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Organic Chemistry

Second Edition

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Chapter 3

Acids and Bases

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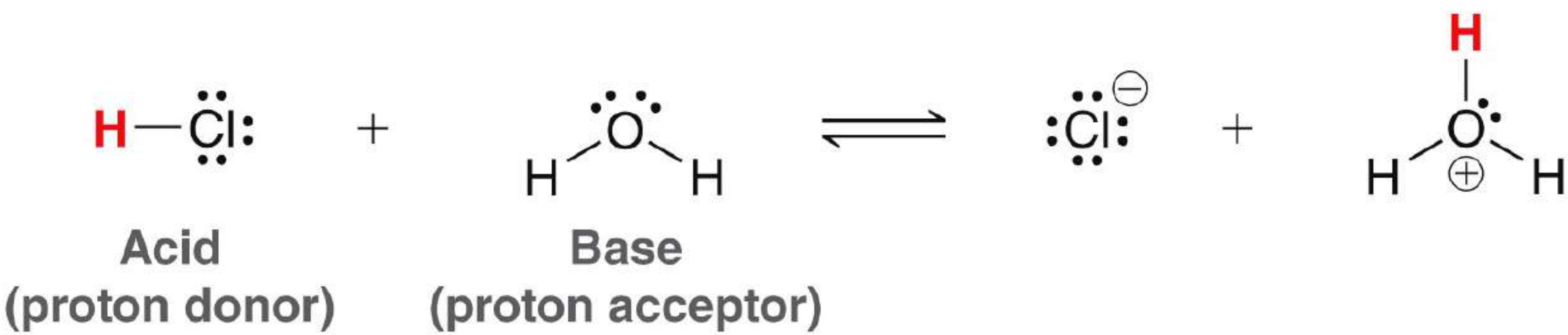
3.1 Acids and Bases

- Brønsted-Lowry definition
  - Acids donate a proton
  - Bases accept a proton
- Recall from General Chemistry this classic example



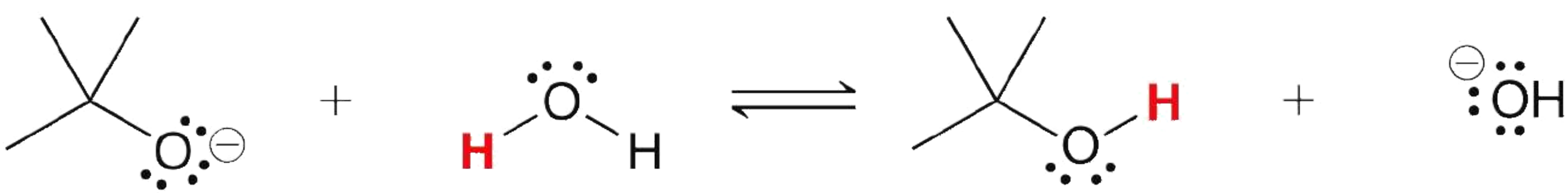
3.1 Conjugate Acids and Bases

- Brønsted-Lowry definition
  - A conjugate acid results when a base accepts a proton
  - A conjugate base results when an acid gives up a proton
- Recall from General Chemistry this classic example

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

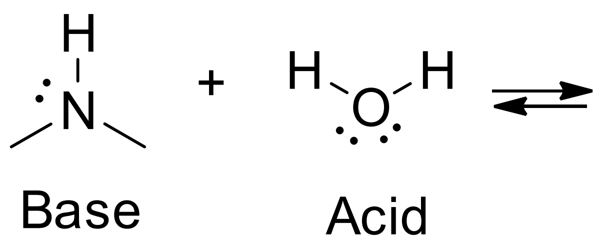
HCl	H_2O	Cl^-	H_3O^+
Acid	**Base**	**Conjugate base**	**Conjugate acid**

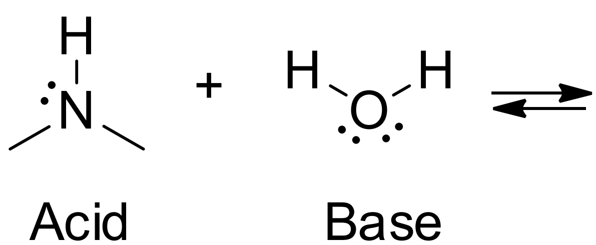
- Label the acid, base, and the conjugates in the reaction below



3.1 Acids and Bases

- Draw reasonable products for the following acid/base reaction, and label the conjugates.





- Water is considered neutral. Does that mean it is neither an acid nor a base?

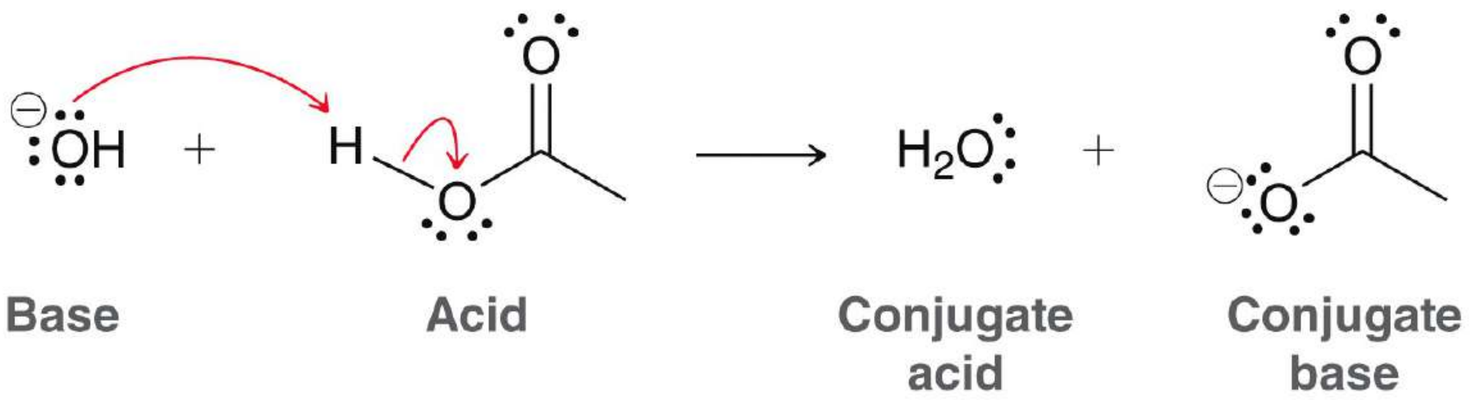
3.2 Curved Arrows in Reactions

- When bonds break and form, **pairs of electrons** move, and we can show their movement with curved arrows
- Consider the following generic acid/base reaction

- How are the curved arrows here different from the ones we use to represent resonance in chapter 2?
- The curved arrows show the reaction **mechanism**
- Learning to draw **mechanisms** is one of the most valuable skills in this class

