Introduction and Review, II

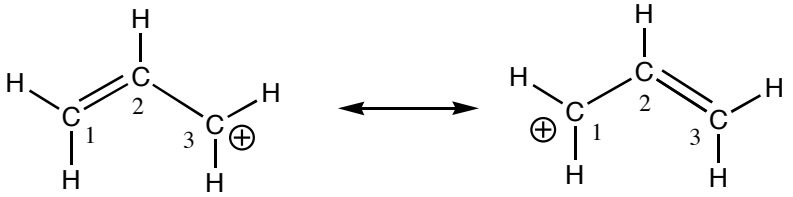
Reading: Wade chapter 1, sections 1-9- 1-14
Study Problems: 1-36, 1-37, 1-40, 1-41, 1-43, 1-44, 1-45

Key Concepts and Skills:

- Draw resonance forms, an use them to predict stabilities
- Predict relative acidities and basicities based on structure, bonding, and resonance of conjugate acid-base pairs; calculate, interpret, use values of K_a and pK_a.
- Identify nucleophiles and electrophiles and be able to show the "curved-arrow formalism" for their reactions

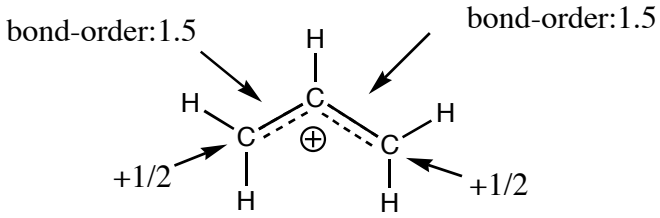
Lecture Topics:
I. Resonance

Some compounds' structures are not adequately represented by a single Lewis structure. When two or more structures are possible, differing only in the placement of electrons, the molecule will show characteristics of both structures. The different structures are called **resonance structures**:
Ex.



resonance structure resonance structure

The actual molecule is a **resonance hybrid** of its **resonance forms**: the combined contribution of both resonance forms.

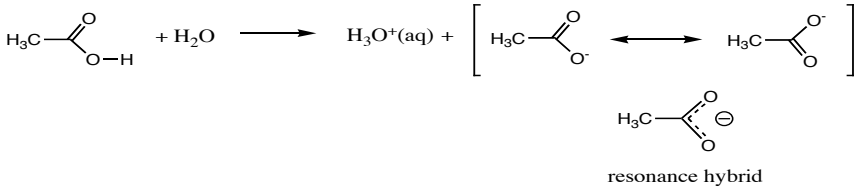


resonance hybrid

Note that the positive charge is spread out or **delocalized** over the two terminal carbons of the propenyl cation.

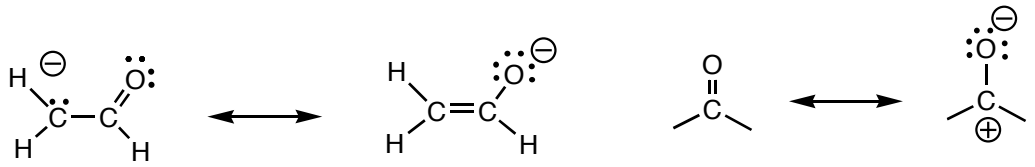
• The spreading out of positive (or negative) charge over two atoms makes the ion more stable than if the entire charge were localized on one atom.

• The acidity of acetic acid is due to resonance stabilization of the carboxylate ion



resonance hybrid

•Individual resonance forms don't exist, the molecule is actually a hybrid with characteristics of both resonance forms.
•Estimate the relative energies of individual resonance forms; more stable resonance forms,"major resonance contributors" are closer representations of the real molecules than less stable ones, "minor resonance contributors"
•Which resonance form is more stable? The most stable resonance form has
-as many octets as possible; as many bonds as possible; any negative charges on electronegative atoms; as little charge separation as possible.



minor major major minor

•The structure of the actual compound resembles the major resonance contributor mor ethan the minor one.

