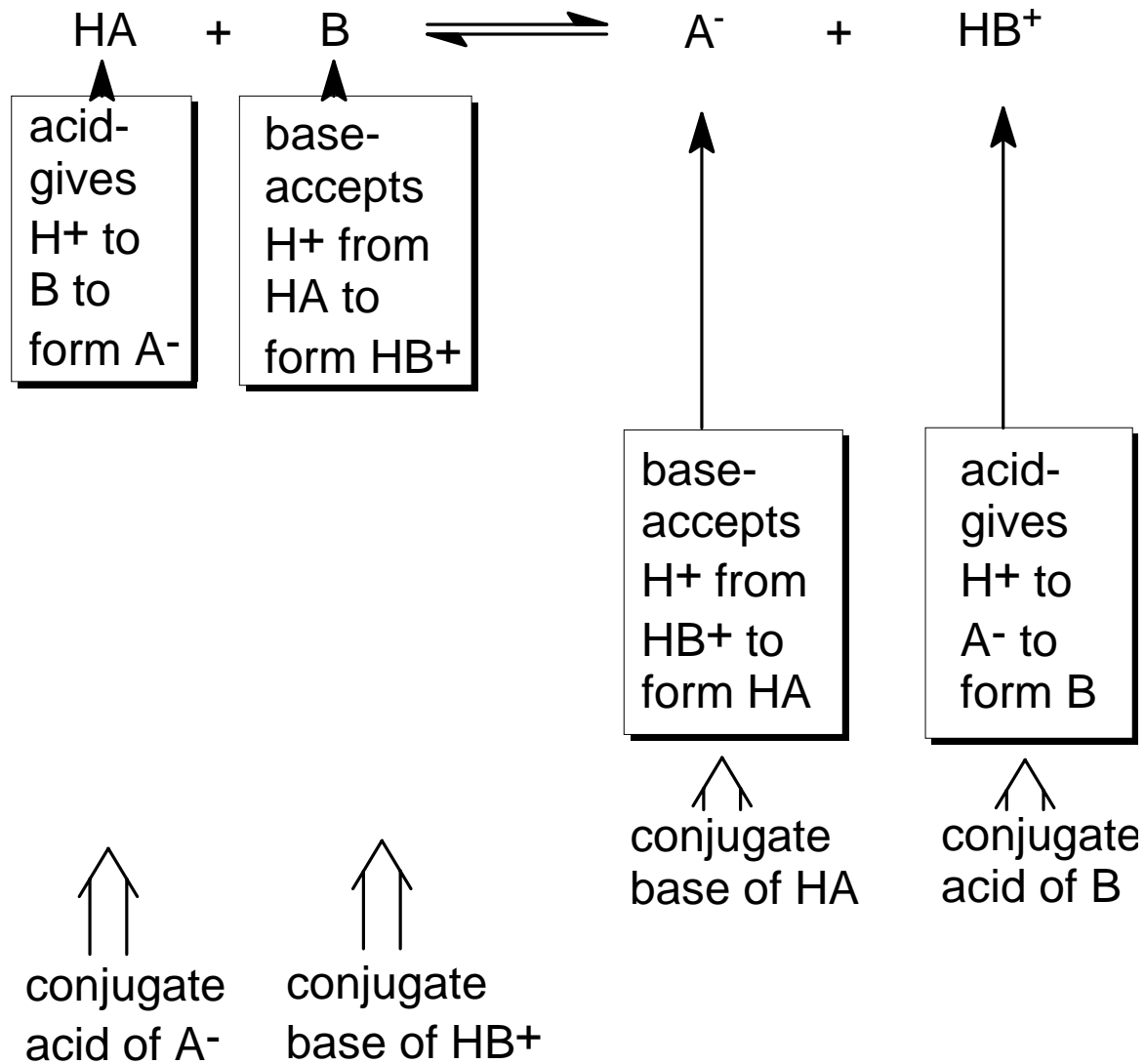


Acids & Bases

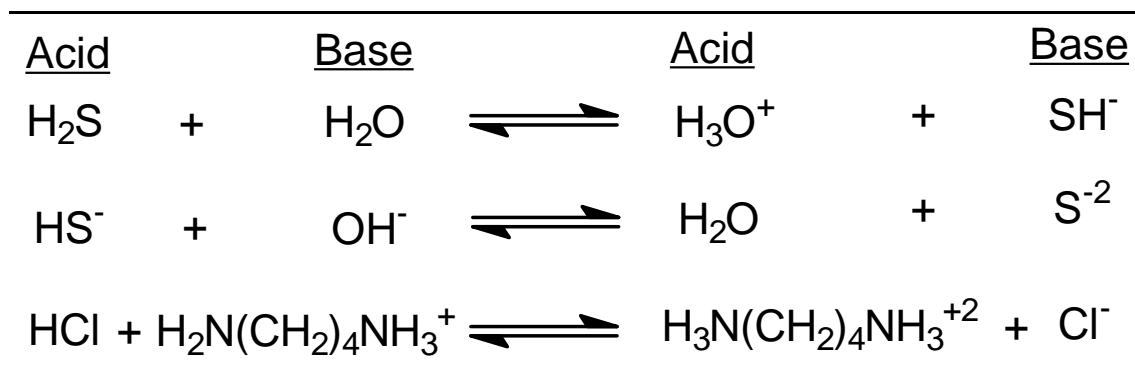
Bronsted/Lowry:

acid: substance which gives up a proton

base: substance which accepts a proton



Acids and bases may be charged or uncharged ---

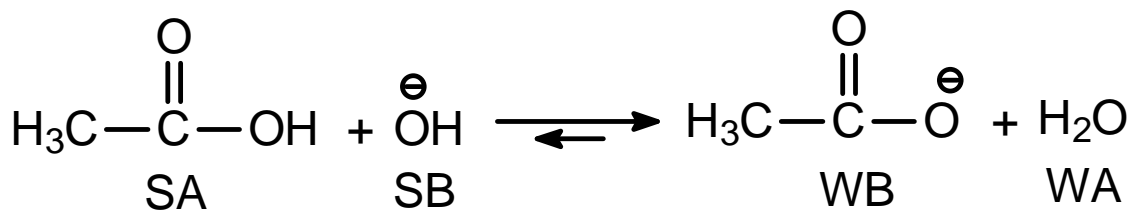
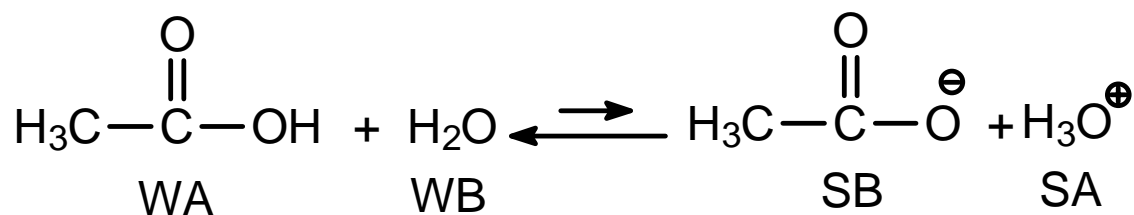
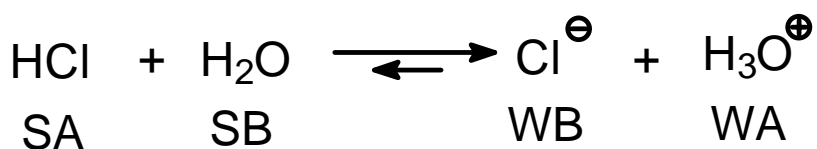


Typically, acids are neutral or positive, bases are neutral or negative.

Acid and Base Strength:

At equilibrium the weaker acid and base are favored.

SA=stronger acid SB=stronger base
 WA=weaker acid WB=weaker base



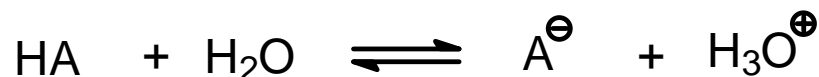
Therefore,

acid strength: $\text{HCl} > \text{H}_3\text{O}^+ > \text{H}_3\text{CCOOH} > \text{H}_2\text{O}$

base strength: $\text{OH}^- > \text{H}_3\text{CCOO}^- > \text{H}_2\text{O} > \text{Cl}^-$

Note that the stronger an acid is, the weaker its conjugate base is. Does this make sense to you? [It should!]

