

# **Chapter 3**

## **Acids and Bases**

# Acids and Bases

## Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid is a proton donor.
- A Brønsted-Lowry base is a proton acceptor.
- $\text{H}^+$  = proton

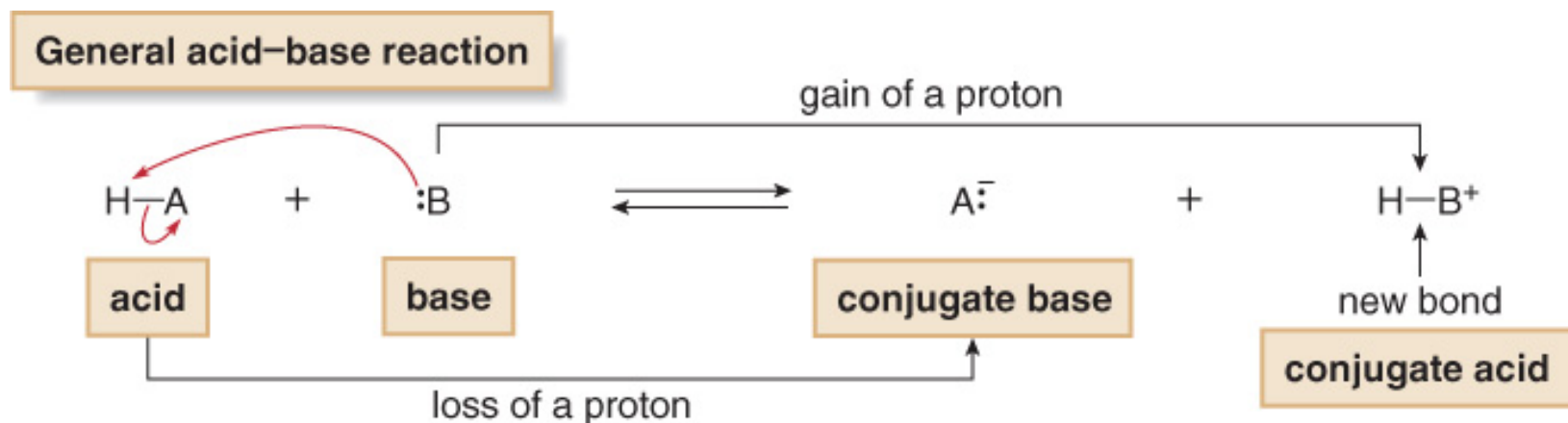
**Figure 2.1** Examples of Brønsted-Lowry acids and bases

Brønsted-Lowry acids [H-A]		Brønsted-Lowry bases [B:]	
Inorganic	Organic	Inorganic	Organic
HCl H <sub>2</sub> SO <sub>4</sub> HSO <sub>4</sub> <sup>-</sup> H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup>	CH <sub>3</sub> CO <sub>2</sub> H acetic acid  $\text{HO}_2\text{CCH}_2-\overset{\text{OH}}{\underset{\text{COOH}}{\text{C}}}-\text{CH}_2\text{CO}_2\text{H}$ citric acid	H <sub>2</sub> Ö:    :NH <sub>3</sub>  $\text{:}\ddot{\text{O}}\text{H}$ $\text{:}\ddot{\text{N}}\text{H}_2$	CH <sub>3</sub> ÑH <sub>2</sub> CH <sub>3</sub> Ö:⁻ methylamine    methoxide  $\begin{array}{c} \text{CH}_3 \\   \\ \text{C}=\ddot{\text{O}} \\   \\ \text{CH}_3 \end{array}$ CH <sub>2</sub> =CH <sub>2</sub> acetone    ethylene
<ul style="list-style-type: none"> <li>• All Brønsted-Lowry acids contain a proton.</li> <li>• The net charge may be zero, (+), or (-).</li> </ul>		<ul style="list-style-type: none"> <li>• All Brønsted-Lowry bases contain a lone pair of electrons or a π bond.</li> <li>• The net charge may be zero or (-).</li> </ul>	

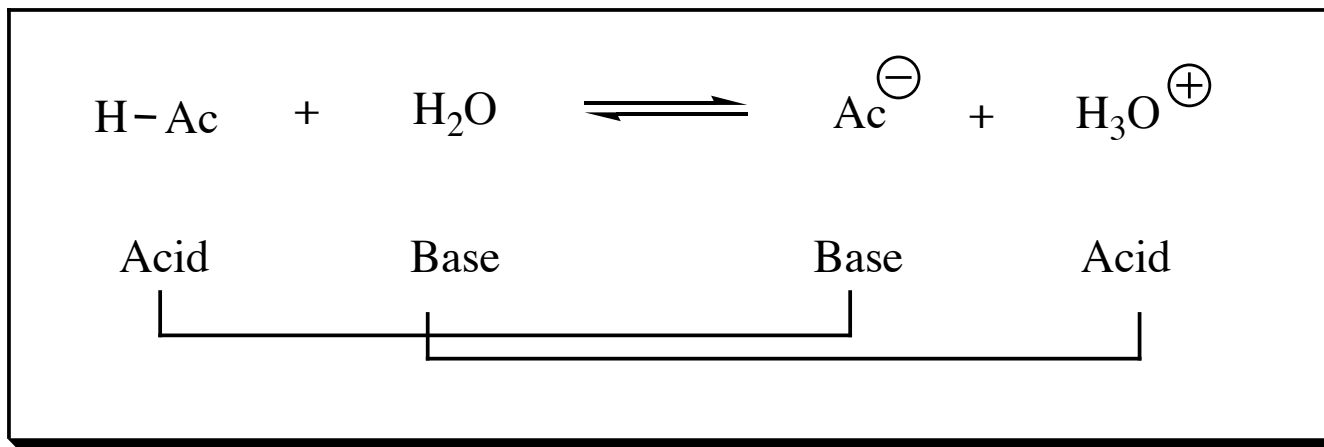
# Acids and Bases

## Reactions of Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid base reaction results in the transfer of a proton from an acid to a base.
- In an acid-base reaction, the electron pair of the base B: forms a new bond to the proton of the acid.
- The acid H—A loses a proton, leaving the electron pair in the H—A bond on A.



# Acids and Bases



Every acid/base reaction has two acids and two bases.



