Acids & Bases in Organic Chemistry

- **Many of the organic reactions you will study involve acid-base reactions.**

- **Understanding these reactions will require you to:**
  - **recognize organic compounds that can serve as acids or bases**

  - **throw away the idea that anything with an OH is a base and anything with an H is an acid!!!**

Acids & Bases in Organic Chemistry

- **Common definitions of acids and bases:**
  - **Arrhenius acids and bases**
  - **Bronsted-Lowry acids and bases**
  - **Lewis acids and bases**

- **Bronsted-Lowry Acid**
  - **any substance that can donate a proton (H^+ ion)**

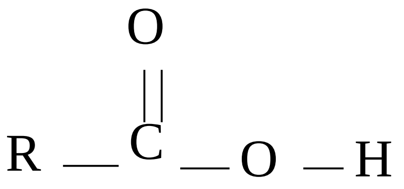
- **Bronsted-Lowry Base**
  - **any substance that can accept a proton**

Acids & Bases in Organic Chemistry

- **Common acids (materials with acidic protons) used in organic chemistry:**
  - **Inorganic acids:**
    - **HCl**
    - **HBr**
    - **HI**
    - **H_2SO_4**
    - **H_3PO_4**

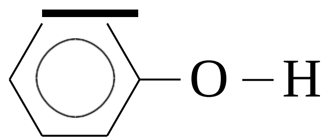
    Strong acids

  - **Carboxylic acids**



Acids & Bases in Organic Chemistry

- **Common acids (materials with acidic protons) used or found in organic chemistry:**
  - **Phenols**

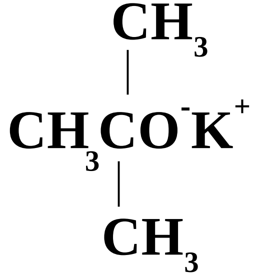


  - **Alcohols** $R - O - \mathbf{H}$
  - **Water** $\mathbf{H} - O - \mathbf{H}$
  - **Terminal Alkynes** $R - C \equiv \quad - \mathbf{H}$

C

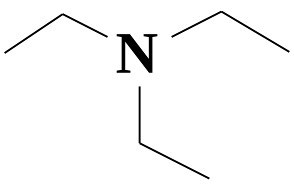
Acids & Bases in Organic Chemistry

- **Common bases (or basic substances) used or found in organic chemistry:**
  - **Hydroxide ion**
    - **NaOH or KOH**
  - **Alkoxide ions**
    - **Sodium methoxide** $CH_3O^-Na^+$
    - **Sodium ethoxide** $CH_3CH_2O^-Na^+$
    - **Potassium t-butoxide**

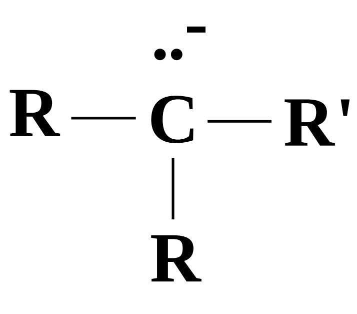


Acids & Bases in Organic Chemistry

- **Common bases (or basic substances) used or found in organic chemistry:**
  - **Sodium hydride** NaH
  - **Sodium amide** $NaNH_2$
  - **Amines or ammonia** $\mathbf{NH_3}$



  - **Carbanions**



Acids & Bases in Organic Chemistry

Example: Complete the following acid-base reactions.

$CH_3CO_2H \quad + \quad NaOH \longrightarrow$

$NaH \quad + \quad CH_3CH_2OH \longrightarrow$

$CH_3 \equiv CH \quad + \quad NaNH_2 \longrightarrow$

C

Acids & Bases in Organic Chemistry

- Acid-base reactions always produce a new acid and a new base:
  - conjugate acid:
    - The new acid formed when the base gains a proton
      - always found on the product side
  - conjugate base:
    - The new base formed by removing a proton from an acid
      - always found on the product side

$$CH_3CO_2H + NaOH \longrightarrow CH_3CO_2Na + H_2O$$

Conj. base (CH₃CO₂Na) Conj. acid (H₂O)

Acids & Bases in Organic Chemistry

- **The strength of an acid or base is determined by the extent to which it ionizes:**

