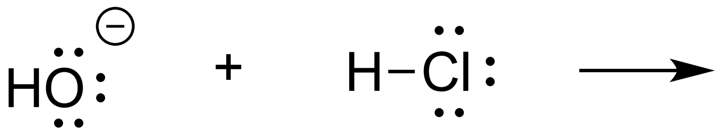


## Curved Arrows to Show Electron Flow

**Curved Arrows**

- **Show electron flow**
- **Always start at the electrons (tail on the electrons)**
- **Arrowhead points to where the electrons are going**

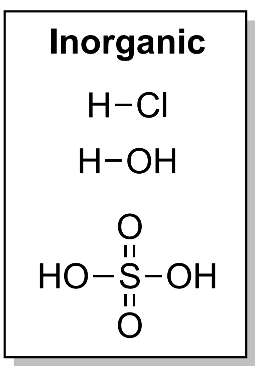


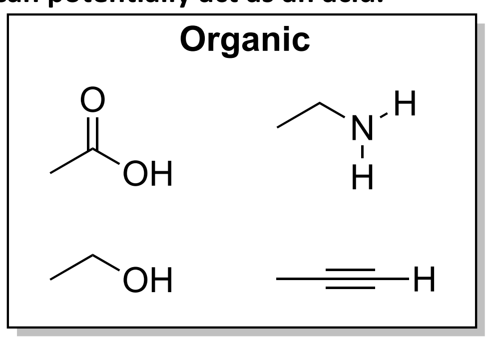



**We used curved arrows to show electron flow in resonance structures. Now we are using them to show electron flow in chemical reactions.**

## Identifying Bronsted-Lowry Acids

**Any species with a hydrogen can potentially act as an acid.**



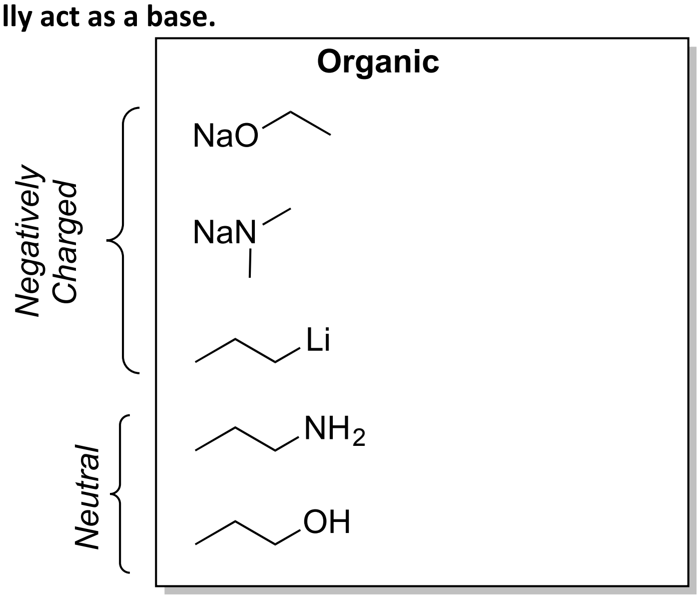

## Identifying Bronsted-Lowry Bases

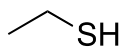
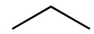
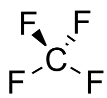
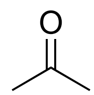
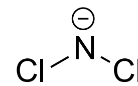
**Any species with a lone pair can potentially act as a base.**

**Inorganic**

*Negatively Charged*
- NaOH
- $LiNH_2$

*Neutral*
- $NH_3$
- $H_2O$

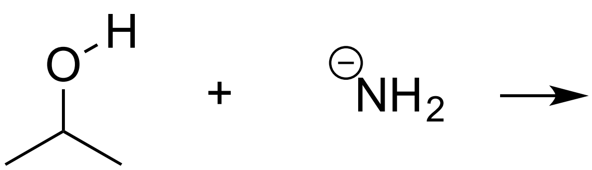


| You Try 4-3 | | |
|---|---|---|
| **Identify each of the following as: an acid, a base, neither an acid nor a base, or both an acid and a base.** | | |
|  |  | H–F |
|  |  |  |

