

2.S: POLAR COVALENT BONDS; ACIDS AND BASES (SUMMARY)

CONCEPTS & VOCABULARY

2.1 Polar Covalent Bonds: Electronegativity

- The difference in electronegativity values of two atoms determines whether the bond between those atoms is classified as either **ionic**, **polar covalent**, or **non-polar covalent**.
- Ionic bonds** result from large differences in electronegativity values, such as that between a metal and non-metal atom (Na and Cl).
- Covalent bonding generally results when both atoms are non-metals, like C, H, O, N and the halides.
- When both atoms the same and/or have the same electronegativity value, then the bonding electrons are shared equally and the bond is classified as **non-polar covalent**.
- Polar covalent** bonds occur when the difference in electronegativity values is small, and the bonding electrons are not shared equally.

2.2 Polar Covalent Bonds: Dipole Moments

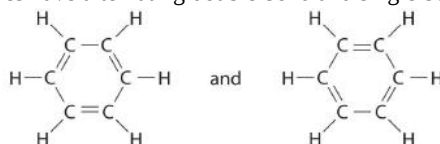
- The **molecular dipole moment** is the sum of all the bond dipoles within a molecule and depends on both the molecular geometry and the bond polarity.
- Molecules that contain no polar bonds, like CH₄, and/or completely symmetrical molecules, like CO₂, generally have no net dipole moment.
- Asymmetrical molecules that contain bonds of different polarities or non-bonding lone pairs typically have a molecular dipole moment.

2.3 Formal Charges

- Formal Charge** compares how many valence electrons surround a free atom versus how many surround that same type of atom bonded with a molecule or ion.
- Formal Charge = (# of valence electrons in free atom) - (# of lone-pair electrons) - (1/2 # of bond pair electrons)** Eqn. 2.3.1
- Formal charges of zero generally represent the most stable structures.
- These bonding patterns for the atoms commonly found in organic molecules result in a formal charge of zero
 - Carbon - 4 bonds, no lone pairs
 - Hydrogen - 1 bond, no lone pairs
 - Nitrogen - 3 bonds, 1 lone pair
 - Oxygen - 2 bonds, 2 lone pairs
 - Halogens - 1 bond, 3 lone pairs.

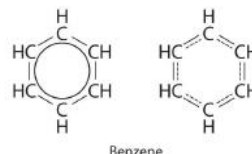
2.4 Resonance

- Resonance Theory** is often used when the observed chemical and physical properties of a molecule or ion cannot be adequately described by a single Lewis Structure. A classic example is the benzene molecule, C₆H₆. The Lewis Structure of benzene could be drawn in two different ways. Both structures have alternating double bond and single bonds between the carbons. The only difference is



the location of the pi bonds.

If these structures are correct, then the benzene molecule should have two different C-C bond lengths and bond energies, corresponding to a C-C single bond and to a C=C double bond. However, analysis shows that benzene contains only one type of carbon-carbon bond and its bond length and energy are half between those of a single bond and double bond. Resonance theory states that benzene exists as the "average" of the two structures called a **resonance hybrid**, in which the six pi electrons **delocalized** over all six carbon atoms. Each C-C bond in benzene would be the average of a single bond and double bond or a "bond and a half". Dashed lines are often used to show type of

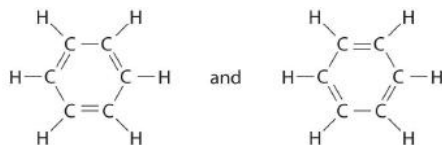


"partial" bonding in a resonance hybrid of benzene

2.5 Rules for Resonance Forms

- The rules for estimating stability of resonance structures are
 - The resonance form in which all atoms have complete valence shells is more stable.
 - The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
 - The structure with the **least number of formal charges** is more stable

- The structure with the **least separation of formal charges** is more stable
 - A structure with a **negative charge on the more electronegative atom** will be more stable
 - **Positive charges on the least electronegative atom** (most electropositive) is more stable
 - **Resonance forms that are equivalent have no difference in stability and contribute equally.** (eg. benzene)
- If these rules are applied to the two Lewis Structures of benzene, the result would be that both structures will have the same relative stability and will both contribute equally to the character of the resonance hybrid.