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

$$B. + H_2O \longrightarrow BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

- **K_a = acid dissociation constant**
- **K_b = base dissociation constant**

Acids & Bases in Organic Chemistry

- **The relative strength of an acid can be determined using:**
  - **the magnitude of Ka (or pKa)**
    - **As K_a increases, the strength of the acid increases.**
    - **As pK_a decreases, the strength of the acid increases.**
  - **structural trends**
    - **The strength of an acid, HX, depends on**
      - **the electronegativity of the atom containing the acidic hydrogen (i.e. the electronegativity of X)**
      - **the stability of the conjugate base, X^-**

Acids & Bases in Organic Chemistry

- **Within the same period (row), acidity increases as the electronegativity of element X increases**
  (i.e. left to right)
  - **electronegative elements can bear a negative charge more easily**

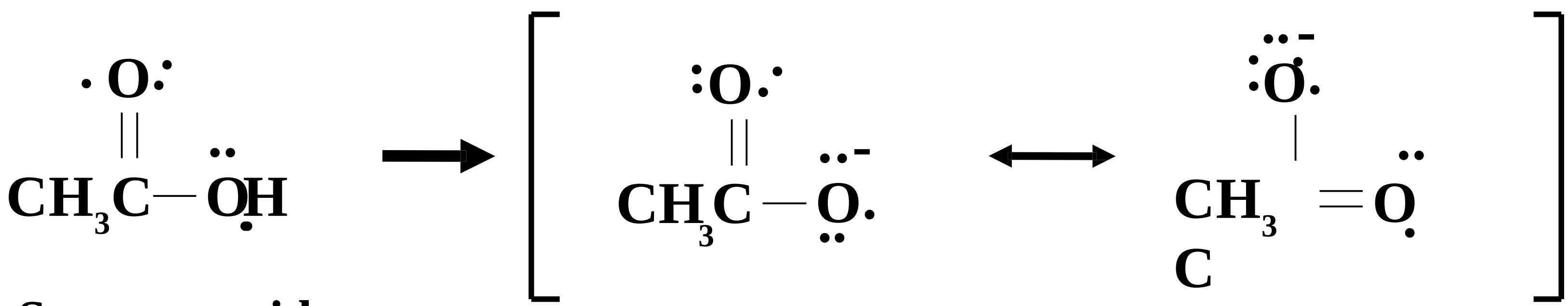
    H-C < H-N < H-O < H-F

- **Within a group, the strength of an acid increases moving down the group**
  - **negative charge is more stable when spread out over a larger region (i.e. larger ion)**

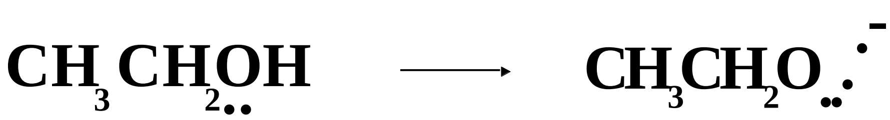
    HCl is stronger than HF

Acids & Bases in Organic Chemistry

- **Acidity increases when the charge on the conjugate base can be delocalized over two or more atoms through resonance.**



Stronger acid
$pK_a = 4.74$



Weaker acid
$pK_a = 15.9$

Acids & Bases in Organic Chemistry

- **You must be able to predict the relative strength of various acids:**
  - **pKa values (see Table 1-5) indicate the following relative acidities:**
    - **strong inorganic acids > carboxylic acids > phenols > alcohols ~ water > terminal alkynes > alkanes**
  - **Be able to use structural trends.**

Acids & Bases in Organic Chemistry

- **The strength of a base is inversely related to its conjugate acid.**
  - **Strong acids form conjugate bases with negligible basicity.**

$$HCl \longrightarrow Cl^-$$

  - **Weak acids form stronger conjugate bases.**

$$CH_3CO_2H \longrightarrow CH_3CO_2^- \qquad CH_3OH \longrightarrow CH_3O^-$$

  - **Substances with negligible acidity form very strong conjugate bases.**

$$NH_3 \longrightarrow NH_2^- \qquad CH_4 \longrightarrow CH_3^-$$

Acids & Bases in Organic Chemistry

- **You should be able to:**
  - **use the relative strength of various acids to predict the relative strengths of their conjugate bases**
  - **use the strength of acids and bases to predict whether an acid/base equilibrium favors reactants or products.**
- **Equilibrium favors the weaker acid (or the weaker base).**