3.2 Curved Arrows in Reactions

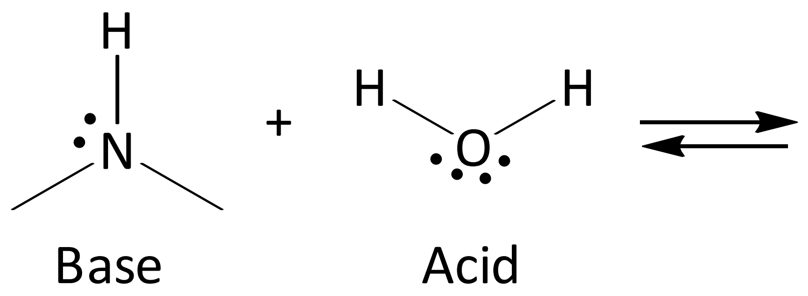
- Consider a specific acid/base example



- You could say the base “attacks” the acid
- The acid cannot lose its proton without the base taking it. All acid/base reactions occur in one step
- The mechanism shows two arrows indicating that two pairs of electrons move simultaneously

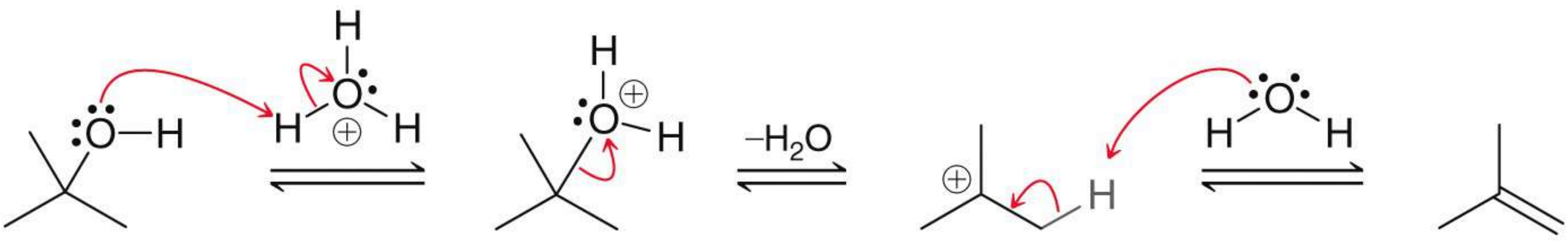
3.2 Curved Arrows in Reactions

- Provide products and curved arrows for the following acid base reaction



3.2 Curved Arrows in Reactions

- Identify the acid/base steps in the following mechanism



- Practice with SkillBuilder 3.1

3.3 Quantifying Acidity

- Recall from General Chemistry, how do "strong" acids/bases differ from "weak" acids/bases?
- The strength of an acid or base is helpful to predict how reactions will progress
  - We will learn to do **Quantitative** strength analysis – using pK_a values to compare the strengths of acids
  - We will learn to do **Qualitative** strength analysis – comparing the general stability of structures.

3.3 Quantifying Acidity

- Quantitative strength analysis – using numerical data to compare how strong acids are.
- Review from General Chemistry K_a and pK_a
- K_a is the equilibrium constant for the reaction between an acid and WATER

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- If the acid is strong, how will that affect the magnitude of K_a, the equilibrium constant?

3.3 Quantifying Acidity

- K_a is the equilibrium constant for the reaction between an acid and WATER

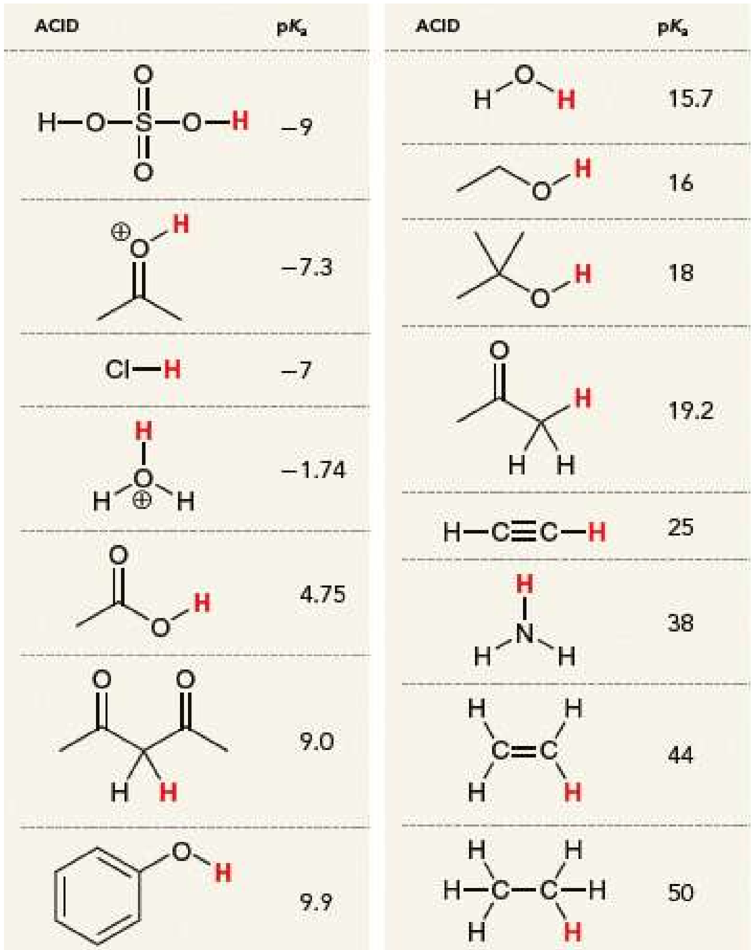
$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- K_a values range from 10^{-50} to 10^{10}
- Such super small and super large numbers can be difficult to imagine
- If you take the -log of the K_a, that will focus you on the exponent of the K_a value, which ranges from -10 to 50

$$pK_a = -\log K_a$$

- Will strong acids have low or high pK_a values?

3.3 Quantifying Acidity



- There are more acids and pK_a values in table 3.1
- Each pK_a unit represents an order of magnitude or a power of 10.
- Which is stronger, HCl or H_2SO_4, and by exactly HOW MUCH?