2.6 Drawing Resonance Forms

- In resonance structures, the electrons are able to move to help stabilize the molecule. This movement of the electrons is called delocalization.
- The rules for drawing resonance structures are:
 - Resonance structures should have the same number of electrons, do not add or subtract any electrons. (You can check the number of electrons by counting them)
 - All resonance structures must follow the rules of writing [Lewis Structures](#).
 - The hybridization of the structure must stay the same.
 - The skeleton of the structure can not be changed (only the electrons move).
 - Resonance structures must also have the same amount of lone pairs.

2.7 Acids and Bases - The Brønsted-Lowry Definition

- A Brønsted-Lowry acid is a proton (H^+) donor and a Brønsted-Lowry base is a proton acceptor.

2.8 Acid and Base Strength

- The strength of Brønsted-Lowry acids is measured indicated by its pKa value. The lower the pKa - the stronger the acid.
- A strong acid will have a weak conjugate base. A strong base will have a weak conjugate acid.

2.9 Predicting Acid-Base Reactions from pKa Values

- The equilibrium of an acid-base reaction favors the formation of weaker acids from stronger acids. To predict the direction of the equilibrium, identify Brønsted-Lowry acid on each side of the reaction. Assign/look up pKa values for each acid. The equilibrium will favor the side that has the weakest acid (the highest pKa).

2.10 Organic Acids and Organic Bases

- Organic acids are stronger when the conjugate base that is formed upon loss of a proton is more stable.
- Some factors that effect the stability of the conjugate base (often an anion) are the anionic atom's size and electronegativity, resonance effects, inductive effects, and solvation.

2.11: Acids and Bases - The Lewis Definition

- A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.

2.12: Non-covalent Interactions between Molecules

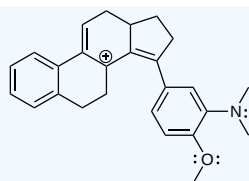
- Non-covalent Interactions, also known as Intermolecular Forces, significantly effect the physical properties of organic molecules. Hydrogen bonding is the most important of these interactions, but others include ion-dipole, dipole-dipole, and London Dispersion Forces.

2.MM: Molecular Models

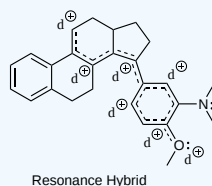
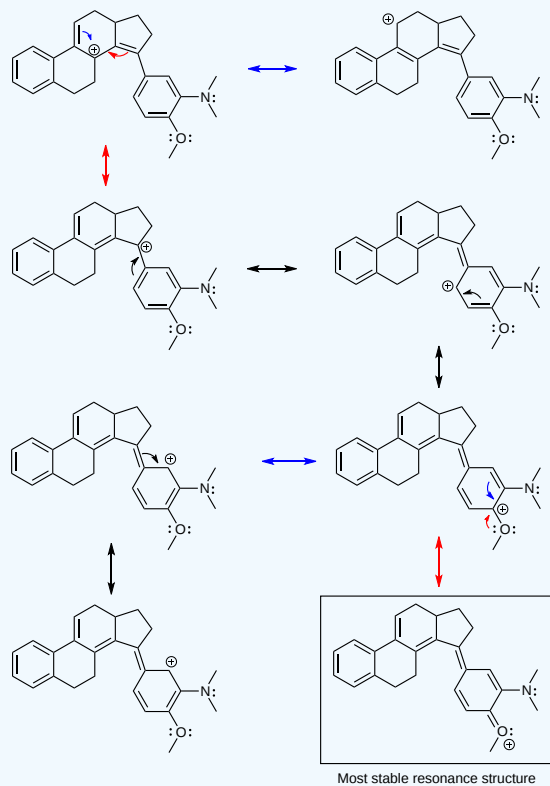
SUMMARY PROBLEMS

? EXERCISE 2.S. 1

Draw all possible resonance structures to demonstrate delocalization of the positive charge in the following molecule. Circle the most stable resonance structure and explain your answer. Also, draw the resonance hybrid.



Answer

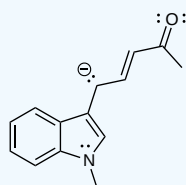


The circled structure is the most stable because it is the only structure with a full octet on all atoms. (Remember that carbocations must have an incomplete octet, and an oxygen with a positive charge and a full octet is more stable than a carbocation.)

