Objective 4: Intro to Reactivity 1: identify acids and bases using Lewis definition. Use curved arrows to show how base reacts with acid. Relate strength to pK_a. Determine direction of equilibrium. Use pK_a table to estimate pK_a of acid based on structure.

Quiz Practice problems

Key ideas:

In General Chemistry, we looked at acids as proton (H^+) donors and bases as proton (H^+) acceptors. This is the Bronsted-Lowry definition.

In organic chemistry, we will look at acids as electron pair acceptors and bases as electron pair donors. This is the Lewis definition.

Organic acids are weak acids. The acid dissociation constant, K_a, is less than 1.

Every acid has a partner or conjugate base.

A pK_a table ranks acids from strong to weak and usually shows the conjugate base of each acid.

An acid reacts with a base. Curved arrows are used to show which bonds break and form. You can use curved arrows to predict the products of an acid-base reaction.

An acid has to be strong enough to react with a base. Or a base has to be strong enough to react with an acid. A pK_a table tells you the direction of equilibrium (more products or more reactants at equilibrium).

Skills:

Relate pK_a to acid strength.

Use pK_a table to identify acidic H and basic atom.

Use pK_a table to identify the conjugate base of an acid.

Use curved arrows to show bonds breaking and forming in an acid-base reaction.

Predict and draw the structures of the products of an acid-base reaction.

Use pK_a table to predict whether an acid-base reaction occurs. In other words, determine the direction of equilibrium (more products or more reactants at equilibrium).

0. a. Every acid has a conjugate base. A strong acid easily donates its proton. Does the conjugate base of a strong acid easily accept a proton?

b. Is the conjugate base of a strong acid strong or weak?

c. What does pK_a of an acid represent?

d. Is an acid with a large pK_a a strong acid or weak acid?

Answers:

a. The conjugate base of a strong acid does not easily accept a proton.

b. A strong acid has a weak conjugate base.

c. pK_a of an acid represents acid strength.

d. An acid with a large pK_a is a weak acid.

1. Water can behave like an acid.

a. When water is an acid, the pK_a is 15.7. Is water a strong acid or weak acid? Does water easily donate its proton to form OH^- or not?

b. What is the conjugate base of water? Is conjugate base of water strong or weak? Does the conjugate base of water easily accept a proton to form water or not?

Answers:

a. Water is a weak acid.

From Chem 1B:	H_2O +	H_2O <==>	H_3O^+	+ OH^-
	Acid	base	conjugate acid of H_2O base	conjugate base of H_2O acid

$pK_a = - \log K_a$

Rearrange and solve for $K_a = 10^{-pKa}$

For water, $K_a = 10^{-15.7} = 2.00 \times 10^{-16}$

$K_a = [H_3O^+] [OH^-] = 2.00 \times 10^{-16}$ ==> this means there are hardly any H_3O^+ and OH^-.

Large pK_a means weak acid.

Water does not easily donate its proton to form OH^-. This is the definition of a weak acid.

b. The conjugate base of water is OH^-.

The conjugate base of water is strong. Strong base ==> weak conjugate acid.

The conjugate base of water easily accepts a proton to form water. This is the definition of a strong base.

2. Water can behave like a base.

a. What is the conjugate acid of water?

b. What is the pK_a of the conjugate acid of water? Is the conjugate acid of water a strong acid or weak acid?

c. Based on the pK_a of the conjugate acid of water, is water a strong base or weak base?

Answers:

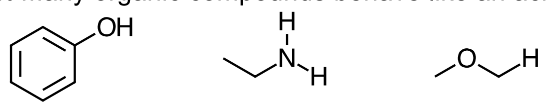
a. The conjugate acid of water is H_3O^+.

From Chem 1B: H_2O + H_2O <==> H_3O^+ + OH^-

Acid	base	conjugate acid of H_2O base	conjugate base of H_2O acid

b. H_3O^+ pK_a = -1.7
H_3O^+ is a strong acid. Small pK_a means strong acid.
c. Water is a weak base.
Strong acid ==> weak conjugate base.

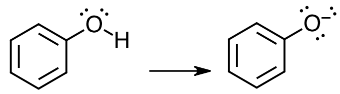
3. Many organic compounds behave like an acid or a base (depending on the conditions).



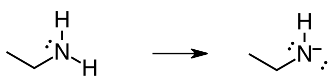
phenol ethyl amine dimethyl ether

a. The acidic H is shown in each compound. Estimate the pK_a of each acid. Draw the conjugate base of each acid.
b. The O or N in each compound is basic. Draw the conjugate acid of each compound. Estimate the pK_a of each acid. Rank the bases from strongest to weakest.
Answers:
a. See pK_a table. Ar = aromatic

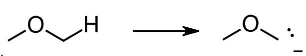
pK_a = 10 (see ArOH)



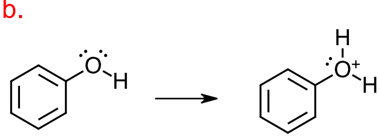
pK_a = 38 (similar to NH_3; RNH_3^+ is the protonated form of ethyl amine)



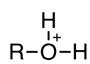
pK_a = 48 (see CH4; C-H bonds are strong and the H is hard to remove)

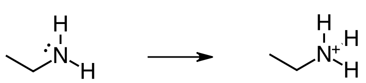


b.