- Practice with SkillBuilder 3.2

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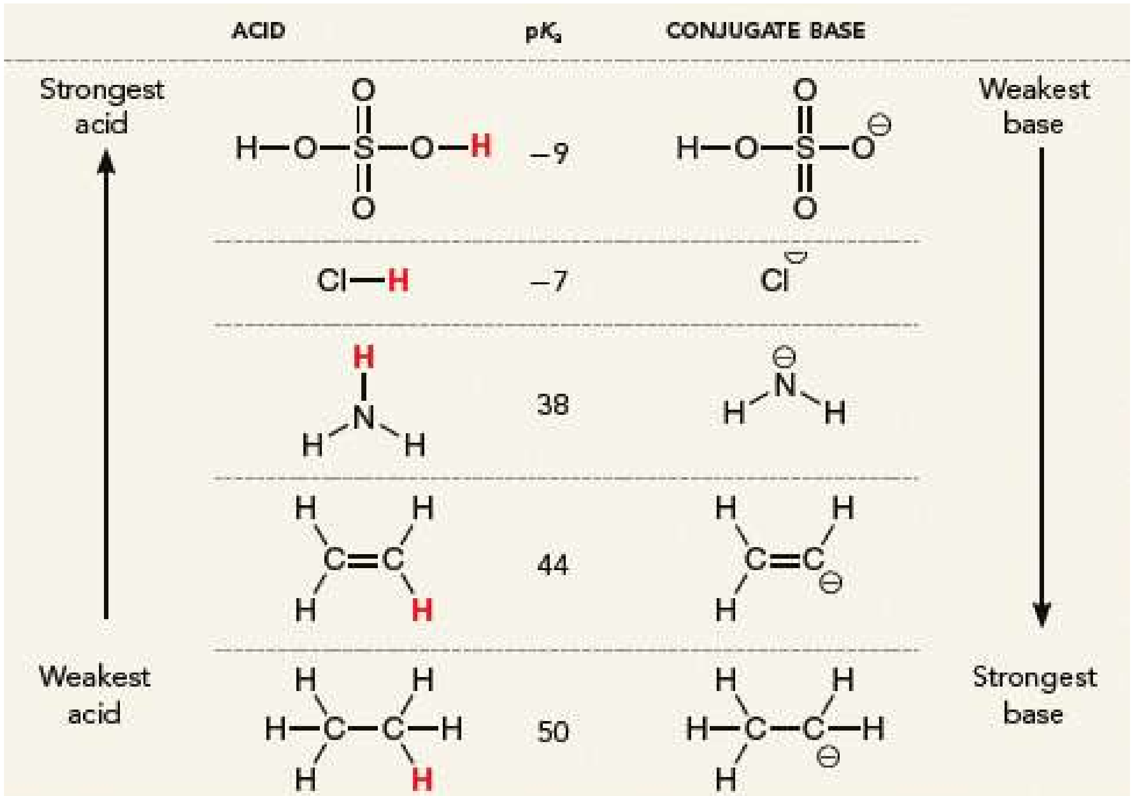
3.3 Quantifying Basicity

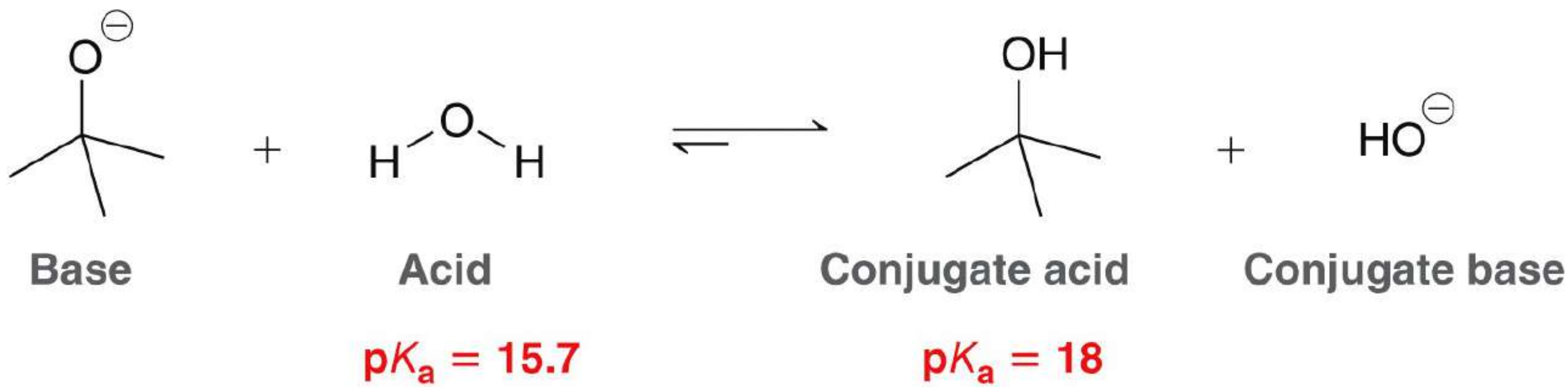


- You can also use pK_a values to compare the strengths of bases
- The stronger the acid the weaker its conjugate base. WHY?

- Practice with SkillBuilder 3.3

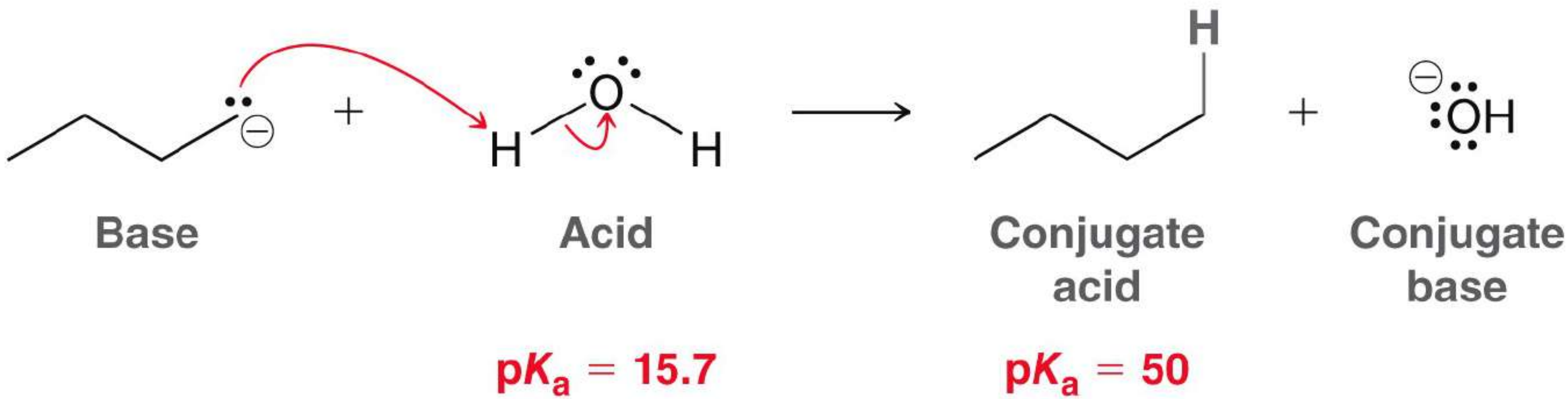
3.3 Using pK_as to analyze Equilibria

- With the relevant pK_a values, you can predict which direction an acid/base equilibrium will favor



- Why is the equilibrium arrow bigger on top than on bottom?

3.3 Using pK_as to analyze Equilibria



- Subtracting the pK_a values, (50 - 15.7 ≈ 34) also tells you that there will be ≈ 10^{34} more products than reactants.
- It's not really much of an equilibrium
- Practice with SkillBuilder 3.4 and conceptual checkpoint 3.12

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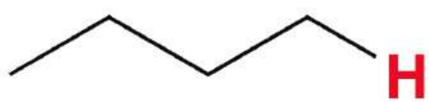
3.4 Qualifying Acidity

- Qualitative analysis – compare structural stability to determine which is a stronger acid
- Formal charge can affect stability
  - The more effectively a reaction product can stabilize its formal charge, the more the equilibrium will favor that product
- Which is a stronger acid, and WHY?