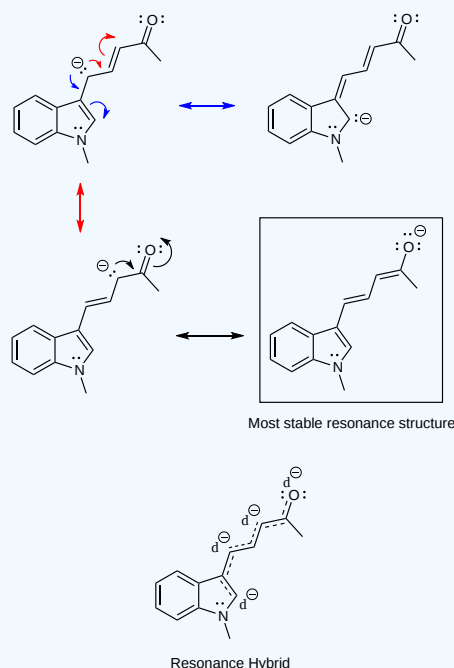
As a reminder, the resonance hybrid structure is a combination of all of your resonance structure showing partial pi bonds and partial formal charges.

? EXERCISE 2.S.2

Draw all possible resonance structures to demonstrate delocalization of the negative charge in the following molecule. Also, draw the resonance hybrid and circle the most stable resonance contributor among all of your resonance structures.



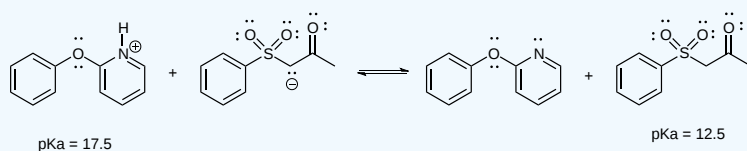
Answer



The circled structure is the most stable because the negative charge is on oxygen, the most electronegative element sharing the negative charge. As a reminder, in resonance structures with negative charges, all of the atoms have octets, so you only need to focus on electronegativity differences to find the most stable structure.

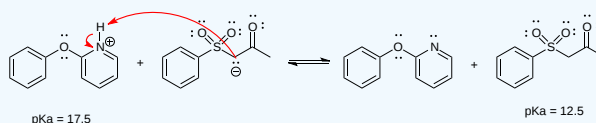
? EXERCISE 2.S.3

For the equilibrium shown below, answer the following questions: a) Draw curved arrows to illustrate bond breakage and formation in the reaction. b) At equilibrium, are the products or reactants favored? Explain. c) What percent reactants and percent products are present at equilibrium? d) Use resonance structures to explain why N is the most basic atom in the conjugate base. e) Use resonance structures to explain why the hydrogen that is removed from the conjugate acid is the most acidic proton.



Answer

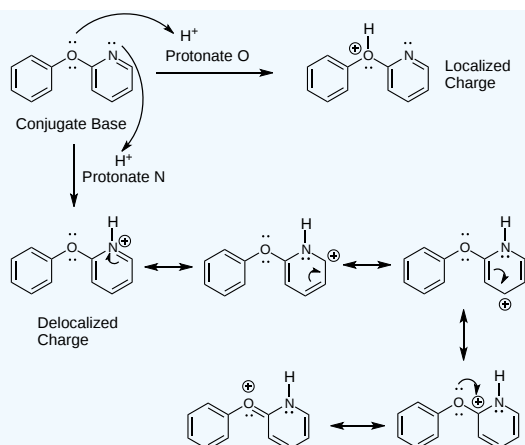
a)



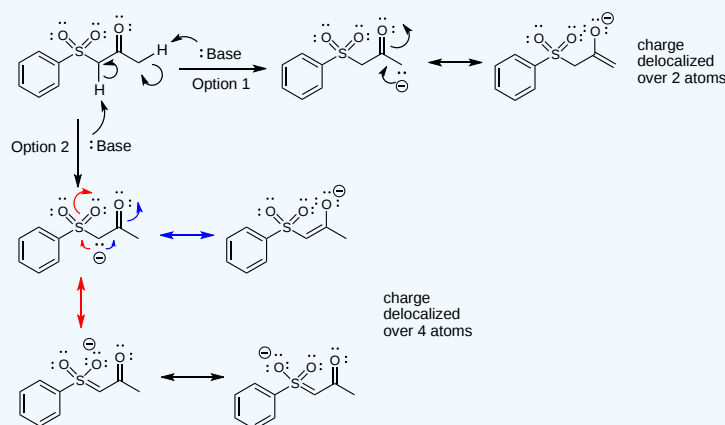
b) The lower pKa is the stronger acid, and the equilibrium will always favor the weak acid (higher pKa), so this reaction favors the reactants. Note: It's normal to assume that the neutral products would be favored, but this is a good example that shows our chemical intuition isn't always right. To make sure we understand the equilibrium, we need to have pKa values to compare.