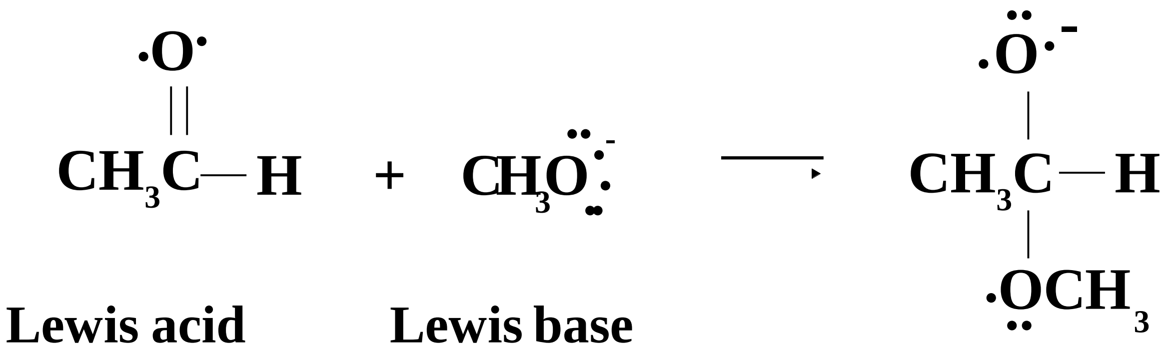
Acids & Bases in Organic Chemistry

Example: Does the following reaction favor the reactants or products?

$$CH_3CH_2OH \;+\; CH_3NH^- \rightleftharpoons CH_3CH_2O^- \;+\; CH_3NH_2$$

Acids & Bases in Organic Chemistry

- The following reaction does not look like a "classic" acid-base reaction...neither reactant gains or loses an H^+.

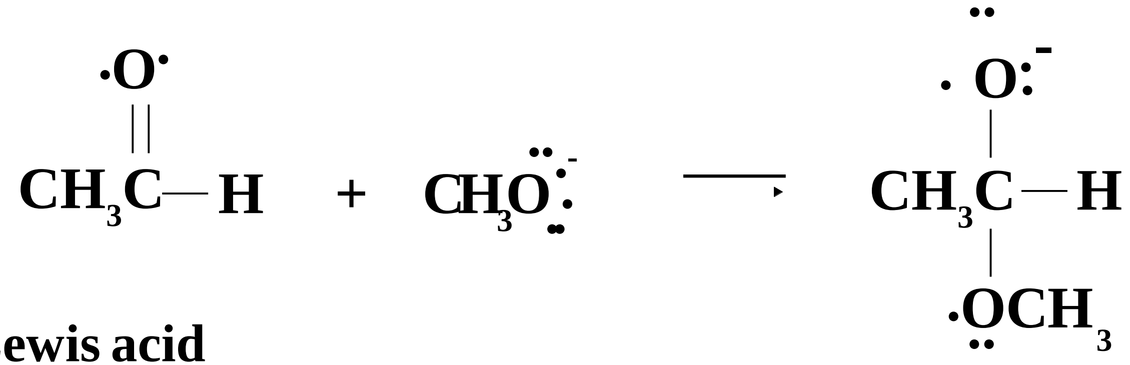


- It is, however, a Lewis acid-base reaction.

- The Lewis acid-base definition is the broadest definition of acids and bases.

Acids & Bases in Organic Chemistry

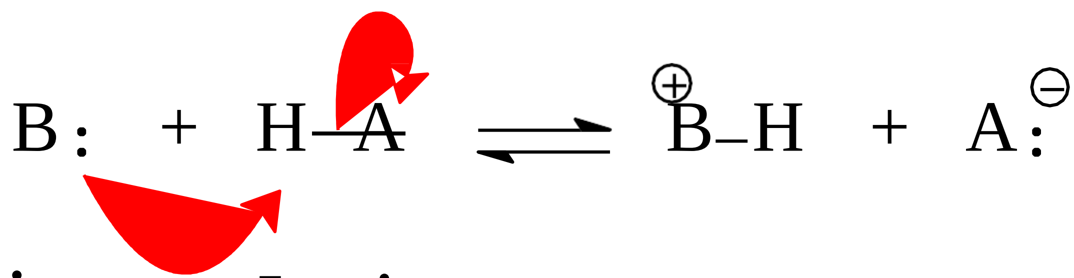
- **Lewis acid:**
  - **an electron pair acceptor**
  - **an electrophile**
    - **“electron lover”**
    - **a substance that accepts a pair of electrons to form a new bond**