Conjugate Acid/Base Pairs

# Acids and Bases

There are two kinds of acids:

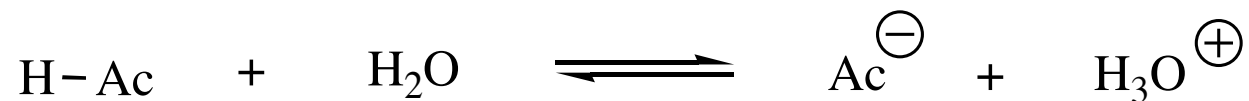
**Strong Acids** (completely dissociated in water)

Example:



**Weak Acids** (partly dissociated in water)

Example:



# Acids and Bases

There are only about 6 “STRONG ACIDS”:



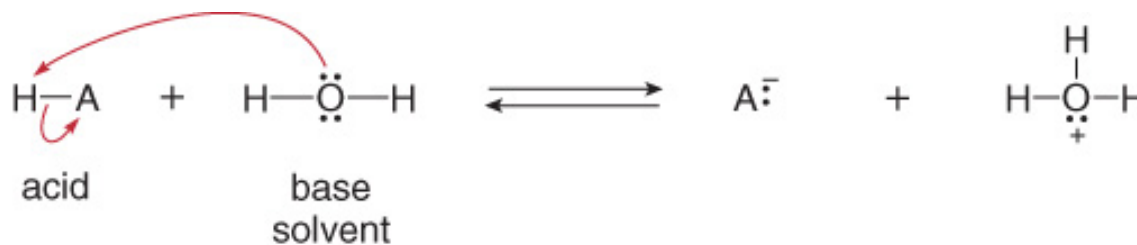
ALL other acids are “WEAK ACIDS”

## For Weak (most) Acids

### Acid Strength and $pK_a$

- Acid strength is the tendency of an acid to donate a proton.
- The more readily a compound donates a proton, the stronger an acid it is.
- Acidity is measured by an equilibrium constant
- When a Brønsted-Lowry acid  $H-A$  is dissolved in water, an acid-base reaction occurs, and an equilibrium constant can be written for the reaction.

Dissolving an acid  
in water



Equilibrium constant

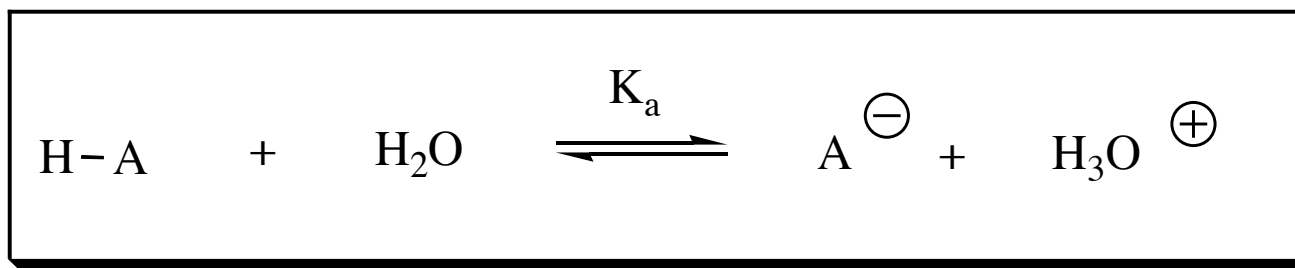
$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{H}-\text{A}][\text{H}_2\text{O}]}$$

# Acids and Bases

## Acid Strength and $pK_a$

Because the concentration of the solvent  $H_2O$  is essentially constant, the equation can be rearranged and a new equilibrium constant, called the acidity constant,  $K_a$ , can be defined.

$$\text{Acidity constant} = K_a = [H_2O]K_{eq} = \frac{[H_3O^+][A^-]}{[H-A]}$$



Larger  $K_a$ , the further to the right, the stronger acid

Smaller  $K_a$ , the further to the left, the weaker the acid.

**Therefore, the value of  $K_a$  is a measure of acid strength**



# Acids and Bases

## Acid Strength and $pK_a$

It is generally more convenient when describing acid strength to use “ $pK_a$ ” values than  $K_a$  values.

Definition:  $pK_a = -\log K_a$

$K_a$	$pK_a = -\log K_a$
$K_a$ values of typical organic acids	$pK_a$ values of typical organic acids
$10^{-5}$ to $10^{-50}$	+5 to +50
larger number stronger acid	smaller number stronger acid
smaller number weaker acid	larger number weaker acid

**Larger  $K_a$  = stronger acid / Smaller  $pK_a$  = stronger acid**  
**Smaller  $K_a$  = weaker acid / Larger  $pK_a$  = weaker acid**

# Acids and Bases

	Acid	Approximate $pK_a$	Conjugate Base	
Strongest acid	HSbF <sub>6</sub>	< -12	SbF <sub>6</sub> <sup>-</sup>	Weakest base
	HI	-10	I <sup>-</sup>	
	H <sub>2</sub> SO <sub>4</sub>	-9	HSO <sub>4</sub> <sup>-</sup>	
	HBr	-9	Br <sup>-</sup>	
	HCl	-7	Cl <sup>-</sup>	
	C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> H	-6.5	C <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> <sup>-</sup>	
	(CH <sub>3</sub> ) <sub>2</sub> OH <sup>+</sup>	-3.8	(CH <sub>3</sub> ) <sub>2</sub> O	
	(CH <sub>3</sub> ) <sub>2</sub> C=OH <sup>+</sup>	-2.9	(CH <sub>3</sub> ) <sub>2</sub> C=O	
	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	-2.5	CH <sub>3</sub> OH	
	H <sub>3</sub> O <sup>+</sup>	-1.74	H <sub>2</sub> O	
	HNO <sub>3</sub>	-1.4	NO <sub>3</sub> <sup>-</sup>	
	CF <sub>3</sub> CO <sub>2</sub> H	0.18	CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	
	HF	3.2	F <sup>-</sup>	
	CH <sub>3</sub> CO <sub>2</sub> H	4.75	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	
	H <sub>2</sub> CO <sub>3</sub>	6.35	HCO <sub>3</sub> <sup>-</sup>	
	CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>	9.0	CH <sub>3</sub> COCH <sup>-</sup> COCH <sub>3</sub>	
	NH <sub>4</sub> <sup>+</sup>	9.2	NH <sub>3</sub>	
	C <sub>6</sub> H <sub>5</sub> OH	9.9	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	
	HCO <sub>3</sub> <sup>-</sup>	10.2	CO <sub>3</sub> <sup>2-</sup>	
	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	10.6	CH <sub>3</sub> NH <sub>2</sub>	
	H <sub>2</sub> O	15.7	OH <sup>-</sup>	
	CH <sub>3</sub> CH <sub>2</sub> OH	16	CH <sub>3</sub> CH <sub>2</sub> O <sup>-</sup>	
	(CH <sub>3</sub> ) <sub>3</sub> COH	18	(CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup>	
	CH <sub>3</sub> COCH <sub>3</sub>	19.2	<sup>-</sup> CH <sub>2</sub> COCH <sub>3</sub>	
	HC≡CH	25	HC≡C <sup>-</sup>	
	H <sub>2</sub>	35	H <sup>-</sup>	
	NH <sub>3</sub>	38	NH <sub>2</sub> <sup>-</sup>	
	CH <sub>2</sub> =CH <sub>2</sub>	44	CH <sub>2</sub> =CH <sup>-</sup>	
Weakest acid	CH <sub>3</sub> CH <sub>3</sub>	50	CH <sub>3</sub> CH <sub>2</sub> <sup>-</sup>	Strongest base



# Acids and Bases

## Amphoteric or Amphiprotic Substances

Substances which can be either acids or bases.