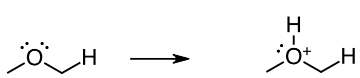


pK_a = -2 (see

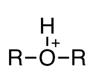




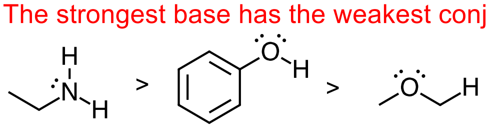
pK_a = 11 (see RNH_3^+)



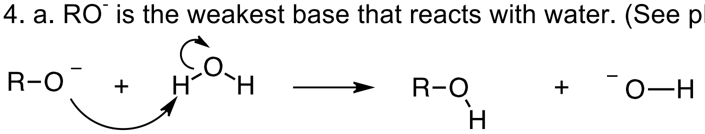
pK_a = -3.5 (see



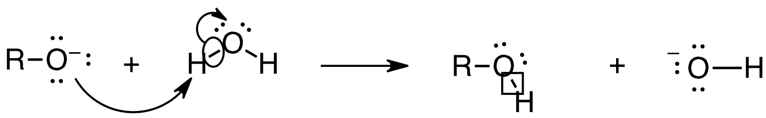
The strongest base has the weakest conjugate acid (highest pK_a).



4. a. RO^- is the weakest base that reacts with water. (See pK_a table.)

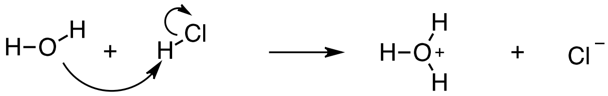


Draw in the H's and lone pairs in each reactant and product.
b. Curved arrows show bonds breaking and forming. A curved arrow starts at the base and ends at the H in an acid.
A lone pair on the O in RO^- behaves like a Lewis base (electron pair donor). The H in H-O-H behaves like a Lewis acid (electron pair acceptor). The lone pair on the O in RO^- forms a bond to the H on H-O-H. Why does the H-O bond in H-O-H have to break?
c. When the H-O bond in H-O-H breaks, what happens to the electron pair?
d. (i) Circle the bond that breaks in the reactants.
(ii) Box the bond that forms in the products.
Answers:
a.

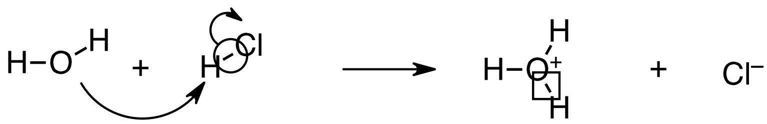


b. The H-O bond in H-O-H has to break because H cannot have two bonds. H has 1 bond only.
c. The bonding pair of electrons between the O and H becomes a lone pair on O.
d. (i) The H-O bond in H-O-H breaks.
(ii) The O-H bond forms to produce ROH.

5. HCl reacts with H-O-H. Curved arrows show how bonds break and form in this reaction.

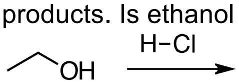


a. Circle the bond that breaks in the reactants.
b. Box the bond that forms in the products.
Answers:

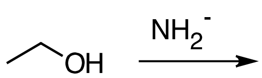


a. The H-Cl bond in HCl breaks.
b. The O-H bond forms to produce H_3O^+.

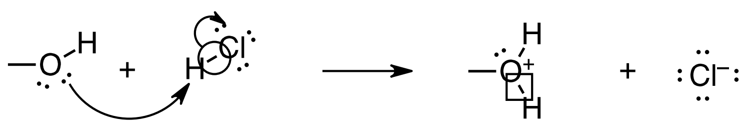
6. a. Ethanol reacts with HCl. Use curved arrows to show how ethanol reacts with HCl. Draw the structures of the products. Is ethanol behaving like an acid or base?



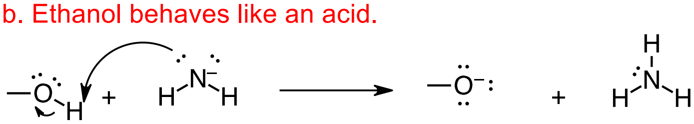
b. Ethanol reacts with NH_2^-. Draw the structure of NH_2^-. Use curved arrows to show how ethanol reacts with NH_2^-. Draw the structures of the products. Is ethanol behaving like an acid or base?