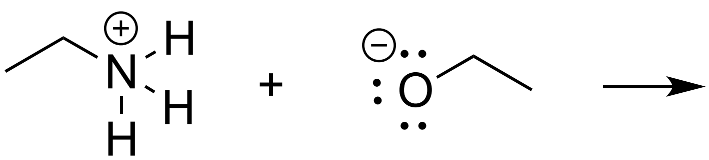
## Acid/Base Reactions

**Maintain Charge Balance!**

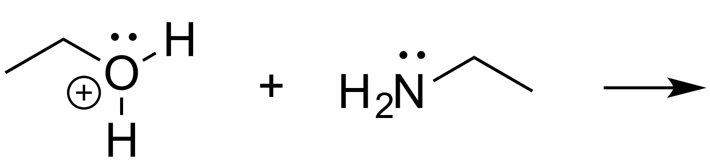
**Neutral Acid + Negatively Charged Base**

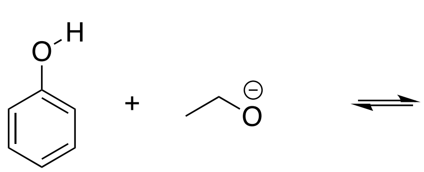


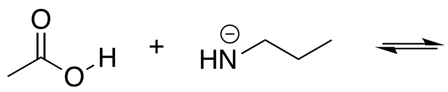
**Positively Charged Acid + Negatively Charged Base**

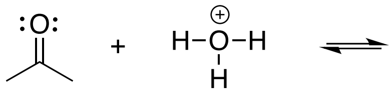


**Positively Charged Acid + Neutral Base**



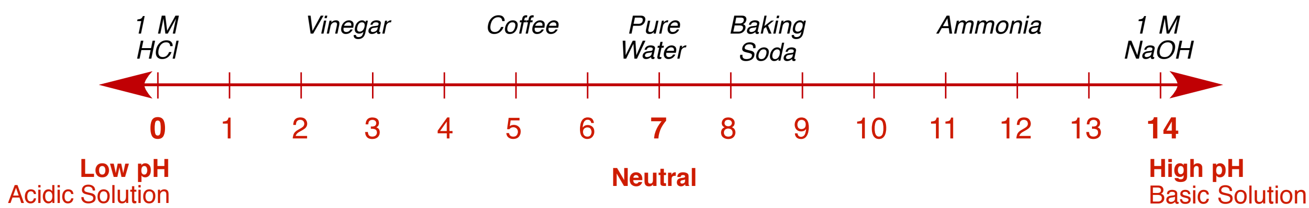
| You Try 4-4 |
|---|
| **Predict the products for each of the following acid/base reactions** |
|  |





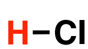
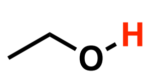
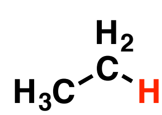
## pH

**pH describes the concentration of $H_3O^+$ in a solution.**
**The pH scale runs from 0 to 14**
**A lower pH value describes a higher concentration of $H_3O^+$**




## $K_a$ and $pK_a$

- **$K_a$ = the acidity constant; describes the exact strength of a given acid in water.**
- **The $K_a$ for an acid is a constant and remains unchanged regardless of concentration.**
- **We typically express acid strength as pKa.**
  **$pK_a = -\log K_a$**
- **Typically encountered $pK_a$ values run from -10 to 50.**
- **A molecule with a lower $pK_a$ is more willing to give up its proton ($H^+$) and is therefore a stronger acid.**

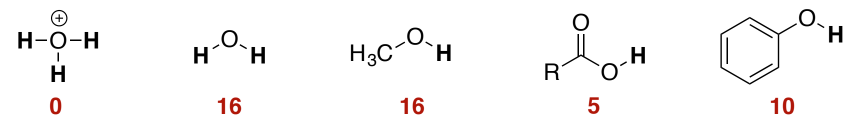
| |  |  |  |
|---|---|---|---|
| $K_a$ | $1 \times 10^{7}$ | $1 \times 10^{-16}$ | $1 \times 10^{-50}$ |
| $pK_a$ | -7 | 16 | 50 |
| | **Most Acidic Proton** | | **Least Acidic Proton** |