For example:  $\text{H}_2\text{O}$

Such compounds exist as two, independent conjugate acid/base pairs with two different  $\text{pK}_a$  values.

$\text{H}_2\text{O}$  as an acid:  $\text{H}_2\text{O} / \text{HO}^-$  ( $\text{pK}_a = 15.7$ )

$\text{H}_2\text{O}$  as a base:  $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$  ( $\text{pK}_a = -1.74$ )

# Acids and Bases

## Factors that Determine Acid Strength

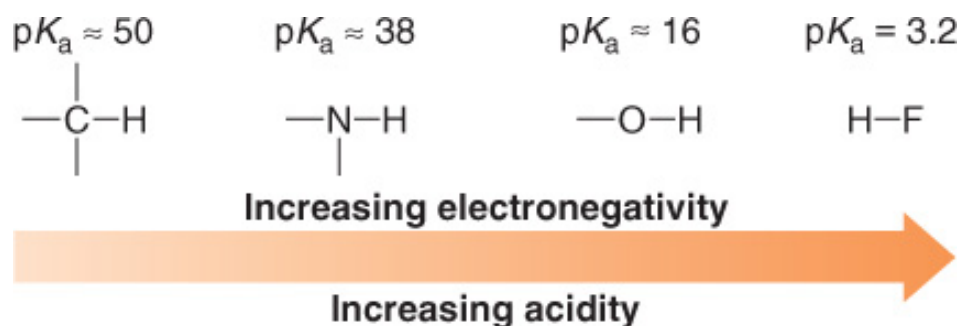
- ❑ Anything that stabilizes a conjugate base  $A:^-$  makes the starting acid  $H-A$  more acidic.
- ❑ Four factors affect the acidity of  $H-A$ . These are:
  - Element effects
  - Inductive effects
  - Resonance effects
  - Hybridization effects
- ❑ No matter which factor is discussed, the same procedure is always followed. To compare the acidity of any two acids:
  - Always draw the conjugate bases.
  - Determine which conjugate base is more stable.
  - The more stable the conjugate base, the more acidic the acid.

# Acids and Bases

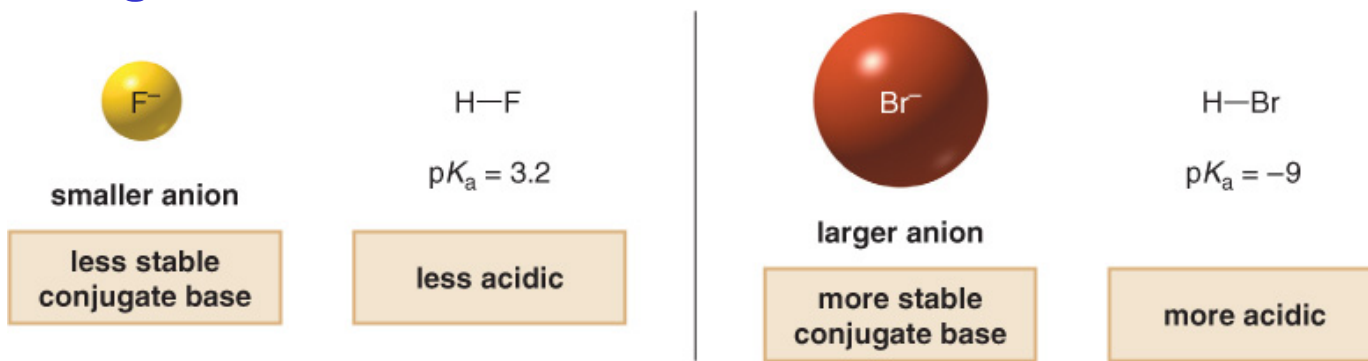
## Factors that Determine Acid Strength

### Element Effects—Trends in the Periodic Table.

Across a row of the periodic table, the acidity of H—A increases as the electronegativity of A increases.



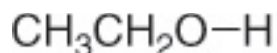
Positive or negative charge is stabilized when it is spread over a larger volume.



# Acids and Bases

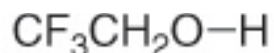
## Factors that Determine Acid Strength—Inductive Effects

- An inductive effect is the pull of electron density through  $\sigma$  bonds caused by electronegativity differences in atoms.
- In the example below, when we compare the acidities of ethanol and 2,2,2-trifluoroethanol, we note that the latter is more acidic than the former.



ethanol

$$\text{p}K_{\text{a}} = 16$$



2,2,2-trifluoroethanol

$$\text{p}K_{\text{a}} = 12.4$$

← stronger acid

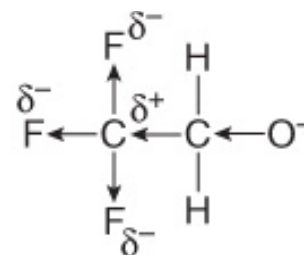
# Acids and Bases

## Factors that Determine Acid Strength—Inductive Effects

- The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.



No additional electronegative atoms stabilize the conjugate base.

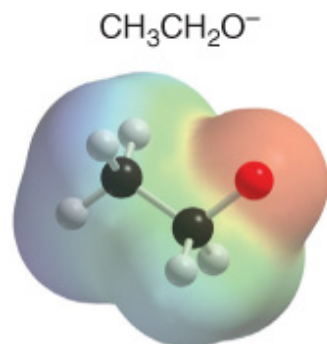


$\text{CF}_3$  withdraws electron density, stabilizing the conjugate base.

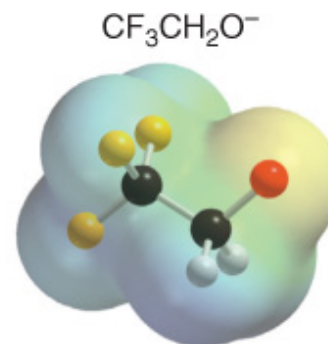
# Acids and Bases

## Factors that Determine Acid Strength—Inductive Effects

- When electron density is pulled away from the negative charge through  $\sigma$  bonds by very electronegative atoms, it is referred to as an **electron withdrawing inductive effect**.
- More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.
- The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- The acidity of H—A increases with the presence of electron withdrawing groups in A.