Quantative measure of Bronsted-Lowry acidity –



$$K_{\text{eq}} = \frac{[\text{A}^{\ominus}] [\text{H}_3\text{O}^{\oplus}]}{[\text{HA}] [\text{H}_2\text{O}]}$$

but in dilute solutions

$[\text{H}_2\text{O}] \sim 55.5\text{M}$

i.e. there are ~55.5 moles of water in a liter of dilute aqueous solution, so...

$$K_{\text{eq}} = \frac{[\text{A}^{\ominus}] [\text{H}_3\text{O}^{\oplus}]}{[\text{HA}] (55.5)}$$

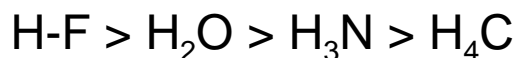
$$\text{or } K_{\text{eq}} (55.5) = \frac{[\text{A}^{\ominus}] [\text{H}_3\text{O}^{\oplus}]}{[\text{HA}]} = K_{\text{a}}$$

$$\text{p}K_{\text{a}} = -\log K_{\text{a}}$$

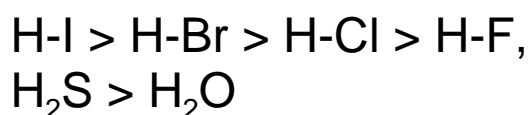
The smaller (or the more negative) the $\text{p}K_{\text{a}}$, the larger the K_{a} , and the stronger the acid.

Prediction of Bronsted-Lowry Acid Strength of H-A ---

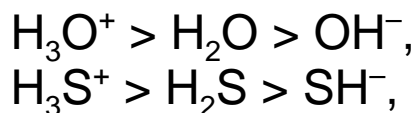
☞ For A within a given row on periodic chart, acidity increases with electronegativity:



☞ For A within a given family on periodic chart, acidity increases with size:



☞ For a given A, acidity increases with + charge, decreases with - charge:



Lewis definitions of acid and base –

Acid: an electron pair acceptor.

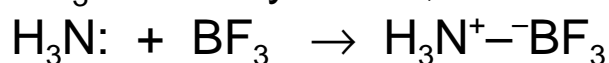
Base: an electron pair donor.

Lowry-Bronsted acids and bases are a subset of Lewis acids and bases; every L-B acid is a Lewis acid, every L-B base is a Lewis base.

H_3O^+ – acid by L-B and Lewis

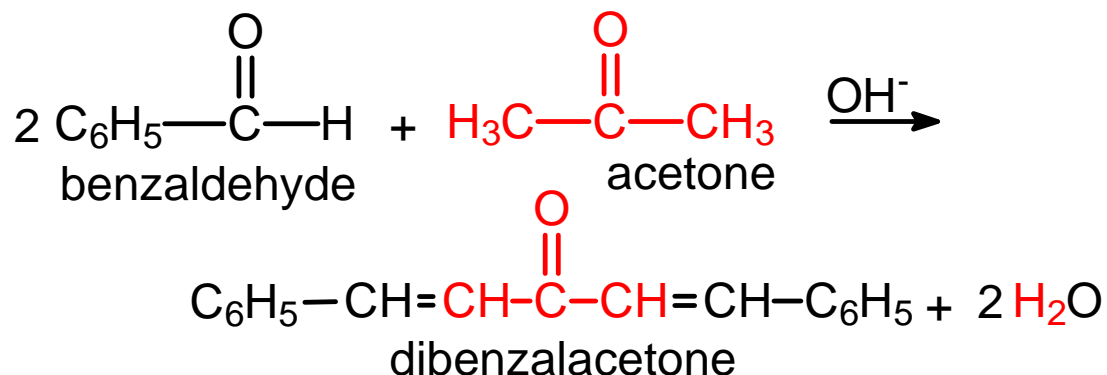
$:\text{NH}_3$ – base by L-B and Lewis

BF_3 – acid by Lewis, but not by L-B (no proton to donate)



Acid-Base Chemistry in Action: Lab Experiment #3, Synthesis of Dibenzalacetone

Overall reaction:



[Sometimes when we write the equations for reactions in organic chemistry we write the formulas of one or more of the reactants above or below the reaction arrow. In this case the hydroxide ion (from sodium or potassium hydroxide) is a catalyst in the reaction and, so, is not consumed.]