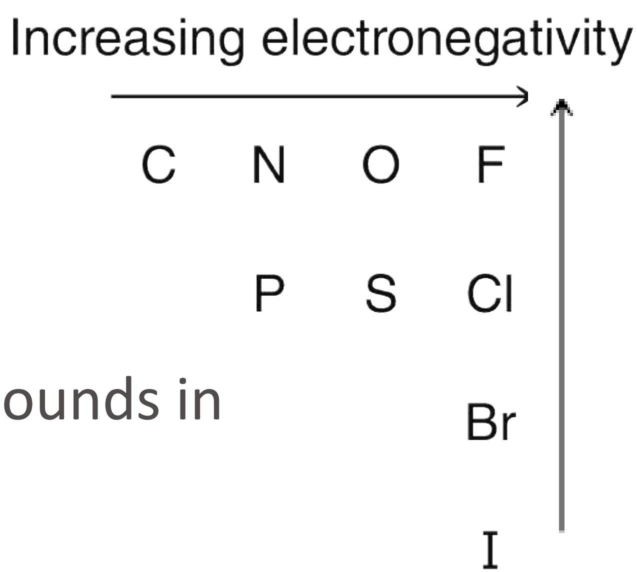
HCl or 

3.4 Qualifying Acidity

- The more effectively a conjugate base can stabilize its negative charge, the stronger the acid
- What factors affect the stability of a negative formal charge?
  - The type of **atom** that carries the charge
  - **Resonance**
  - **Induction**
  - The type of **orbital** where the charge resides
- These factors can be remembered with the acronym, **ARIO**

3.4 Qualifying Acidity

- **A**RIO - The type of **atom** that carries the charge
  - More electronegative atoms are better at stabilizing negative charge. WHY?
  - Compare the acidity of the two compounds below

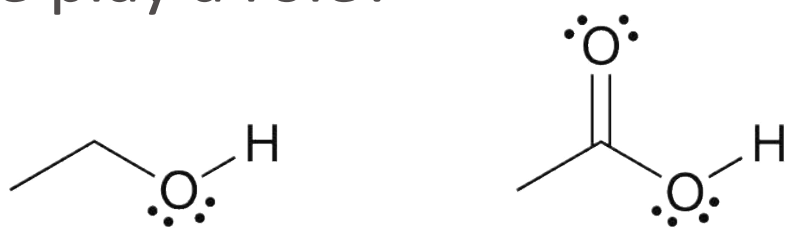


  - Look up the pK_a values for similar compounds in table 3.1 to verify your prediction

- Practice with SkillBuilder 3.5

3.4 Qualifying Acidity

- ARIO - **Resonance** can greatly stabilize a formal negative charge by spreading it out into partial charges
- Compare the acidity of the two compounds below by comparing the stabilities of their conjugate bases. How does resonance play a role?

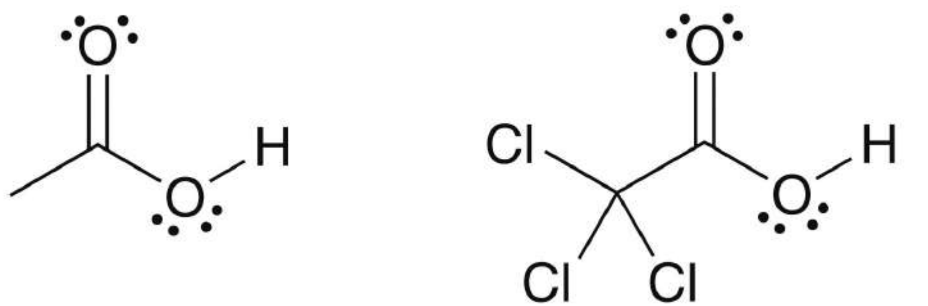


Ethanol   Acetic acid

- Look up the pK_a values in table 3.1 to verify your prediction
- Practice with SkillBuilder 3.6

3.4 Qualifying Acidity

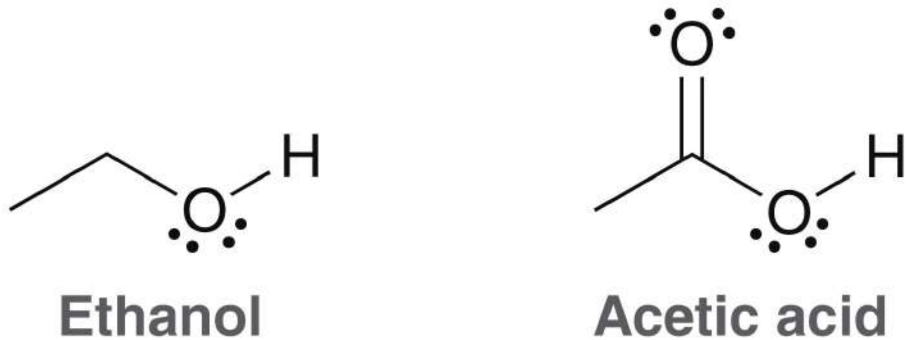
- ARIO - **Induction** can also stabilize a formal negative charge by spreading it out. How is induction different from resonance?
- Compare the acidity of the two compounds below by comparing the stabilities of their conjugate bases. How does induction play a role?



Acetic acid Trichloroacetic acid

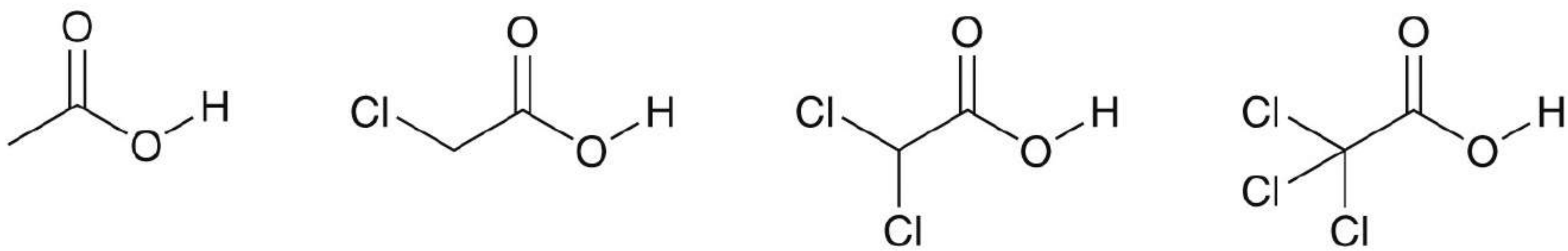
3.4 Qualifying Acidity

- Does **induction** also play a role in explaining why acetic acid is stronger than ethanol?