II. Acids and Bases

-Review the definitions of Arrhenius acids and bases, Bronsted acids and bases, conjugate acid/base pairs, K_a, K_b, pK_a
•Note that most organic acids are weak acids ($K_a=10^{-4}$ or less). Strong acids have low pKa values (0,1,2); weak acids have high pKa values (4,5,…40)
• Remember that $K_a \bullet K_b=K_w$ and $K_a = K_w/K_b$ for conjugate acid/base pairs; thus a weak acid makes a strong conjugate base and a strong acid makes a weak conjugate base. Compare the strong acid HCl (weak conjugate base Cl^-) with the weak acid CH_4 (strong conjugate base: CH_3^-)
•In acid-base reactions , the strongest acid in the medium reacts with the strongest base in the medium to produce the weaker acid and the weaker base.
• An acid will donate a proton to the conjugate base of a weaker acid.
Using tables of K_a/pKa values in the book, predict the direction of the following equilibria:

$NaOCH_3 + HCN$ $\qquad$ $HOCH_3 + CN^-$

III. Structural Effects on Acidity:

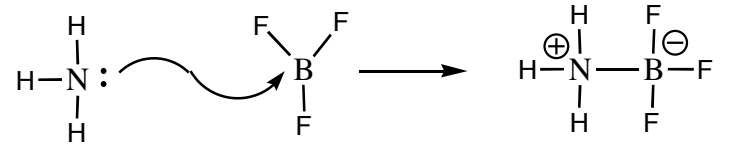
$$\mathbf{HA + H_2O \Leftrightarrow H_3O^+ + A^-}$$

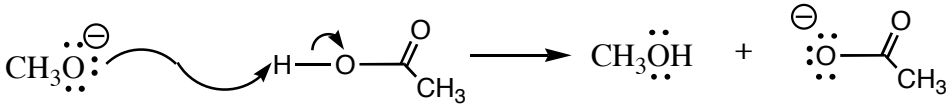
The more stable the conjugate base of an acid (A^-, the species bearing a negative charge), the stronger the acid. What factors influence the stability of the negative charge on the conjugate base?
Three major factors affect the acidity of a given compound: electronegativity, size, and charge.

1. A negative charge on a more electronegative element is more stable, making a weaker conjugate base and thus a stronger conjugate acid; Consider: acidity: $CH_4<NH_3<H_2O<HF$; and basicity: $H_3C^- > H_2N^- > HO^- > F^-$
2. The negative charge on an anion is more stable if it is spread out over a larger region of space. Acidity: $HF<HCl<HBr<HI$, size, stability: $I^- > Br^- > Cl^- > F^-$
3. The greater the extent of resonance stabilization/ charge delocalization, the more stable the anion is, the greater the acidity of the corresponding conjugate acid. Consider: CH_3SO_3H is more acidic that CH_3CO_2H. Why?

IV. Lewis acids and Bases

1. A Lewis acid is a species that can accept a pair of electrons to form a new bond (BF_3, $AlCl_3$), often containing an empty orbital; a Lewis base is a species that can donate a pair of electrons to form a new bond (NH_3, $(CH_3)_3P$)
2. In organic reactions, Lewis acids are termed "electrophiles", and Lewis bases are termed "nucleophiles"
3. In organic reactions, the "curved arrow formalism" shows the direction of flow of electrons in a chemical process; The arrow originates at the lone pair of the nucleophile and is pointed toward the electrophilic atom of the acceptor molecule.





Additional Problems for practice

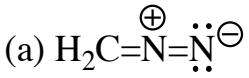
1. Rank each of the following compounds from the most to the least acidic:
   a. HCO_2H, HNO_3, NH_3
   b. CH_3CH_2OH, $CH_3CH_2CO_2H$, $CH_3CH_2NH_2$
   c. CH_4, HCN, H_2O, CH_3CO_2H

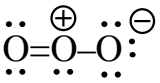
2. Classify the following reagents as Lewis acids or Lewis bases
   (a) $AlBr_3$ (b)HF (c)BH_3 (d)$TiCl_4$ (e) CH_3SCH_3 (f)$CH_3CH_2NH_2$

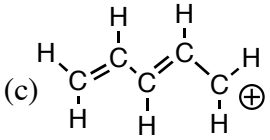
3. Which of the following compounds have polar bonds, and which have dipole moments?

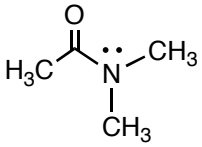
   (a) CH_3Cl (b) Cl_2 (c)CH_3OH (d)$(CH_3)_4Si$ (e)CH_4
   (f) CH_3Li (g) CBr_4 (h) CH_3COCH_3

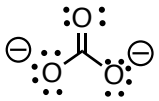
4. Draw all important resonance structure for the following species. If applicable, indicate major and minor resonance contributors

(a) 

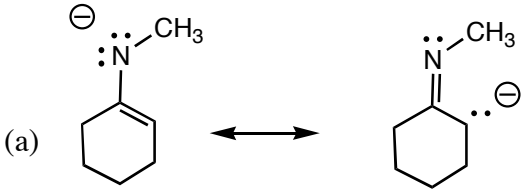
(b) 

(c) 

(d) 

(e) 

5. Predict the major and minor resonance contributors in each case.

(a) 

(b)