Lewis acid

Acids & Bases in Organic Chemistry

- **Lewis Base:**
  - **an electron pair donor**
  - **a nucleophile**
    - **“nuclei lover”**
    - **a substance with a pair of electrons that can be donated to another nucleus to form a new bond**

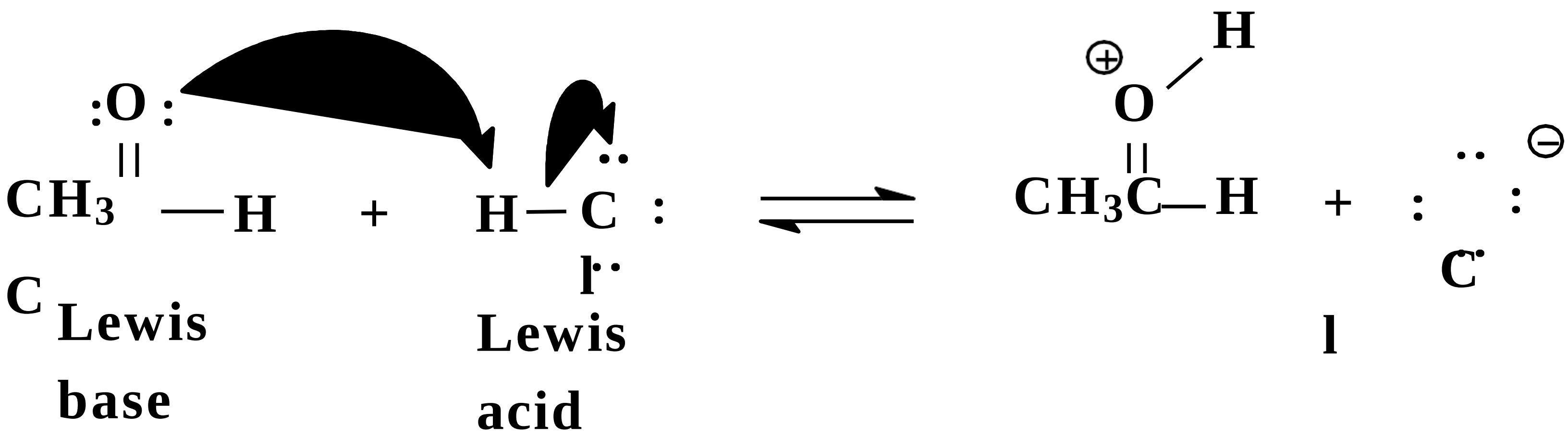


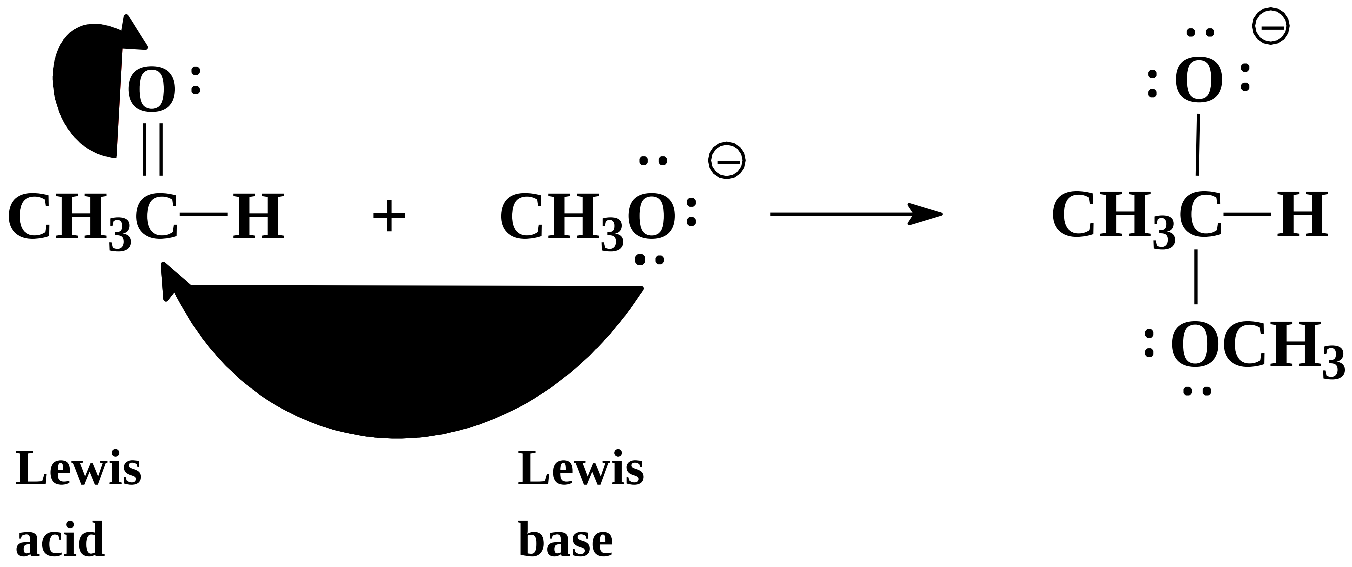
Lewis Base

Lewis Acid

Acids & Bases in Organic Chemistry

Examples of Lewis Acid/Base Reactions





Curved Arrows

- **Curved arrows are used to show the *movement of electrons* during a chemical reaction.**
  - **Electrons always move from the electron donor to the electron acceptor.**