The dark red of the O atom indicates a region of high electron density.



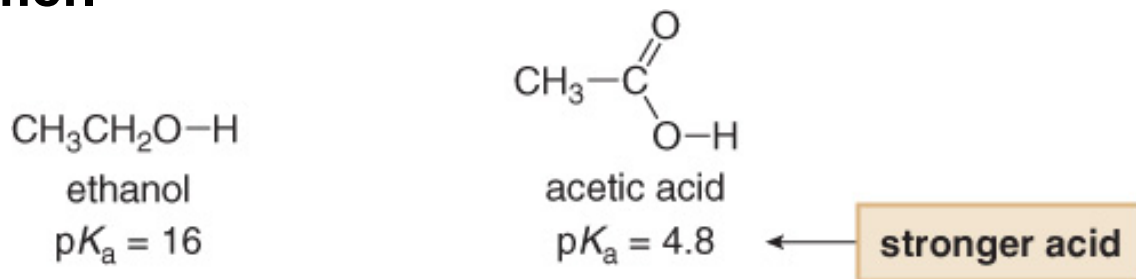
The O atom is yellow, indicating it is less electron rich.



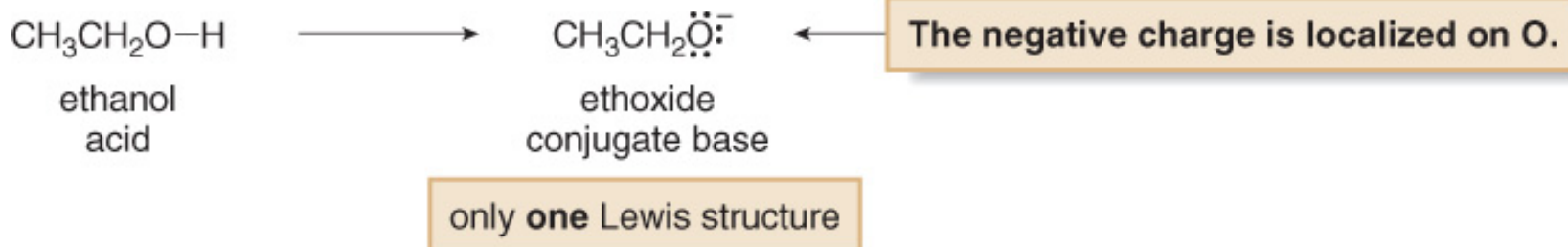
# Acids and Bases

## Factors that Determine Acid Strength—Resonance Effects

- Resonance is a third factor that influences acidity.
- In the example below, when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.



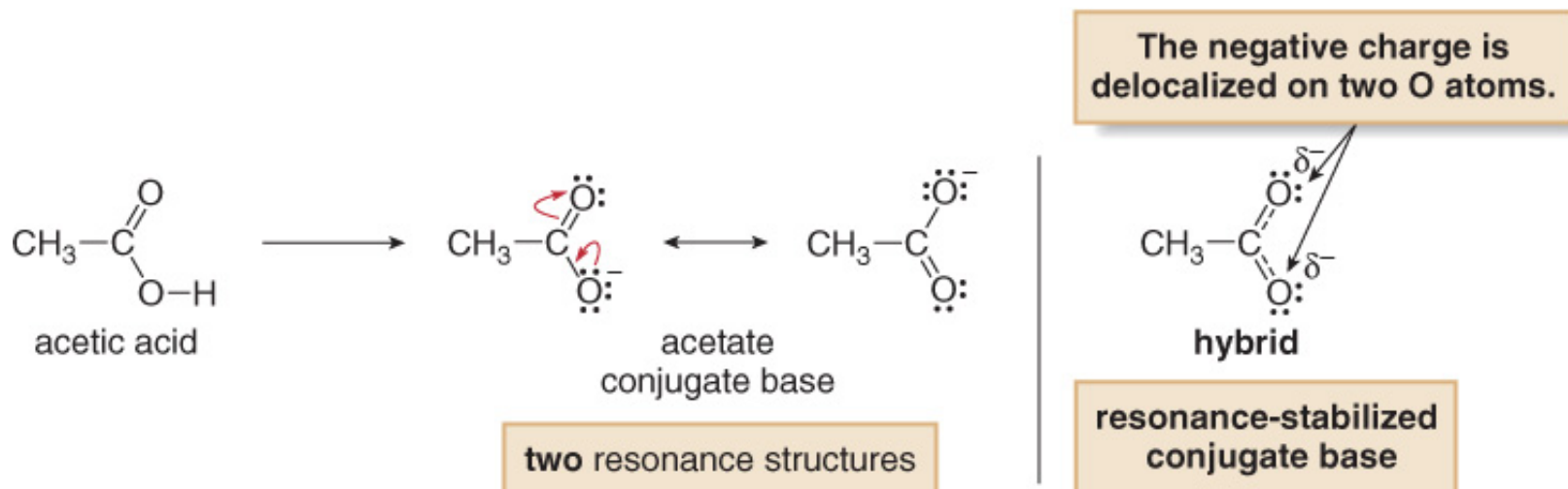
- When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.



# Acids and Bases

## Factors that Determine Acid Strength—Resonance Effects

- Resonance delocalization makes  $\text{CH}_3\text{COO}^-$  more stable than  $\text{CH}_3\text{CH}_2\text{O}^-$ , so  $\text{CH}_3\text{COOH}$  is a stronger acid than  $\text{CH}_3\text{CH}_2\text{OH}$ .



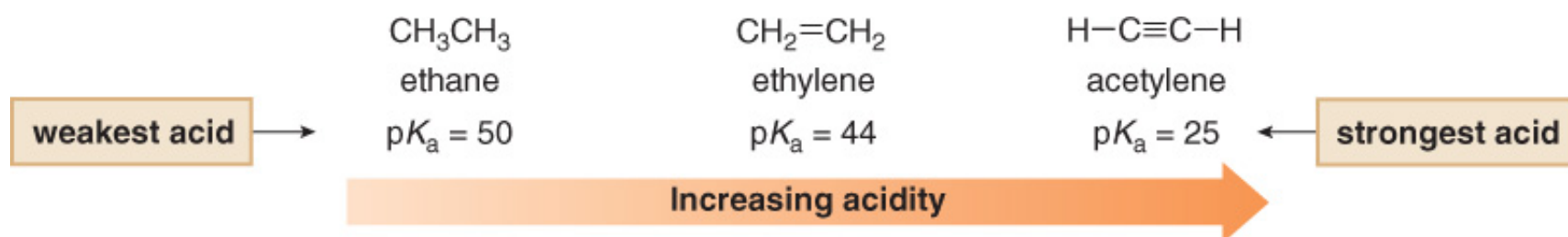
- The acidity of  $\text{H—A}$  increases when the conjugate base  $\text{A}^-$  is resonance stabilized.