c) $K_{eq} = 10^{12.5-17.5} = 10^{-5} = 0.00001$. So, the ratio of reactants to products is 1:0.00001. The percent reactants is 99.999% and the percent products is 0.001%.

d) There are two atoms with lone pairs in the conjugate base, O and N, so we should evaluate both to show that N is the most basic atom. Protonating O yields a positive charge localized on O. Protonating N yields a charge delocalized over 3 Cs, 1 N, and 1 O. The N is most basic because the charge in the acid is delocalized and there are two structures with full octets (positive charge on N and O).

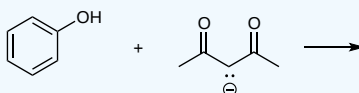


e) To find the most acidic proton, we should focus on Hs on atoms next to (not on) double bonds. This will yield a delocalized negative charge when the H is removed. In the conjugate acid, we have two options. Option 1 yields a compound with a negative charge delocalized over 2 atoms, O and C. Option 2 yields the base from the original reaction because the charge is delocalized over 4 atoms, C and 3 Os. This is very stable because it is spread over 3 electronegative oxygen atoms.



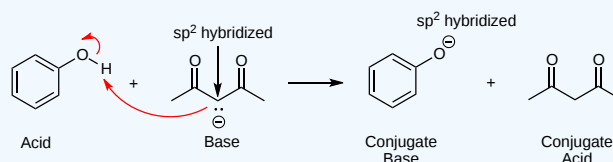
? EXERCISE 2.S. 4

This question focuses on the reaction of the two molecules shown below. a) Draw an acid-base reaction of these molecules. Clearly label the acid, the base, the conjugate acid, and the conjugate base. Draw curved arrows to clearly indicate electron movement involved in bond formation and bond cleavage. For the base and the conjugate base, label the hybridization of the charged atoms. b) If you drew the reaction correctly, the pK_a of the conjugate acid is 9. Use the table in Section 2.8 to determine the pK_a of the acid. Are the reactants or products favored at equilibrium? What is the approximate ratio of reactants to products? What is the approximate percentage of reactants and products? c) Draw the structures of the two charged molecules in the reaction. Draw resonance structures to illustrate charge delocalization in these molecules. Based on your analysis in part b, which charged molecule is more stable? Briefly explain this result.



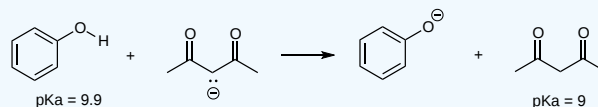
Answer

a)



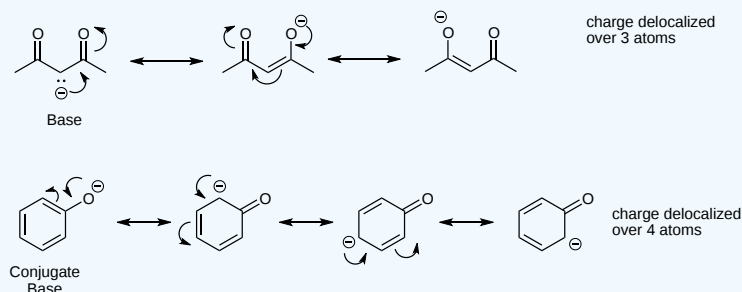
Don't forget that the charged atoms in the base and conjugate base are sp^2 hybridized so that the lone pair can be in a p orbital and then delocalized by resonance. For negative charges to be delocalized, the lone pair must be in a p orbital so that electrons can flow to adjacent pi bonds by resonance.

b)



The acid has the larger pKa, so it is the weaker acid and the reactants are favored. The approximate difference in pKa values is 1. So, K_{eq} is 10^{-1} and for every 1 product molecule there are 10 reactant molecules. (Remember, since the reactants are favored, there are more reactants and the K_{eq} must be less than 1.) The approximate percentage of reactants is 90% and products is 10%. ($10/(10+1)$ is approximately 90% and $1/(10+1)$ is approximately 10%)