3.4 Qualifying Acidity

- Explain the pK_a differences below

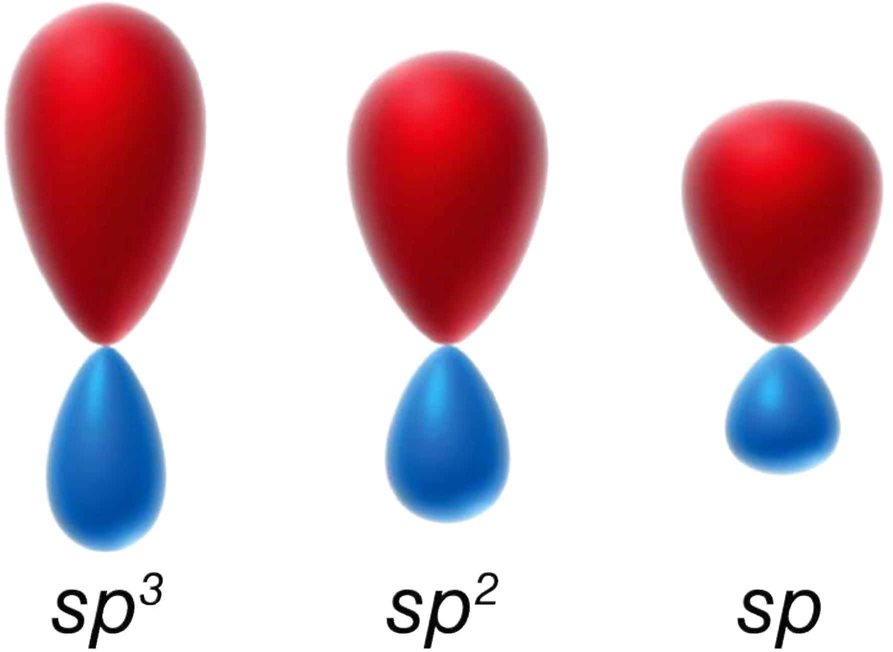


pK_a = 4.75　　pK_a = 2.87　　pK_a = 1.25　　pK_a = 0.70

- Practice with SkillBuilder 3.7

3.4 Qualifying Acidity

- ARI**O** - The type of **orbital** also can affect the stability of a formal negative charge
- Is a negative charge more stable or less stable if it is held closely to an atom's nucleus? WHY?
- Rank the ability of these orbitals (2*s*, 2*p*, sp^3, sp^2, and *sp*) to stabilize electrons, and explain.



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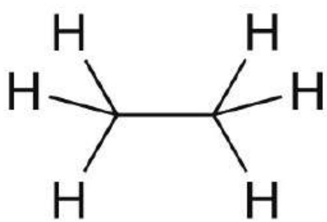
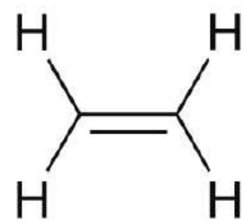
3.4 Qualifying Acidity

- Compare the acidity of the compounds below by comparing the stabilities of their conjugate bases. How does the type of **orbital** play a role?



Ethane
$pK_a = 50$



Ethylene
$pK_a = 44$

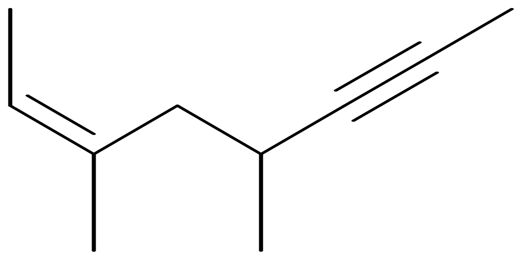
Acetylene
$pK_a = 25$

- Explain the pK_a differences above

- Practice with SkillBuilder 3.8

3.4 Qualifying Acidity

- If a strong base were to react with the following molecule, which proton would most likely to react?

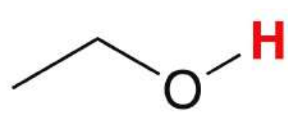


- Why would a very strong base be required?

- How could the molecule above act as a base in the presence of a strong acid?

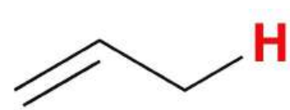
3.4 Qualifying Acidity

- When assessing the acidity of protons, we generally use **ARIO** as our order of priority
  1. The type of **atom** that carries the charge
  2. **Resonance**
  3. **Induction**
  4. The type of **orbital** where the charge resides
- Compare ethanol and propylene. Which has a more stable conjugate base? WHY?



Ethanol

pK_a = 16



Propylene

pK_a = 43

3.4 Qualifying Acidity

- ARIO is a good general guideline, but it sometimes fails
- Compare acetylene and ammonia. Using ARIO, which should be a stronger acid?

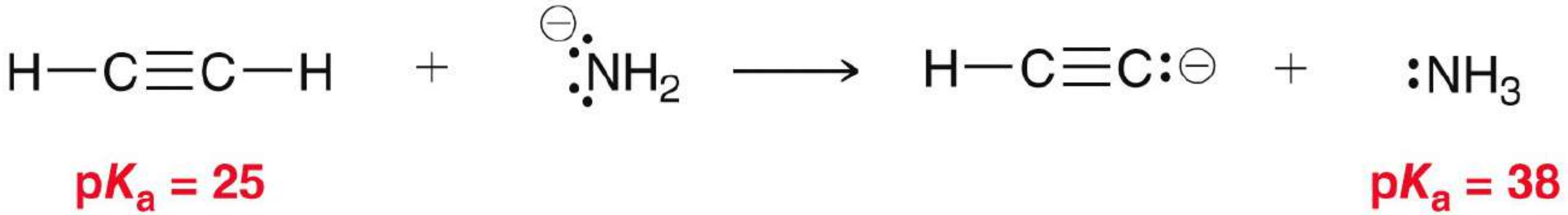
Acetylene

Ammonia

- To determine the **actual** acidities, the pK_a values must be experimentally measured and compared – see next slide

3.4 Qualifying Acidity

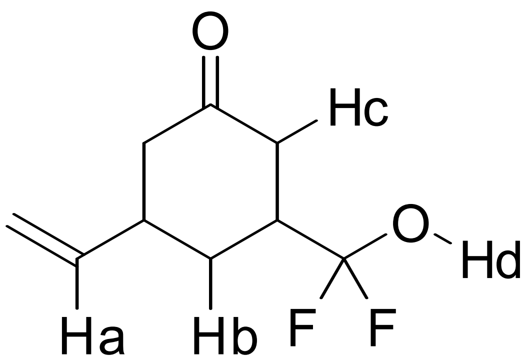
- **ARIO** is a good general guideline, but it sometimes fails
- Using the pK_a values, you can never go wrong. Which acid is truly stronger? Which direction will the following equilibrium favor?

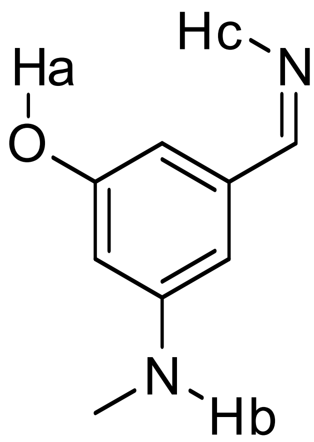


- Practice with SkillBuilder 3.9

3.4 Qualifying Acidity

- For each of the molecules below, rank the labeled Hydrogen atoms in order of increasing pK_a value





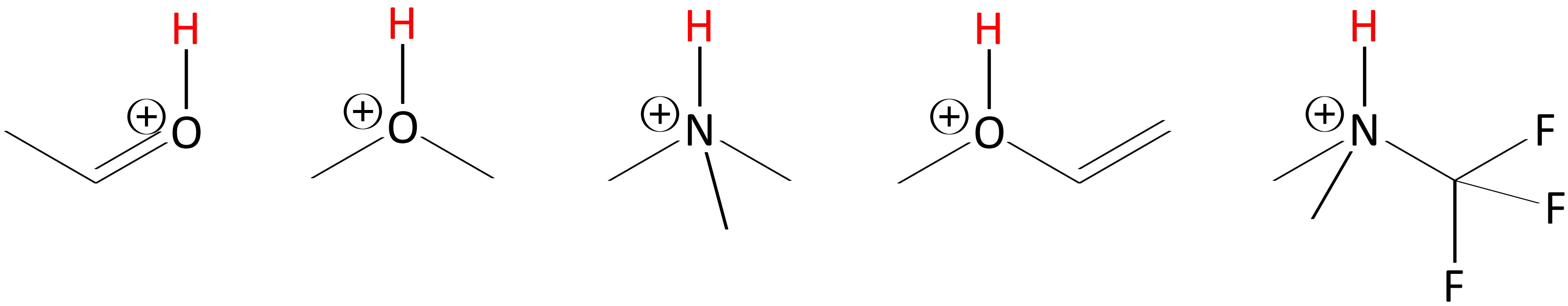
3.4 Qualifying Acidity

- Sometimes acids will carry a formal positive charge
- For such acids, their conjugate bases will be neutral. WHY?