# Acids and Bases

## Factors that Determine Acid Strength—Hybridization Effects

- The final factor affecting the acidity of H—A is the hybridization of A.

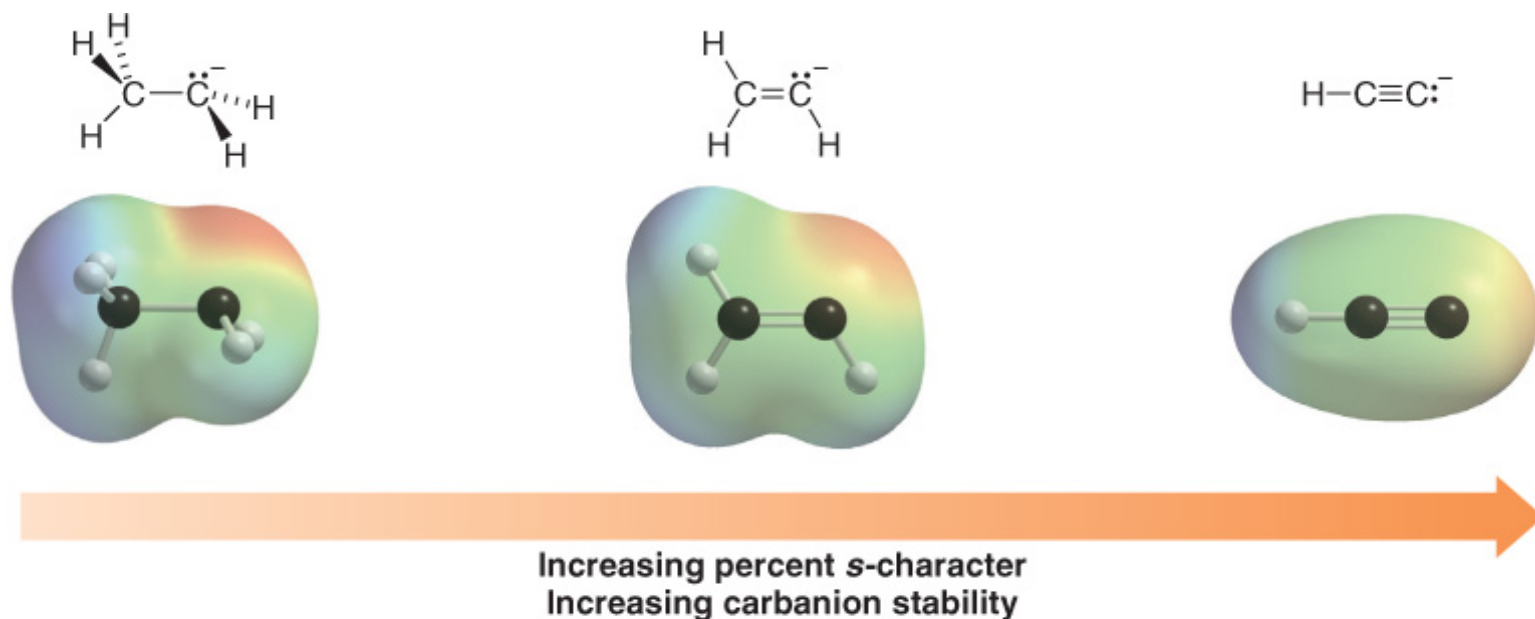
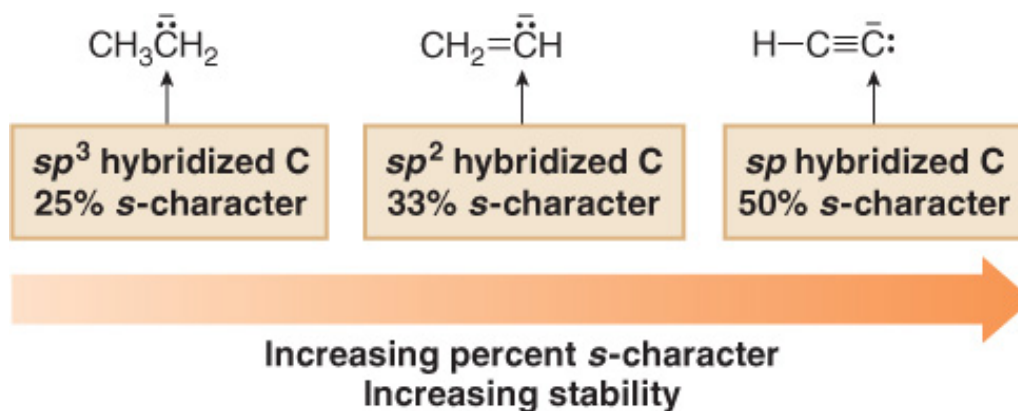
Let us consider the relative acidities of three different compounds containing C—H bonds.



- The higher the percent of s-character of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.

# Acids and Bases

## Factors that Determine Acid Strength—Hybridization Effects



- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

# Acids and Bases

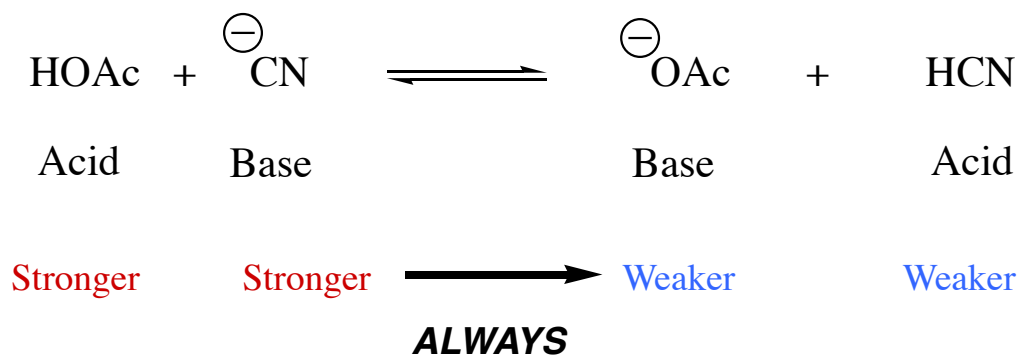
## Summary of Factors that Determine Acid Strength—Hybridization Effects