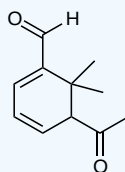
c)



We know that the equilibrium favors the reactants. We also know that in acid base reactions, the stronger acid reacts with the stronger base to yield the weaker base and the weaker acid. In this reaction, the products are the stronger acid-base pair. We also know that "stronger" means more reactive and less stable, while "weaker" means less reactive and more stable. So, since the reactants are favored, that means the base (as labeled above) is more stable than the conjugate base. This seems strange since the charge is more delocalized in the conjugate base. This comparison highlights the importance of quality of resonance structures versus quantity of resonance structures. The charge is more stable in the base since in two of the resonance structures, the negative charge is on O. In the conjugate base, only one of the structures has the negative charge on O.

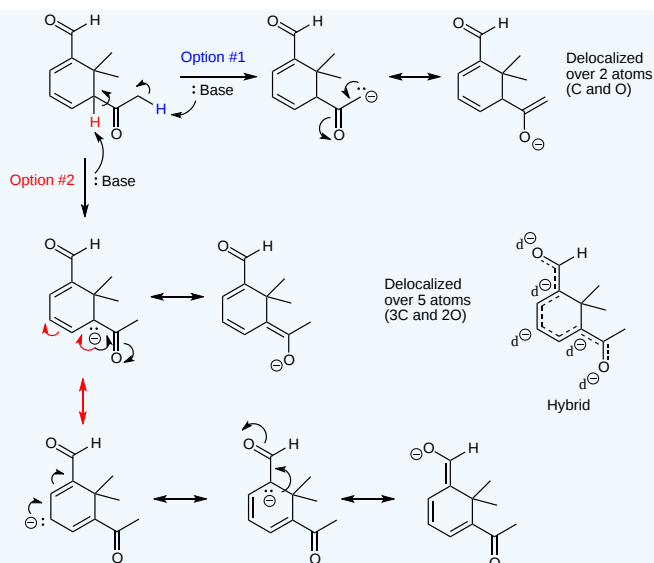
? EXERCISE 2.S. 5

Determine the position of the most acidic proton in the following molecule. You should draw resonance structures and a resonance hybrid to justify your answer.



Answer

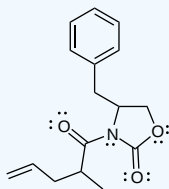
Donation of the most acidic proton (H^+) yields the most stable conjugate base; the one that has the charge on the most electronegative element and/or the most delocalized charge. You should focus on protons attached to electronegative elements (e.g., O or N) and protons on atoms next to pi bonds, but not attached to atoms with pi bonds. In this molecule, all Hs are attached to carbon. So, we should focus on the Hs next to pi bonds. These are Hs on sp^3 hybridized carbons next to sp^2 hybridized carbons. Loss of these protons will yield a negative charge that can be delocalized by resonance.



Option #1 yields a conjugate base with the charge delocalized over 1 carbon and 1 oxygen. Option #2 yields a conjugate base with a charge delocalized over 3 carbons and 2 oxygens. This is the most stable conjugate base, so the most acidic proton is the red proton (removed in option #2).