- In such cases, we can use **ARIO** to compare the stability of the acids directly to see which is best at stabilizing its positive charge

3.4 Qualifying Acidity

- For acids that carry a formal positive charge, we can use **ARIO** to compare the stability of the acids directly to see which is best at stabilizing its positive charge
- Rank the following acids in order of increasing strength



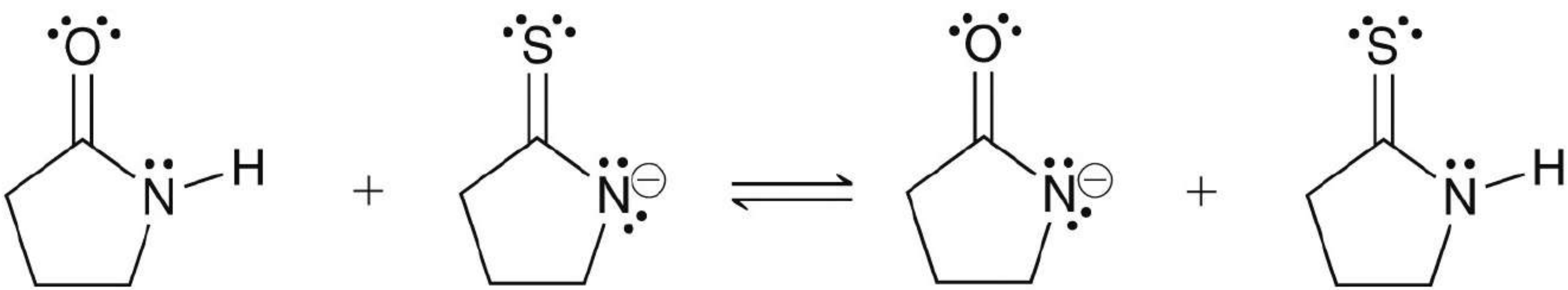
3.5 Predicting Equilibrium Position

- If pK_a values are known, they are a sure-fire way to predict the position of an equilibrium
- If pK_a values are not known, relative stability of conjugates should be used

- Practice with SkillBuilder 3.10

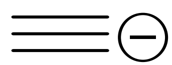
3.5 Predicting Equilibrium Position

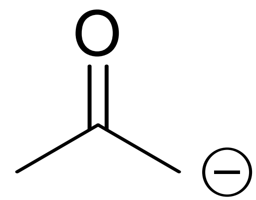
- If pK_a values are not know, relative stability of conjugates should be used
- Is the reaction below, reactant or product favored?

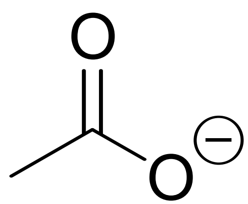


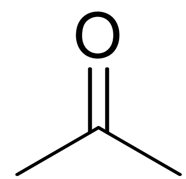
3.5 Choosing a Reagent

- Another important skill is to be able to choose an appropriate **reagent** for a acid/base reaction
- Choose an **acid** from table 3.1 that could effectively **protonate** each of the following molecules



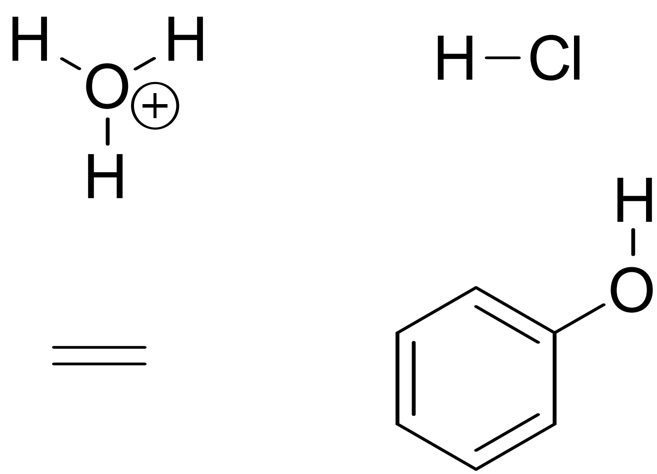






3.5 Choosing a Reagent

- Another important skill is to be able to choose an appropriate **reagent** for a acid/base reaction
- Choose a **conjugate base** from table 3.1 that could effectively **deprotonate** each of the following molecules



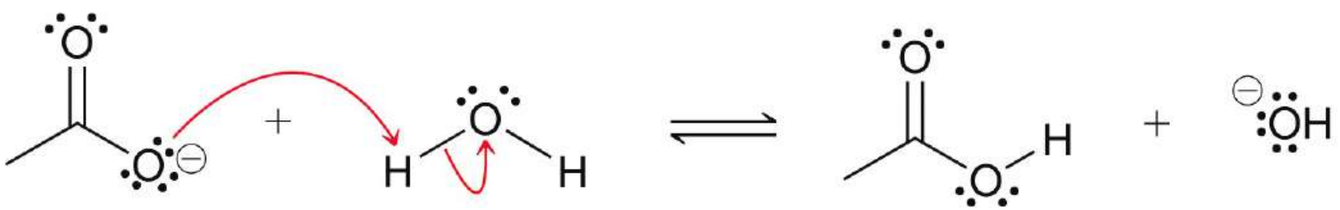
- Practice with SkillBuilder 3.11

3.6 Leveling Effect

- Another important skill is to be able to choose an appropriate **solvent** for a acid/base reaction
- The solvent should be able to surround the reactants and facilitate their collisions without itself reacting
- Because water can act as an acid or a base, it has a **leveling effect** on strong acids and bases
  - Acids stronger than H_3O^+ can not be used in water. WHY? – see next few slides
  - Bases stronger than OH^- can not be used in water. WHY? – see next few slides