Answers:
a. Ethanol behaves like a base.



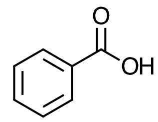
b. Ethanol behaves like an acid.



7. When you do an acid-base reaction, make sure you choose a base that is strong enough to react with the acid (or vice versa).
(i) See a pK_a table. Remember that an acid reacts with a base below it on the table.
(ii) Another way: Remember in an acid-base reaction:

acid + base ---> conjugate base of reactant acid + conjugate acid of reactant base

Compare the pK_a of the acids in the reaction.
If the reactant acid is stronger than the product acid, the reaction occurs (equilibrium favors products).
If the reactant acid is weaker than the product acid, the reaction does not occur (equilibrium favors reactants).
a. Phenol (from Question 3) reacts with $NaHCO_3$. Draw the structure of HCO_3^-. Use curved arrows to show how this reaction occurs. Draw the structures of the products. Does the equilibrium favor the products or reactants?
b. Phenol (from Question 3) reacts with NaOH. Draw the structure of OH^-. Use curved arrows to show how this reaction occurs. Draw the structures of the products. Does the equilibrium favor the products or reactants?
c. Does benzoic acid react with $NaHCO_3$ or NaOH? Give reasons.



benzoic acid

d. In Lab 2, you will try to separate a mixture of three compounds by an acid-base extraction. You have a mixture of benzoic acid and phenol. Which base would you use that reacts with one compound in the mixture but not the other?

Answers:

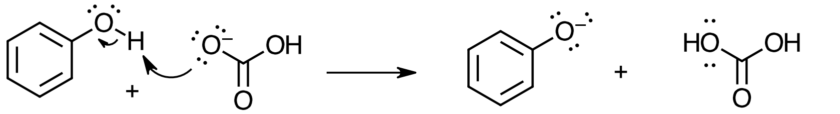
a. Equilibrium favors reactants.

Phenol is a weak acid (see ArOH at pK_a = 10) and HCO_3^- is not a strong enough base (above ArOH in pK_a table) to react with phenol.

This reaction shows a weaker acid (phenol) forming a stronger acid (H_2CO_3) ==> reaction does not occur.

If the reactant acid is stronger than the product acid, the reaction occurs (equilibrium favors products).

If the reactant acid is weaker than the product acid, the reaction does not occur (equilibrium favors reactants).



$pK_a = 10$
weaker acid

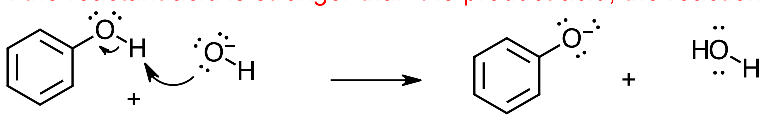
$pK_a = 6.4$
stronger acid

b. a. Equilibrium favors products.

Phenol is a weak acid (see ArOH at pK_a = 10) and OH^- is a strong enough base (below ArOH in pK_a table) to react with phenol.

This reaction shows a stronger acid (phenol) forming a weaker acid (H_2O) ==> reaction does occur.

If the reactant acid is stronger than the product acid, the reaction occurs (equilibrium favors products).



$pK_a = 10$
stronger acid

$pK_a = 15.7$
weaker acid

c. Benzoic acid (pK_a = 4.2) reacts with both $NaHCO_3$ and NaOH. These bases are strong enough to react with the weak acid.

d. Choose a base between benzoic acid and phenol. E.g., HCO_3^-, HS^-, NH_3 reacts with benzoic acid but not phenol.

8. Acetylene, C_2H_2, is an acid. It is used as a fuel but is also used to make many organic compounds.

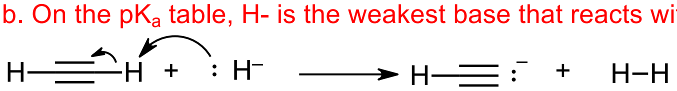
a. What is the pK_a of the acidic proton in acetylene?

b. What is the weakest base that reacts with acetylene? Use curved arrows to show how acetylene reacts with this base. Draw the structures of the products.

Answers:

a. pK_a of the acidic proton in acetylene = 25.

b. On the pK_a table, H- is the weakest base that reacts with acetylene.



9. Acetone, $(CH_3)_2CO$, can behave like an acid or a base.

a. What is the pK_a of the acidic proton in acetone?

b. What is the weakest base that reacts with acetone? Use curved arrows to show how acetone reacts with this base. Draw the structures of the products.