## Some Common $pK_a$ Values

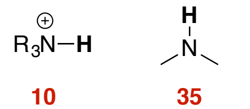
**Halo Acids**

| | |
|---|---|
| HF | 3 |
| HCl | -7 |
| HBr | -9 |
| HI | -10 |

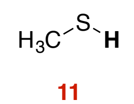
**Oxygen Acids**



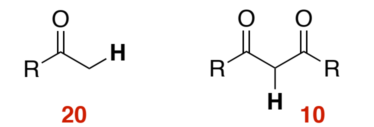

**Nitrogen Compounds**



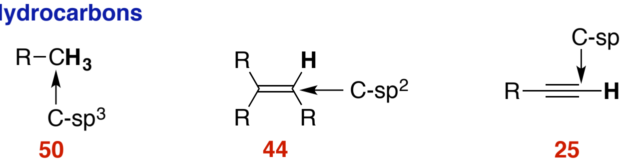

**Sulfur Compounds**




**Carbonyl Alpha Hydrogen**



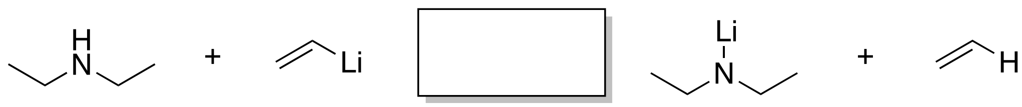

**Hydrocarbons**




## Using $pK_a$ to Predict the Direction of an Acid/Base Reaction

**In an acid base reaction, the reaction lies to the side opposite the stronger acid.**

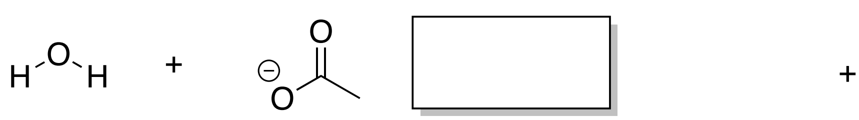
- If the acid has a smaller $pK_a$, the reaction lies to the right.
- If the conjugate acid has a smaller $pK_a$, the reaction lies to the left.




*Acid* *Base* *Conjugate Base* *Conjugate Acid*

**$pK_a$**

**Draw the products for the following acid/base reaction and determine the direction of the reaction equilibrium.**

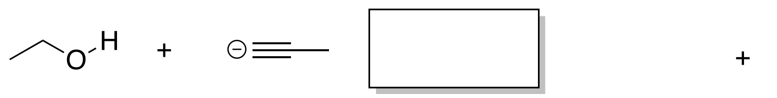



*Acid* *Base* *Conj. Base* *Conj. Acid*

**$pK_a$**

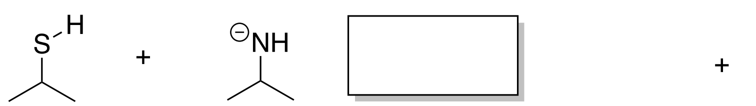
## You Try 4-5

**For each reaction below, predict the products, write the pKa of the acid and conjugate acid, and predict the direction of the reaction equilibrium.**



*Acid* — *Base* — *Conj. Base* — *Conj. Acid*

**$pK_a$** [ ] (Acid) [ ] (Conj. Acid)



*Acid* — *Base* — *Conj. Base* — *Conj. Acid*

**$pK_a$** [ ] (Acid) [ ] (Conj. Acid)

## Further Use of $pK_a$

**A stronger acid has a more stable conjugate base.**

**Acids**: $H_3C{-}O{-}H$ pKa = 16 *vs* $H_3C{-}S{-}H$ pKa = 11

**Conj. Bases**: $H_3C{-}O^{\ominus}$ *less stable* — $H_3C{-}S^{\ominus}$ *more stable*

**A more stable conjugate base (base) is less reactive and therefore less basic.**

$H_3C{-}O^{\ominus}$ stronger base — $H_3C{-}S^{\ominus}$ weaker base

**To analyze relative basicity, just look at the $pK_a$ values of the conjugate acids.**

## You Try 4-6

**Using the table below, rank the compounds from most basic (1) to least basic (4).**

| | |
|---|---|
| $CH_3NH_3^{\oplus}$ | pKa 10 |
| $CH_3NH_2$ | pKa 35 |
| $CH_3OH_2^{\oplus}$ | pKa -3 |
| $CH_3OH$ | pKa 16 |