3.6 Leveling Effect

- Appropriate use for water as a solvent

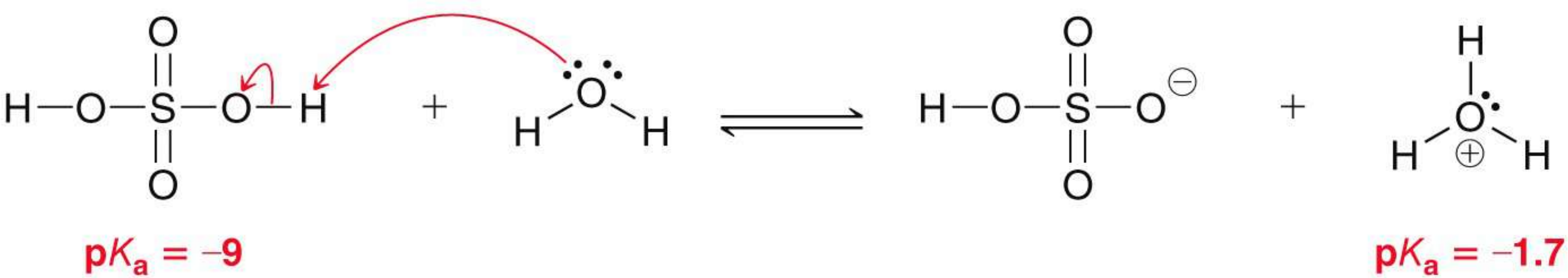


pK_a = 15.7 pK_a= 38

- With water as the solvent, the $CH_3CO_2^-$ will react with the water, but the equilibrium greatly favors the reactant side, so water is an appropriate solvent

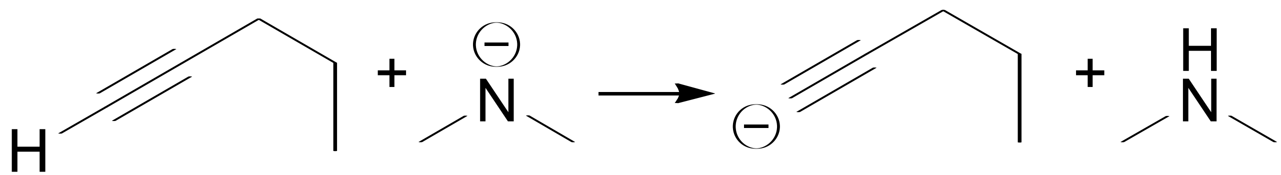
3.6 Leveling Effect

- Because water can act as an acid or a base, it has a leveling effect on strong acids and bases
  - Acids stronger than H_3O^+ cannot be used in water. For example, water would react with sulfuric acid producing H_3O^+. Virtually no sulfuric acid will remain if we wanted it to be available to react with another reagent

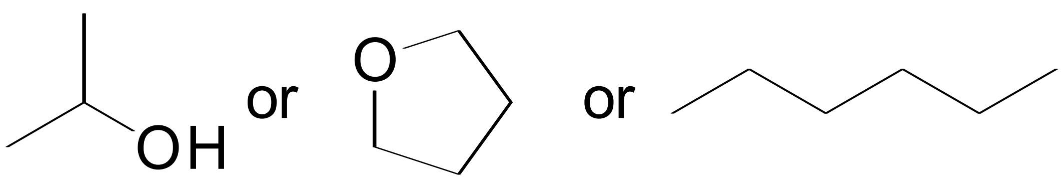


3.6 Leveling Effect

- Because water can act as an acid or a base, it has a leveling effect on strong acids and bases
  - Bases stronger than OH^{-} can not be used in water. For example, water would not be an appropriate solvent for the following reaction. WHY?

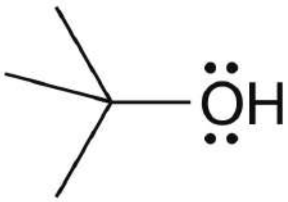


  - Which of the following solvents would be a better choice?

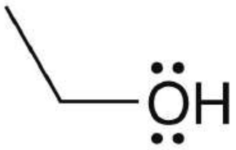


3.7 Solvation

- Because they are so similar, **ARIO** can not be used to explain the pK_a difference comparing ethanol and *tert*-Butanol



***tert*-Butanol**
pK_a = 18

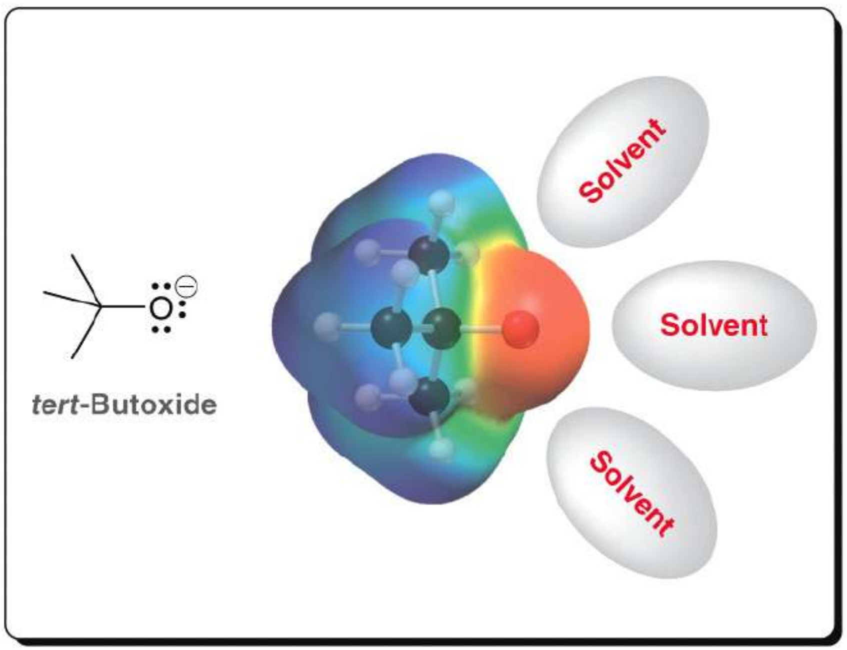


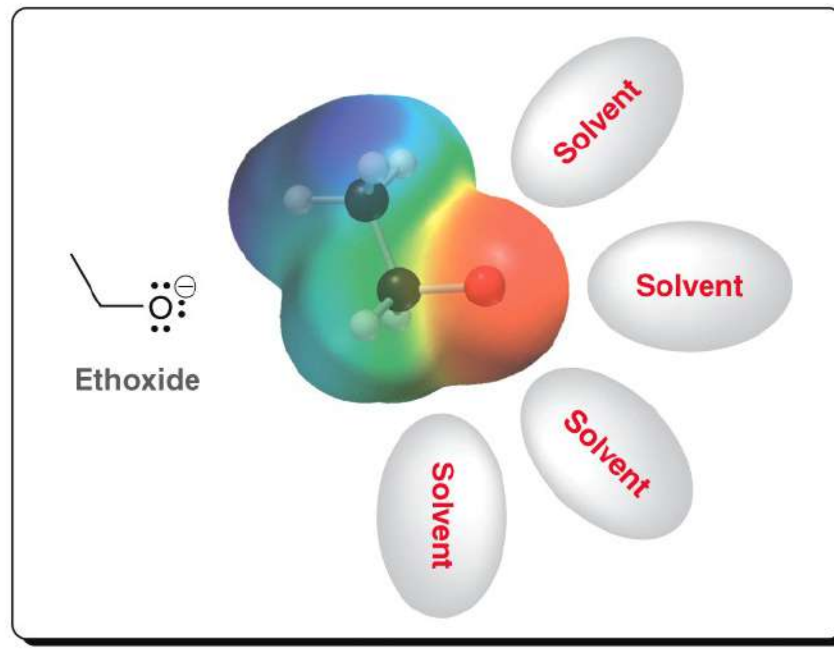
Ethanol
pK_a = 16

- Considering that pK_a values are measured in solution, how might the solvent act to make ethanol a slightly stronger acid? Think about how the solvent could stabilize its conjugate base.