Factor	Example
1. <b>Element effect:</b> The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.	<p style="text-align: center;">Increasing acidity →</p> $\begin{array}{cccc} \begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array} & \begin{array}{c} -\text{N}-\text{H} \\   \end{array} & \begin{array}{c} -\text{O}-\text{H} \\ -\text{S}-\text{H} \end{array} & \begin{array}{c} \text{H}-\text{F} \\ \text{H}-\text{Cl} \\ \text{H}-\text{Br} \\ \text{H}-\text{I} \end{array} \end{array}$ <p style="text-align: right; vertical-align: middle;">↓ Increasing acidity</p>
2. <b>Inductive effects:</b> The acidity of H–A increases with the presence of electron-withdrawing groups in A.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$ $\text{CF}_3\text{CH}_2\text{O}-\text{H}$ <span style="margin-left: 150px;"><b>more acidic</b></span>
3. <b>Resonance effects:</b> The acidity of H–A increases when the conjugate base $\text{A}^-$ is resonance stabilized.	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$ $\text{CH}_3\text{COO}-\text{H}$ <span style="margin-left: 150px;"><b>more acidic</b></span>
4. <b>Hybridization effects:</b> The acidity of H–A increases as the percent s-character of $\text{A}^-$ increases.	$\text{CH}_3\text{CH}_3$ $\text{CH}_2=\text{CH}_2$ $\text{H}-\text{C}\equiv\text{C}-\text{H}$ <p style="text-align: center;">→ Increasing acidity</p>

# Acids and Bases

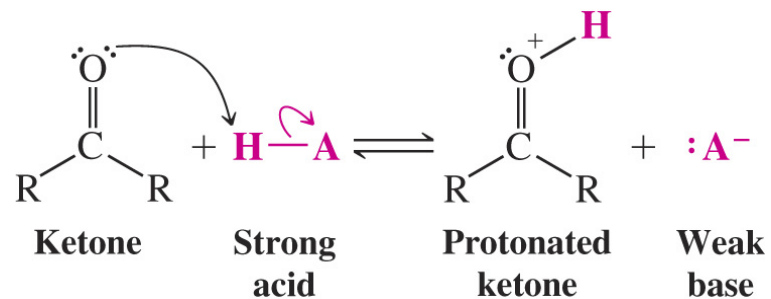
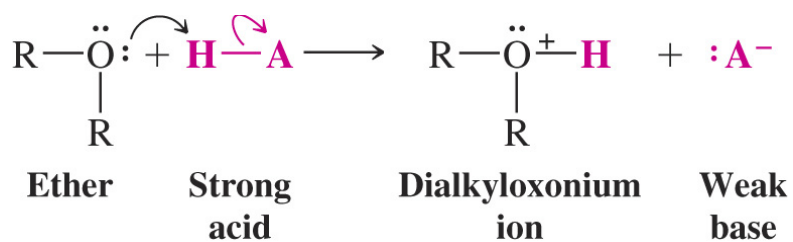
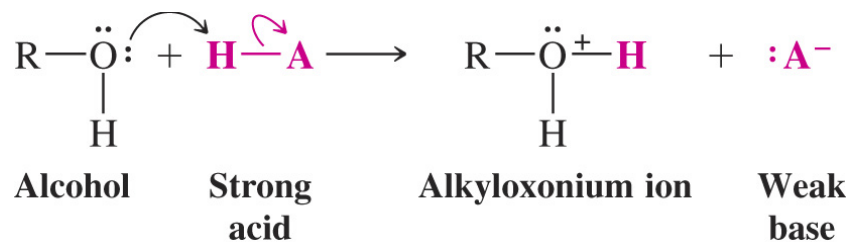
Acid/base equilibria always favor the side of the weaker acid and the weaker base

For Example:



## ◆ What Makes a Compound Behave as a Base?

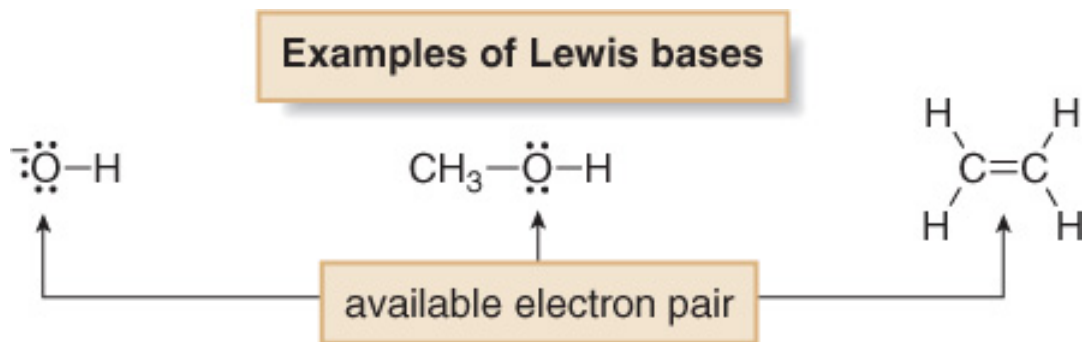
➔ Any organic compound containing an atom with a lone pair (O,N) can act as a base



# Acids and Bases

## Lewis Acids and Bases

- The Lewis definition of acids and bases is more general than the Brønsted-Lowry definition.
- A Lewis acid is an electron pair acceptor.
- A Lewis base is an electron pair donor.
- Lewis bases are structurally the same as Brønsted-Lowry bases. Both have an available electron pair—a lone pair or an electron pair in a  $\pi$  bond.
- A Brønsted -Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.