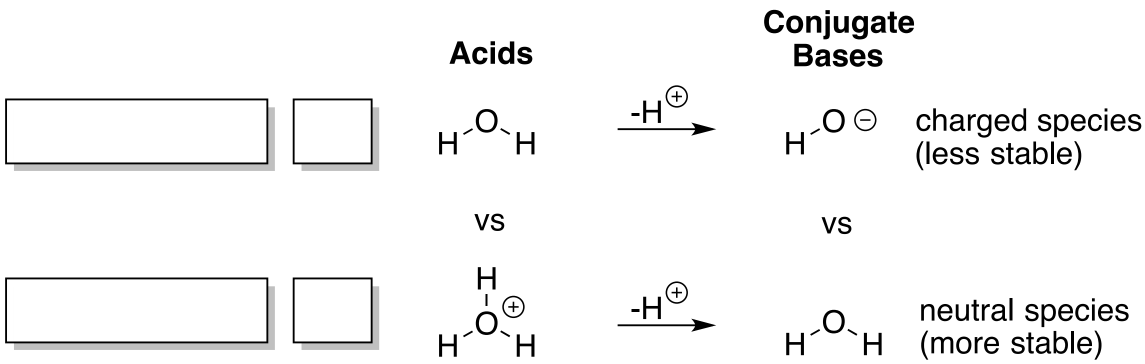
$CH_3O^{\ominus}$ [ ] $CH_3OH$ [ ] $CH_3NH^{\ominus}$ [ ] $CH_3NH_2$ [ ]

# Understanding Relative Acidity

**Acidity is essentially how willing a molecule is to donate its proton.**

**A molecule is more willing to donate its proton if the resulting product (its conjugate base) is more stable.**

**We can analyze the relative acidity of two or more compounds by comparing the relative stability of the conjugate bases.**

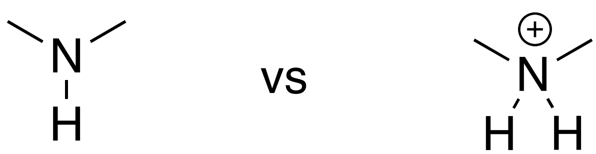



# Predicting Relative Acidity

**To predict relative acidity, you should analyze the following effects in order.**

**1. Charge Effect**

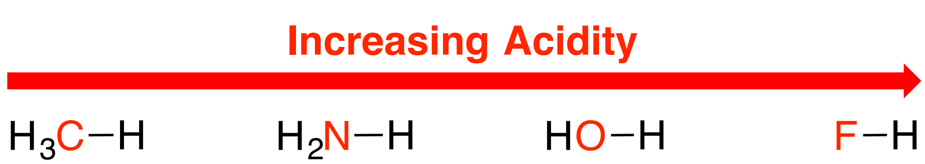
When comparing a positively charged acid and a neutral acid, the positively charged acid is typically more acidic.




**2. Atom Effects**

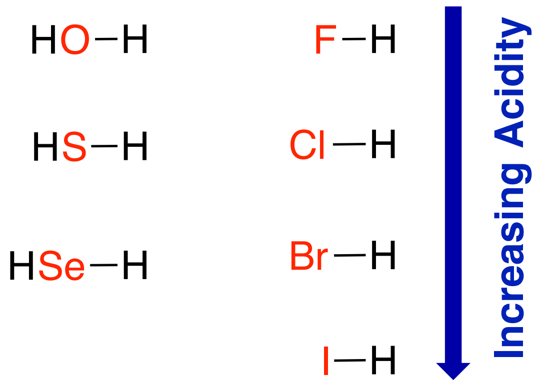
**a. Comparing atoms in the same row**

The compound that has the proton bonded to the more electronegative atom is more acidic.



**b. Comparing atoms in the same column**

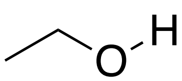
The compound that has the proton bonded to the larger atom is more acidic.



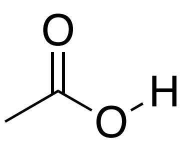

### 3. Structural Effects (Non-Atom Effects)

**a. Resonance stabilization of the conjugate base**

An acid that has a resonance stabilized conjugate base will be more acidic than one that does not.