3.7 Solvation

- The solvent must form ion-dipole attractions to stabilize the formal negative charge
- If the *tert*-Butoxide is sterically hindered, it won’t be as well solvated as the ethoxide





3.7 Solvation

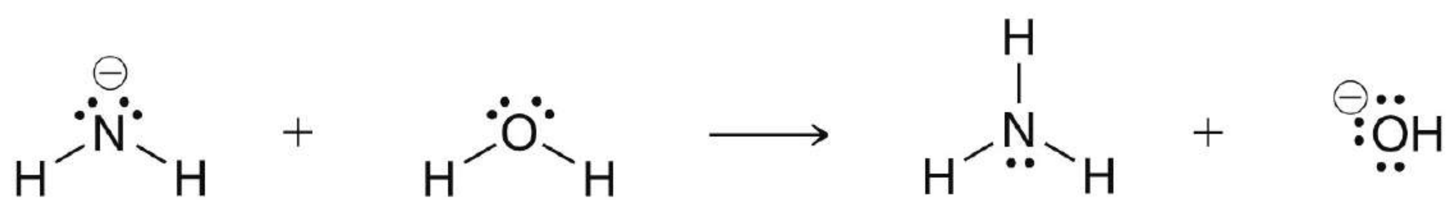
- **Solvation** is critically important in reactions. The solvent is often needed to stabilize transition states, intermediates, and/or products to allow a reaction to occur
- Explain why the pK_a for acetic acid is 4.75 in water while it is 23.5 in CH_3CN
- Practice with conceptual checkpoint 3.33

3.8 Counterions

- Counterions are also known as spectator ions.
- There are always present, because they are necessary to balance the overall charge of a solution
- Full reaction with couterion included:

$$NaNH_2 + H_2O \longrightarrow NH_3 + NaOH$$

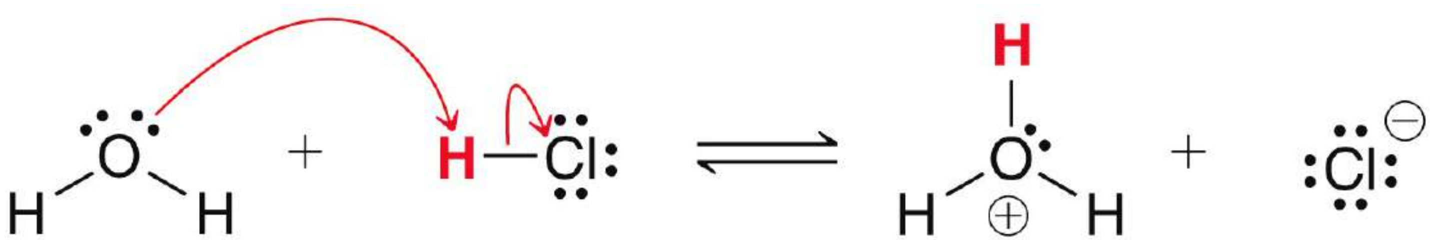
- Reaction without counterion even though it is present



- Why are they often left out of an equation?

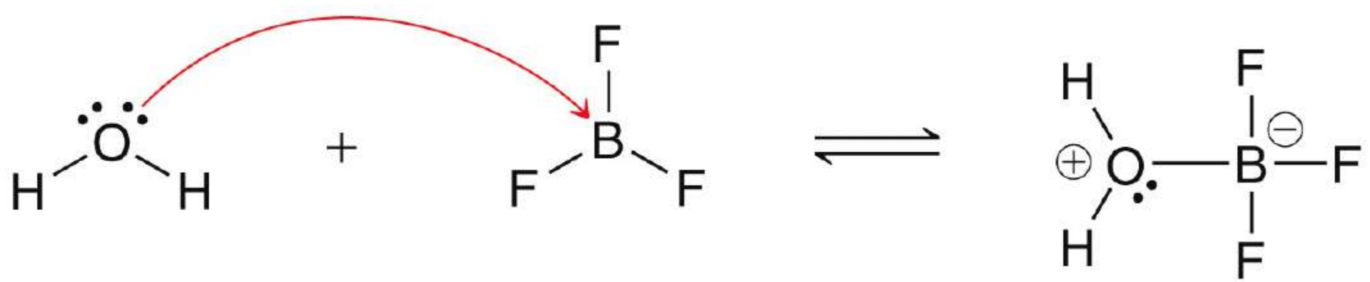
3.9 Lewis Acids and Bases

- Lewis acid/base definition
  - A Lewis acid accepts and shares a pair of electrons
  - A Lewis base donates and shares a pair of electrons
- Acids under the Brønsted-Lowry definition are also acids under the Lewis definition
- Bases under the Brønsted-Lowry definition are also bases under the Lewis definition
- Explain how this reaction fits both definitions



3.9 Lewis Acids and Bases

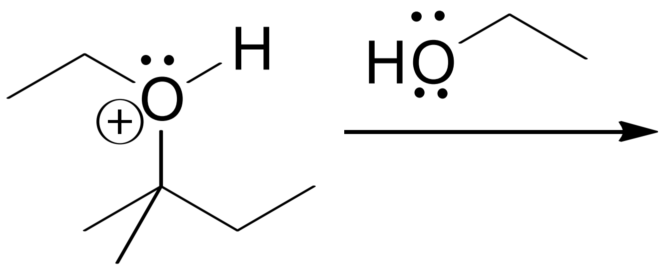
- Lewis acid/base definition
  - A Lewis acid accepts and shares a pair of electrons
  - A Lewis base donates and shares a pair of electrons
- Some Lewis acid/base reactions can not be classified using the Brønsted-Lowry definition
- Explain how this reaction fits the Lewis definition but not the Brønsted-Lowry definition



- Practice with SkillBuilder 3.12

Additional Practice Problems

- Provide products and curved arrows for the following acid base reaction



Additional Practice Problems

- For a base with an especially large value for K_b. Will its conjugate acid have a relatively low or high pK_a? Explain why using the relative pK_a values to illustrate.

Additional Practice Problems

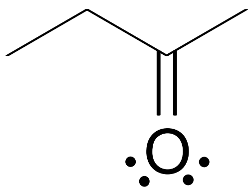
- Which side of the following generic reaction will be favored, and what will the ratio of products/reactants be?

  HA + B: $\rightarrow$ HB + A:

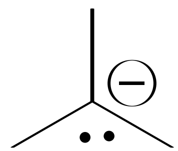
  pK_a = 5 8

Additional Practice Problems

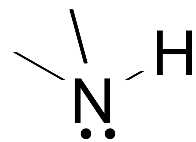
- Rank the following bases in order of increasing strength and rank their conjugates in order of increasing pK_a.



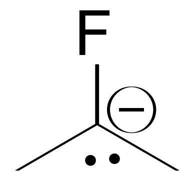
A



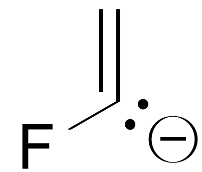
B



C



D



E