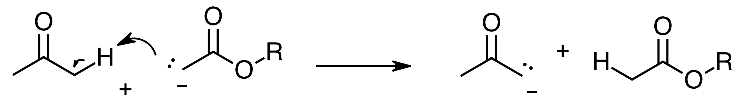
c. The oxygen in acetone behaves like a base. What is the pK_a of the conjugate acid of acetone?

d. What is the weakest acid that reacts with acetone? Use curved arrows to show how acetone reacts with this acid. Draw the structures of the products.

Answers:

a. pK_a of the acidic proton in acetone = 20.

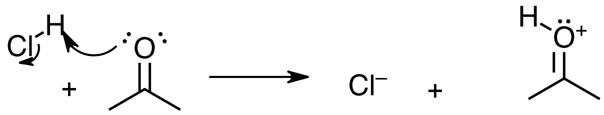
b. From the pK_a table, the weakest base (the base just below acetone) that reacts with acetone is the conjugate base of the ester ($ROOCCH_2^-$).



$pK_a = 20$
stronger acid

$pK_a = 24$
weaker acid

c. The pK_a of the conjugate acid of acetone is -7.
d. The weakest acid that reacts with acetone is HCl (the acid just above acetone).



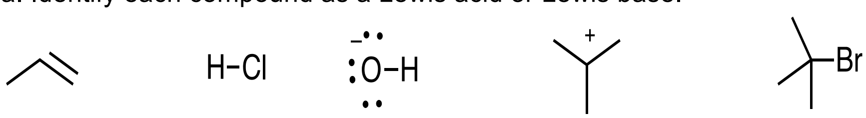
$pK_a = -7$
stronger acid

$pK_a = -7$
weaker acid

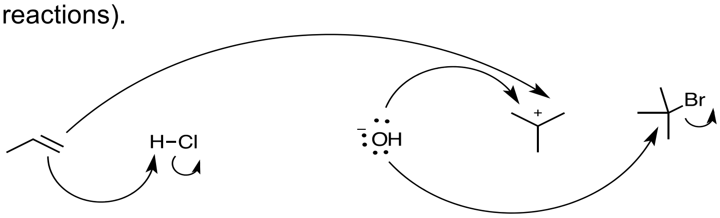
10. So far, we have looked at acids as electron pair donors and bases as electron pair acceptors, specifically H^+. Most organic reactions are "polar" reactions. This means an electron pair donor (Lewis base) reacts with an electron pair acceptor (Lewis acid). Other Lewis acids and bases are shown in the Table.
Table. Examples of Lewis acids and bases.

Lewis base	***Lewis acid***
Electron pair donor	Electron pair acceptor, e.g., H^+
(-) charge	(+) charge
(-) pole (δ-)	(+) pole (δ+)
Nucleophile ($Nu:^-$)	**Electrophile** (E^+)
Electron Source	Electron Sink
lone pair, e.g., OH^-	electron deficient species
π bond	less EN atom in polar bond

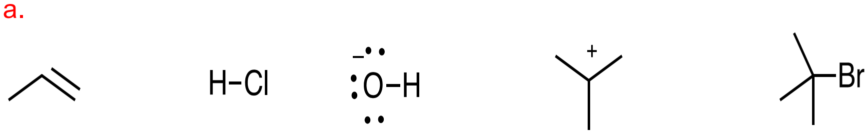
a. Identify each compound as a Lewis acid or Lewis base.



b. Curved arrows are used to show how reactants form products. Curved arrow starts at a Lewis base (nucleophile) and ends at a Lewis acid (electrophile). For the reactions below, draw the structure of the product of each reaction (4 reactions).

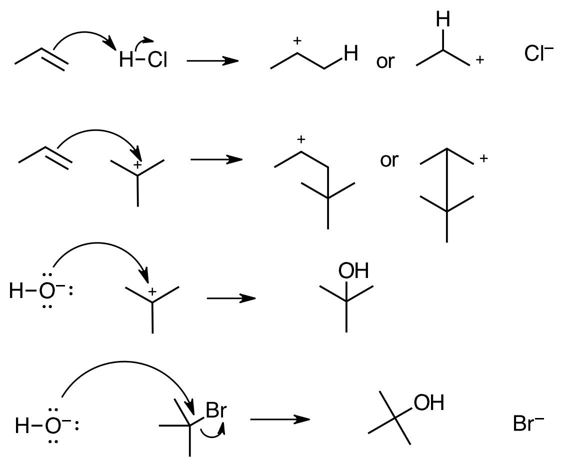


Answers:
a.



Lewis base pi bond	Lewis acid H	Lewis base lone pair on O	Lewis acid carbocation (+)	Lewis acid C bonded to Br (less electronegative atom in polar bond)

b.



We will look at these reactions later in Chem 12A.

1st reaction is the 1st step in a reaction mechanism for an addition reaction.

2nd reaction is the 1st step in a reaction mechanism for an addition reaction.

3rd reaction is the 2nd step in a reaction mechanism for a substitution reaction.

4th reaction is a substitution reaction.