Acid-Base Chemistry

1. The species shown below are all Lewis acids. Considering the individual bond dipoles, **draw a circle around any Lewis acidic atoms**. *Which of the circled atoms are also Brønsted acids*?



Lewis acidic atoms are able to *accept electrons* and can be identified by the positive end of a bond dipole or an open shell (as is also true in the case of B in BF_3)



Bronsted acids donate protons, therefore only two of the species above can be classified as proton donors. Notice that both have protons at the end of polarized bonds.

2. **Draw the conjugate base** for each of the following acids. Assume that deprotonation only occurs one time.



Deprotonation of an acid generates its conjugate base. In the first example, loss of one proton results in a neutral molecule (ethanol). In the second example, loss of one proton results in an anion. The proton is lost from the O-H bond as opposed to the C-H bond because O is more electronegative than C. In the third example, S and O are in the same group. Since S is larger than O, the S-H bond is more acidic than the O-H bond, therefore the anion is formed on S.

3. **Draw the conjugate acid** of each of the following bases. Assume that protonation only occurs one time.

Base	Conjugate Acid
н–с≡с ^Θ	H—С≡С—Н
∕∩он	$\frown_{OH_2}^{\oplus}$
\succ	⊕——— Н

Protonation of a base generates its conjugate acid. In the first example, adding one proton results in a neutral molecule (acetylene, C_2H_2). In the second example, adding one proton results in an cation. The proton is added to the O atom because the lone pairs (not shown) can form a new O-H bond. In the third example, the electrons act as the base. Since these electrons are associated with **two** C atoms, only <u>one C atom</u> can accept the proton, generating one C-H bond, while the other C atom becomes a carbocation. More on this when addition reactions are discussed.

4. Select the more acidic molecule in each pair below. Then, provide a brief explanation of your reasoning (e.g. eN, bond length, resonance, hybridization, etc...)



O is more electronegative than N, therefore the carboxylic acid is more acidic than the amide



Phenol has a resonance stabilized conjugate base, therefore it is more acidic than cyclohexanol



Stronger acids have more stable conjugate bases. Although both molecules have resonance stabilized conjugate bases (shown below), the more stable conjugate base exists with deprotonated ketone (lone pair on less electronegative C "moves" to more electronegative O).

CI 3 2 1 OH

Cl at C-2 is closer to acidic O-H bond, thus this compound is more acidic than one with similar structure but Cl is at C-3.

5. Using the process outlined on page 2 of the Acid-Base Core Concepts, **draw the products** of the following acid/base reactions and **determine which side of the reaction is favored at equilibrium**. In your own words, explain your selection.



Explanation:

Thiol is a **stronger acid** than alcohol because S is below O (Group 6) Reactants are favored at equilibirum



Explanation:

Trifluoroacetic acid is a stronger acid than acetic acid due to the presence of the electronegative F atoms

Products favored at equilibrium

6. The acid-base mechanisms below are incorrect. In your own words, explain why and draw correct arrow pushing mechanisms.



As depicted above, the bond dipole of the O-H bond indicates that the partial positive charge exists at the H end of the bond, not the O as the formal charge suggests. Remember that formal charges are simply a method of counting electrons and do not always accurately predict where charge exists in a molecule or ion.

Correct mechanism:



In the correct arrow pushing shown above, the red arrow shows the lone pair on NH₃ forming a new N-H σ bond. The blue arrow shows the O-H σ bond breaking which creates a lone pair on O.



As depicted above, the bond dipole of the O-H bond indicates that the partial positive charge exists at the H end of the bond, therefore electrons from hydroxide should move towards the H shown. Remember that arrows do not indicate where atoms move but rather where electrons move.

Correct mechanism:



In the correct arrow pushing shown above, the red arrow shows a lone pair on hydroxide (lone pairs implied by the negative charge) forming a new O-H σ bond. The blue arrow shows the O-H σ bond of the carboxylic acid breaking which creates a third lone pair on O (two are implied in the reactant carboxylic acid).

7. Hydroxide is often presented as a strong base, but in some reactions it is not strong enough. Given the pK_a values shown below, explain why the reaction below is disfavored in the forward reaction.



Explanation:

In order for an acid-base reaction to favor the products at equilibrium, the reactant acid must be a stronger acid (lower pK_a) than the conjugate acid that is produced. That is not the case here.

If strong acids have stable conjugate bases, **weak acids have more reactive conjugate bases**. With this in mind, explain why NaNH₂ **is** an appropriate base for the reaction below.



Explanation:

In this case, the conjugate acid formed, NH_3 , is a weaker acid than the reacting alkyne. Because of this, the product side of this equilibrium is favored and therefore $NaNH_2$ will deprotonate this (and most) alkyne C-H bonds.

Using the example above, **select which base** (¹⁻OH or ¹⁻H) is reactive enough for deprotonating the most acidic proton in ethanol.



In order for an acid-base reaction to favor the products at equilibrium, the reactant acid must be a stronger acid (lower pK_a) than the conjugate acid that is produced. Therefore, the hydride ion (H^{1-}) is an appropriate base for this reaction. Given the reported pK_a values, it is appropriate to say that hydride is a **stronger base** than hydroxide (^{1-}OH).