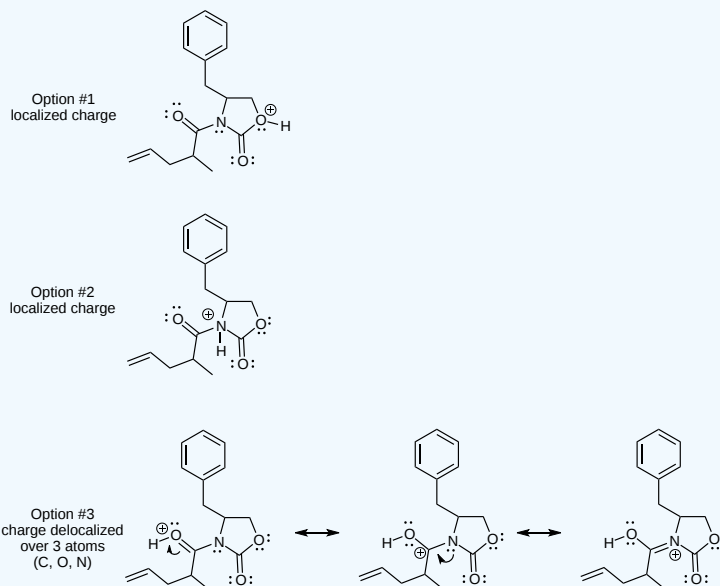
? EXERCISE 2.S. 6

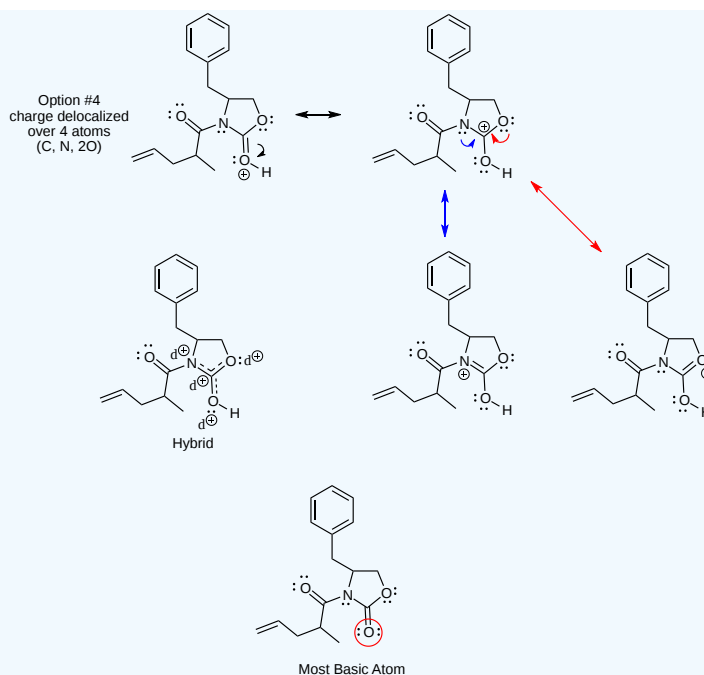
Determine the position of the most basic atom in the following molecule. You should draw resonance structures and a resonance hybrid to justify your answer.



Answer

There are four basic atoms (atoms with lone pair electrons) in this molecule. The strongest base will yield the most stable conjugate acid (the one with the most delocalized positive charge and/or the charge on the least electronegative atom).





Options #1 and #2 yield conjugate acids with localized charges. Options #3 and #4 yield conjugate acids with delocalized charges. This illustrates a key point: For atoms that can't have an expanded octet, atoms with a lone pair and no pi bond will accept a proton and yield a localized charge in the conjugate acid while atoms with both a lone pair and a pi bond will accept a proton and yield a delocalized charge in the conjugate acid. So, we should focus our energy on the latter atoms. In this problem, that means Options #3 and #4. In option #3, the charge is delocalized over 3 atoms, 2 that have full octets on all atoms (positive charge on N and O). In option #4, the charge is delocalized over 4 atoms, 3 that have full octets on all atoms (positive charge on N and 2 Os). So, Option #4 has more total resonance structures and more structures that have a full octet. This is the most stable conjugate acid which means the circled O is the most basic atom.

SKILLS TO MASTER

- Skill 2.1 Predict whether a bond is ionic, polar covalent, or non-polar covalent based on the position of the atoms in the periodic table.
- Skill 2.2 Identify the partial positive and partial negative atoms of a polar covalent bond based on relative electronegativity.
- Skill 2.3 Determine the dipole moment of a molecule based on molecular geometry and bond polarity.
- Skill 2.4 Identify the chemicals in a reaction as Brønsted-Lowry acids or bases, and conjugate acids and bases.
- Skill 2.5 Predict the products of an acid-base reaction.
- Skill 2.6 Use pKa values to predict the equilibrium direction of an acid-base reaction.
- Skill 2.7 Predict the relative strength of an organic acid by examining the stability of the conjugate base.
- Skill 2.8 Use molecular structure and analysis of intermolecular forces to rank a series of organic molecules with respect to physical properties like melting point and boiling point.
- Skill 2.9 Identify the chemicals in a reaction as Lewis acids or bases.

MEMORIZATION TASKS (MT)

- MT 2.1 Memorize that the C-H bond is considered to be non-polar.
- MT 2.2 Memorize the common bonding patterns for C, H, N, O and the halogens that have a zero formal charge.
- MT 2.3 Memorize the factors that affect the relative stability of conjugate bases.

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