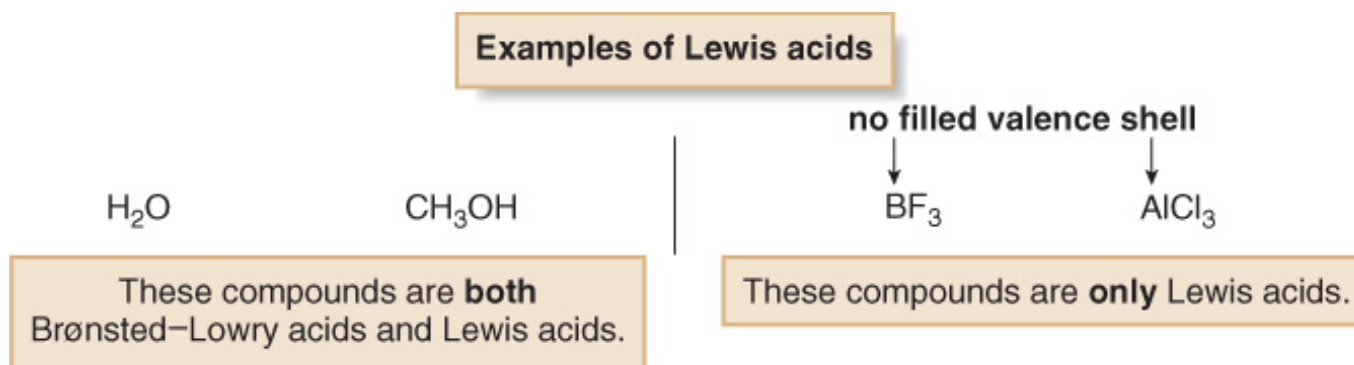




# Acids and Bases

## Lewis Acids and Bases

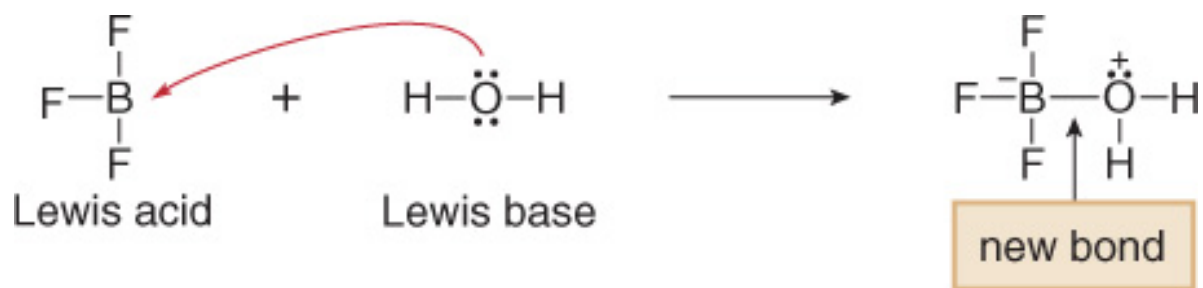
- A Lewis acid must be able to accept an electron pair, but there are many ways for this to occur.
- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.
  - Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.
- Common examples of Lewis acids (which are not Brønsted-Lowry acids) include  $\text{BF}_3$  and  $\text{AlCl}_3$ . These compounds contain elements in group 3A of the periodic table that can accept an electron pair because they do not have filled valence shells of electrons.



# Acids and Bases

## Lewis Acids and Bases

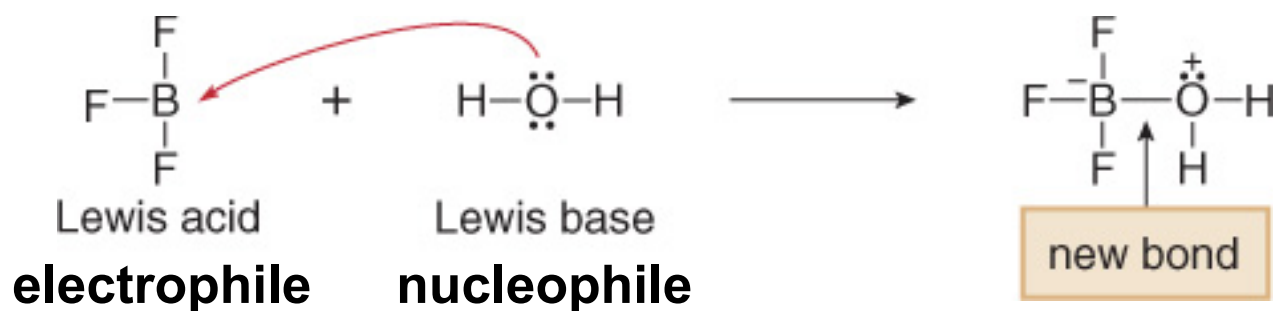
- Any reaction in which one species donates an electron pair to another species is a Lewis acid-base reaction.
- In a Lewis acid-base reaction, a Lewis base donates an electron pair to a Lewis acid.
- Lewis acid-base reactions illustrate a general pattern in organic chemistry. Electron-rich species react with electron-poor species.
- In the simplest Lewis acid-base reaction one bond is formed and no bonds are broken. This is illustrated in the reaction of  $\text{BF}_3$  with  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  donates an electron pair to  $\text{BF}_3$  to form a new bond.



# Acids and Bases

## Lewis Acids and Bases

- A Lewis acid is also called an **electrophile**.
- When a Lewis base reacts with an electrophile (other than a proton), the Lewis base is also called a **nucleophile**. In this example,  $\text{BF}_3$  is the electrophile and  $\text{H}_2\text{O}$  is the nucleophile.



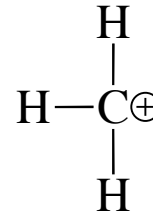
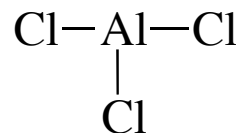
# Nucleophiles and Electrophiles

## The Organic chemistry terms for Lewis acids and bases

**Electrophiles (“electron-loving” reagents): seek electrons to obtain a stable valence shell of electrons**

➔ Are electron-deficient themselves

Some Examples are:



### NOTE:

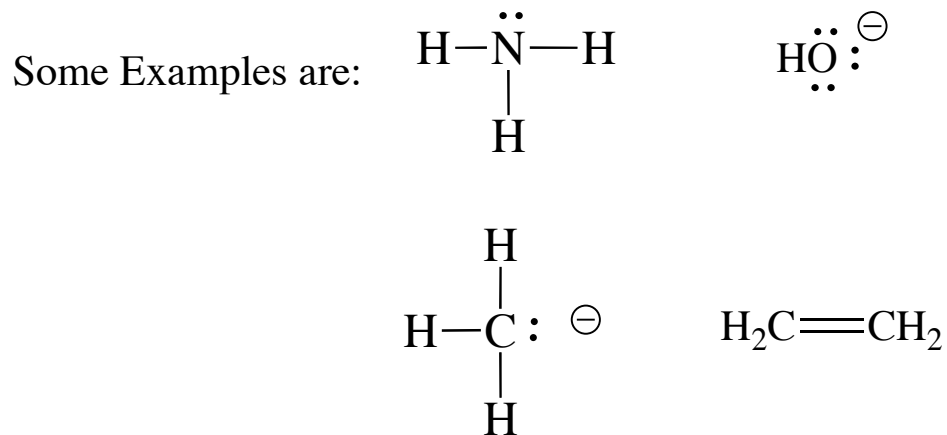
An electrophile can either be neutral or have a positive charge.

The important thing is that they have "room" for a pair of electrons.