    - **The curved arrow always starts at the pair of electrons used to form the new bond.**

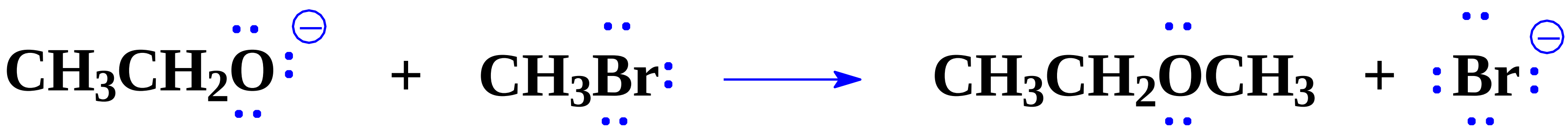
    - **Curved arrows DO NOT show the movement of atoms or charges!!!!**

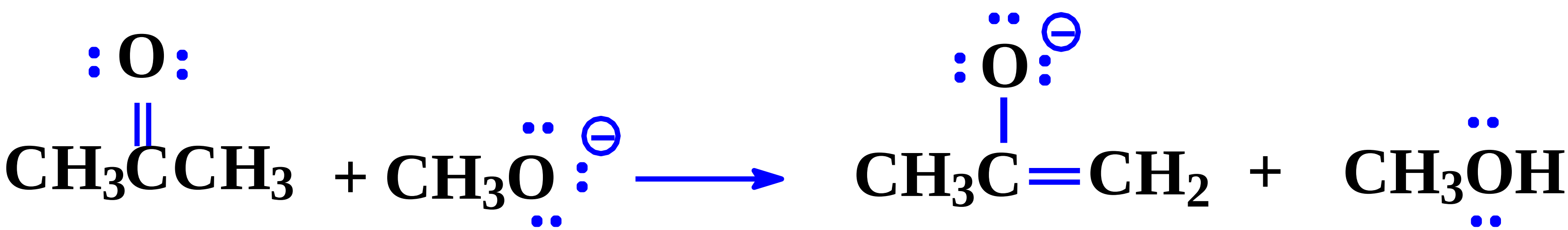
Curved Arrows

- **You should be able to used curved arrows correctly to show the movement of electrons for:**
  - **Converting one resonance structure into another**
  - **Lewis acid/base reactions**

Curved Arrows

Example: Used curved arrow to show the movement of electrons in the following reactions. Identify the nucleophile and the electrophile.





Curved Arrows

Example: Use curved arrows to show the interconversion of the following resonance structures.