Color is used here to show how fragments within the dibenzalacetone molecule derive from the two components that react.]

The Reaction Mechanism

The equation above tells us what happens, overall, in the reaction. The equation tells us that two molecules of benzaldehyde react with one molecule of acetone, in the presence of hydroxide ion, to give one molecule of dibenzalacetone and two molecules of water; it does not tell us how this happens. The *reaction mechanism* tells us how the reactants are converted into products. To use

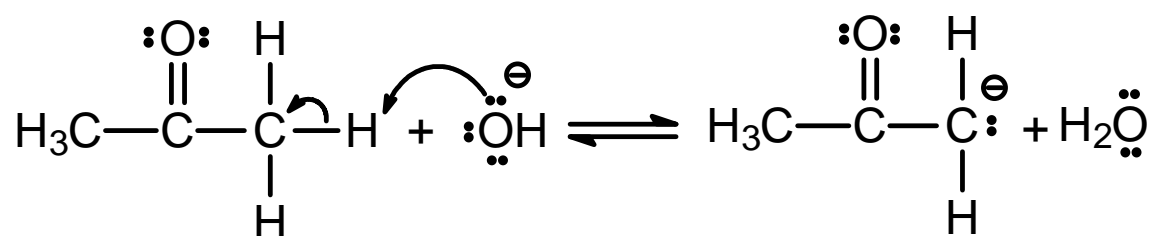
a sports analogy, knowing the overall reaction is like knowing that the Dodgers played the Mets last night and the Mets won, 3 to 2. Knowing the details of the reaction mechanism is like knowing the play-by-play of the game.

The reaction mechanism for this reaction involves a lot of acid-base chemistry as do many, if not most, reaction mechanisms.

The Mechanism –

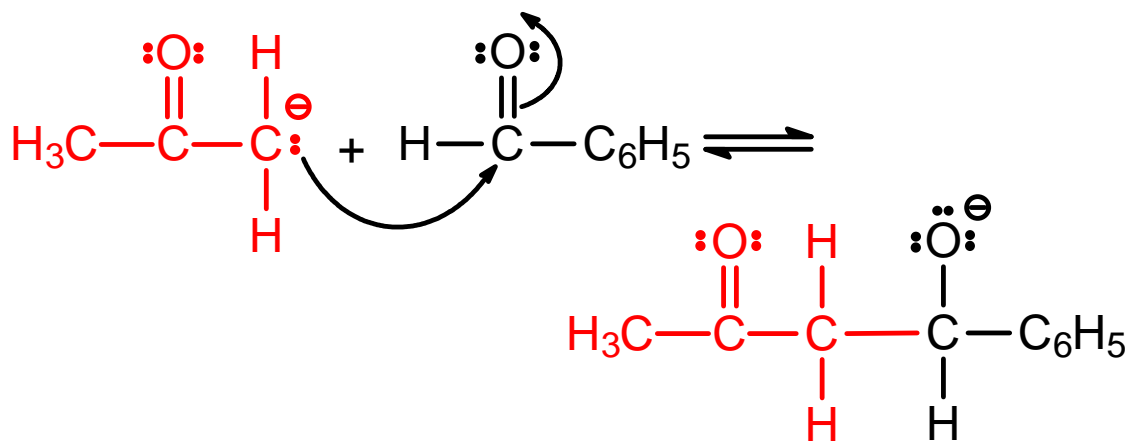
In the first step, acetone functions as an L-B acid and hydroxide as a base. Note that the equilibrium for this step is not favorable: water ($pK_a = 15.7$) is a stronger acid than acetone ($pK_a \sim 20$). Nevertheless, the overall reaction is successful because the equilibrium for the final step in the mechanism is favorable.

Note the use of curved arrows in the mechanism. The curved arrows are “bookkeeping” devices – they track the movements of **electrons**.