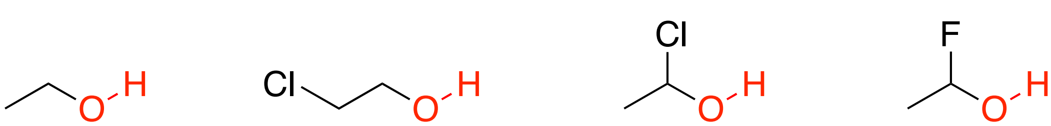


*vs*



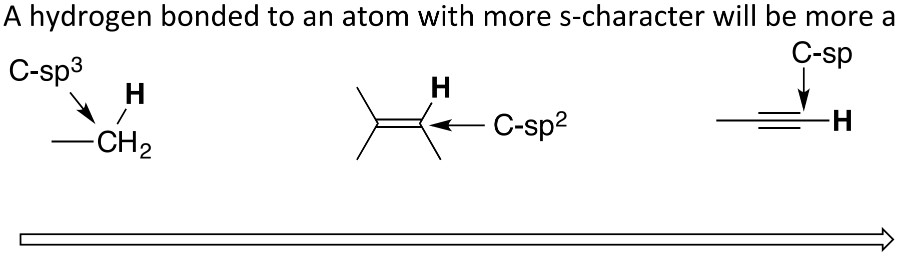
**b. Inductive effects**

Nearby electronegative atoms (not bonded directly to the acidic H) will enhance the acidity of the proton.



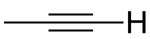
**c. Hybridization effects**

A hydrogen bonded to an atom with more s-character will be more acidic.




**Increasing s-Character**
**Increasing Acidity**

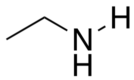
**A couple of exceptions**



pKa = 25

*more acidic*

*vs*

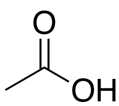


pKa = 35

An alkyne C-H is more acidic than an amine N-H despite rule 2a where the proton bonded to the more electronegative atom is typically more acidic.

H−Br

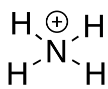
pKa = -9



pKa = 5

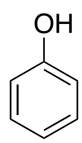
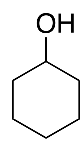
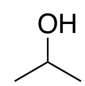
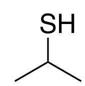
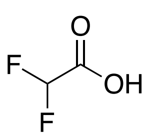
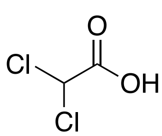
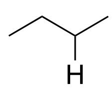
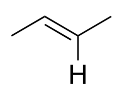
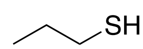
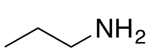
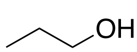
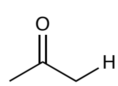
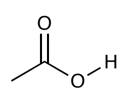
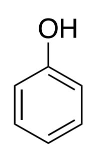
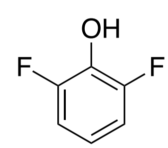
*more acidic*

*vs*



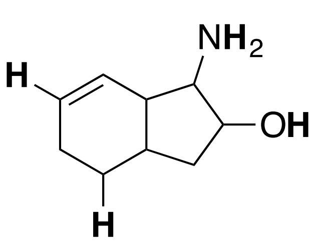
pKa = 10

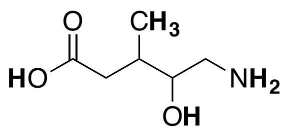
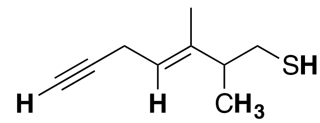
Despite rule 1, there are several neutral acids that are more acidic than the ammonium ion.

| You Try 4-7 | | |
|---|---|---|
| **For each pair below, identify the more acidic species.** | | |
| H−Br and H−F |  and  |  and  |
|  and  |  and  |  and H−Cl |
|  and  |  and  |  and  |

## Ranking the Acidity of Protons in a Molecule

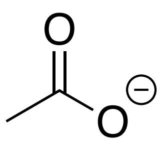
**Find the acidic protons in the molecule. Look at them independently and rank them based on the factors discussed previously.**



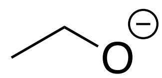
| You Try 4-8 | |
|---|---|
| **Rank the indicated protons in each molecule below from most acidic (1) to least acidic (4).** | |
|  |  |

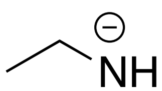
## Qualitative Assessment of Basicity

**Analyze the conjugate acids. The base that has the less acidic conjugate acid is the stronger base.**

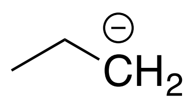


*VS*

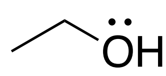


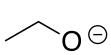
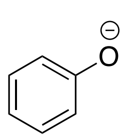
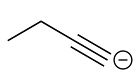
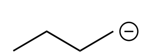
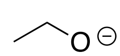
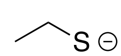


*VS*



*VS*



| You Try 4-9 | | |
|---|---|---|
| **Circle the stronger base in each pair below.** | | |
|  or  |  or  |  or  |