# Nucleophiles and Electrophiles

**Nucleophiles (“nucleus-loving” reagents): seek a proton or some other positively charged center**

➡ Are electron-rich themselves



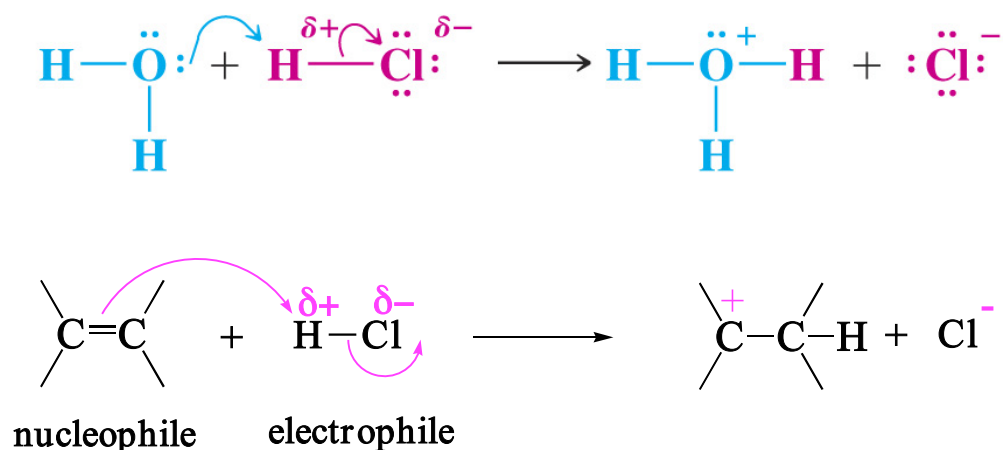
## NOTE:

A nucleophile can either be neutral or have a negative charge.

The important thing is that it be able to donate a pair of electrons (either from a lone pair or from a pi-bond)

## Use of Curved Arrows in Illustrating Reactions

- ◆ Curved arrows show the movement of electrons in a reaction
- ◆ An arrow starts at site of higher electron density (a covalent bond or unshared electron pair) and points to site of electron deficiency
- ◆ Examples:



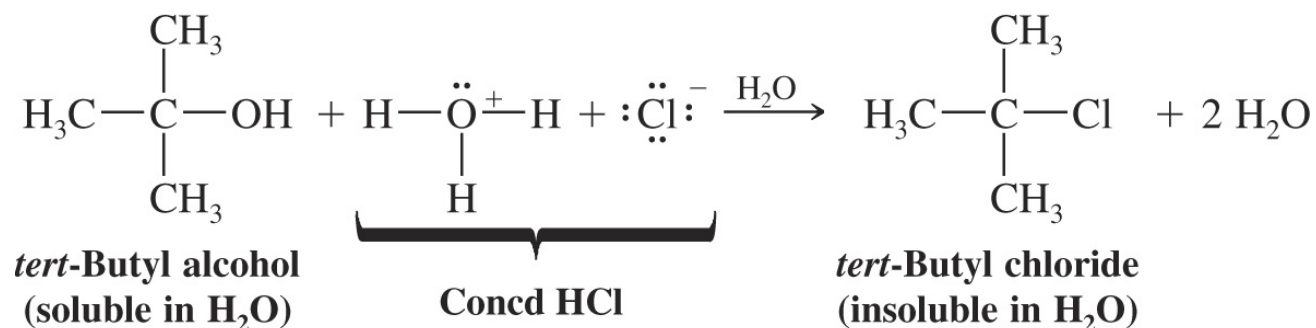
**NOTE:** Electron pairs move from the nucleophile to the electrophile

# A Mechanism for an Organic Reaction

## (The First Example of Many)

### The Substitution Reaction of *tert*-Butyl Alcohol

This is the overall reaction:

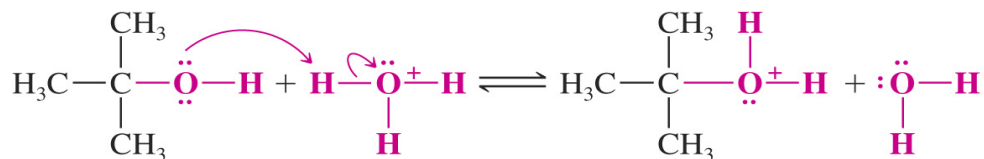


You will be doing this exact reaction in the lab this semester

# The Mechanism Has Three Steps

➡ All steps are actually acid-base reactions

Step 1:

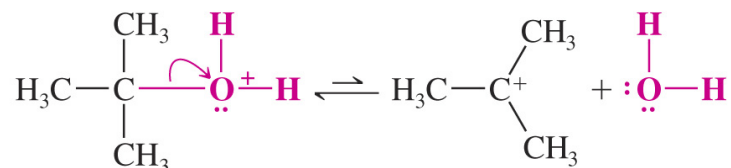


*tert*-Butyloxonium ion

*tert*-Butyl alcohol acts as a base and accepts a proton from the hydronium ion. (Chloride anions are spectators in this step of the reaction.)

The products are a protonated alcohol and water (the conjugate acid and base).

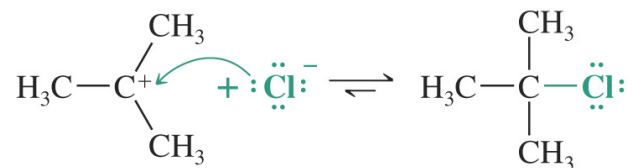
Step 2:



Carbocation

The bond between the carbon and oxygen of the *tert*-butyloxonium ion breaks heterolytically, leading to the formation of a carbocation and a molecule of water.

Step 3:



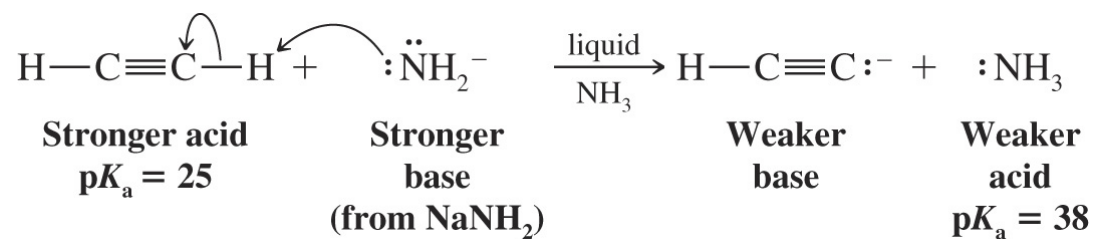
*tert*-Butyl chloride

The carbocation, acting as a Lewis acid, accepts an electron pair from a chloride ion to become the product.



## Acids and Bases in Nonaqueous Solutions

Sodium amide ( $\text{NaNH}_2$ ) can be used as a strong base in solvents such as liquid  $\text{NH}_3$



We need to use non-protic solvents when we use strong bases

- ◆ Alkyl lithium reagents in hexane are extremely strong bases