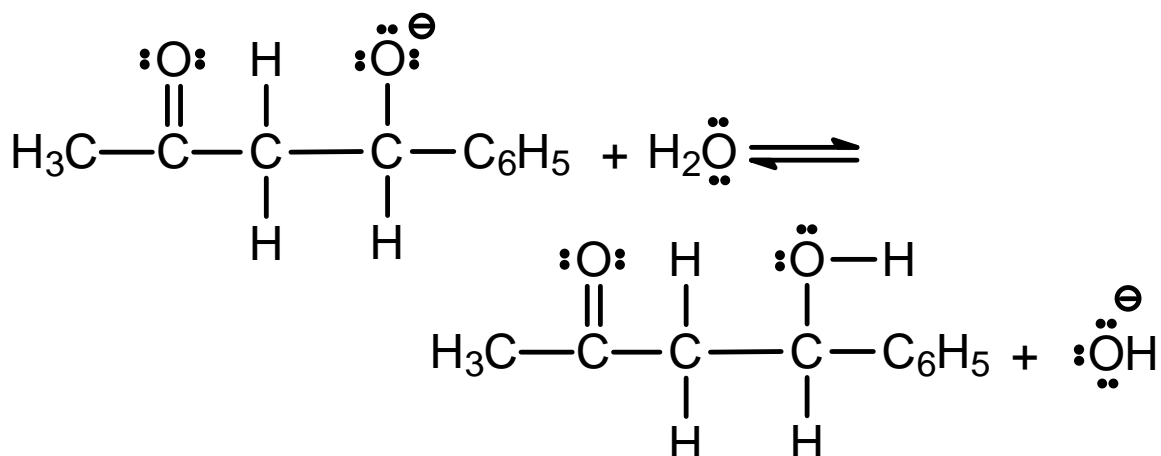


There is another resonance form for this anion. Can you draw it?

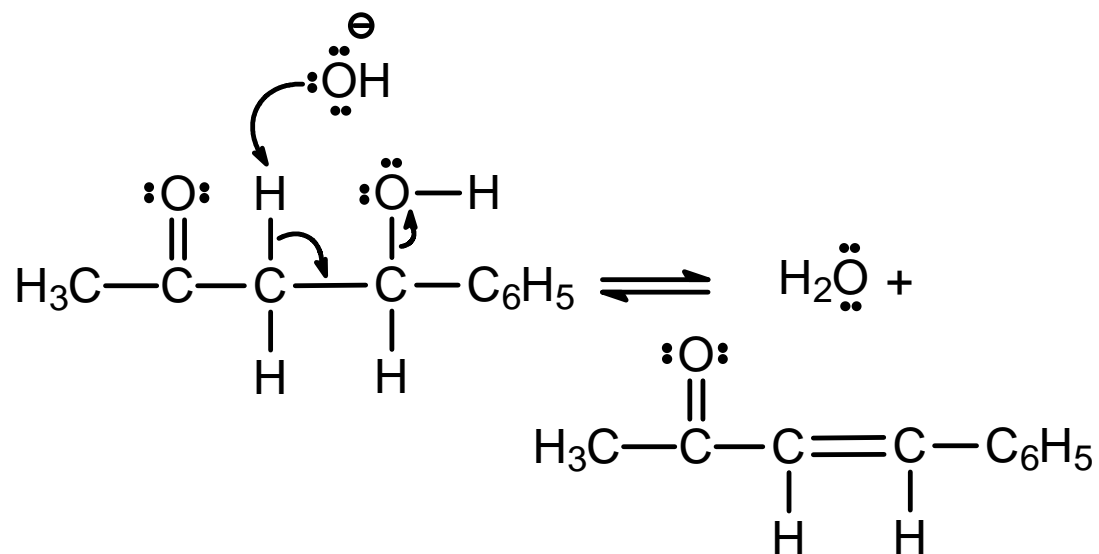
The next step involves the anion formed in the first step acting as a Lewis base in its attack on the partially positively charged C=O carbon of benzaldehyde to form a covalent bond that joins these two moieties together.



The next step is simply a Lowry-Bronsted acid-base reaction with water functioning as the acid.



The next step involves what is known as an *elimination reaction*. In an elimination reaction a couple of moieties (atoms or groups of atoms) are removed from a molecule generating the products. In this case the elimination reaction involves a L-B acid-base reaction with hydroxide as the base.



At this point we are halfway to the final product. Looking back, we started with acetone and converted the $-\text{CH}_3$ group on the right side into a $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ group. Using the same series of steps, it is now possible to convert the remaining $-\text{CH}_3$ into a $\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ group to produce the final product.

Do it!