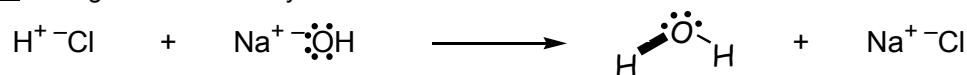


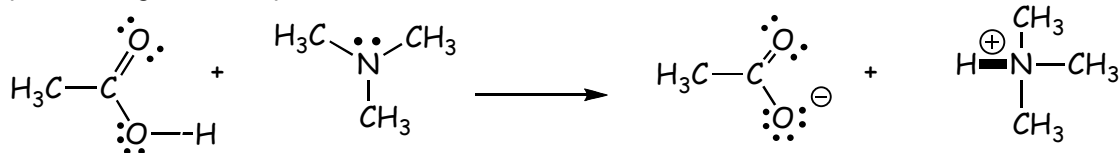
5 Brønsted Acid/Bases

- A Brønsted acid **DONATES** a proton
- A Brønsted base **ACCEPTS** a proton

Example from general chemistry



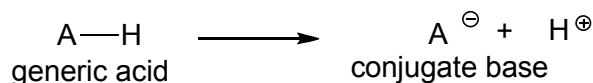
Example from organic example



- hydrogen moves from the acid to the base, but leaves its electron "behind" (is given to the oxygen). A hydrogen with no electron is a proton, therefore a proton is transferred from the acid to the base.

6 Factors Controlling Brønsted Acidity

- Focus attention on the electrons that are involved, BEFORE and AFTER bond heterolysis
- Think of acidity as a reaction. The stronger acid "wants" to go from left to right more than a weaker acid



- note, **HETEROLYTIC BOND CLEAVAGE** (this is NOT given the bond dissociation energy, which is homolytic)
- in general, an acid will be stronger if the electrons in the bond are high in energy, i.e. if the bond is weak
- in general, an acid will be stronger if the energy of the now non-bonding electrons on the conjugate base (usually on an ANION) are lower in energy, e.g. if A is an electronegative atom
- PROBLEM, these two effects sometimes OPPOSE, how to know which one "wins"

SOME RULES HELP! Acidity increases.....

Rule #1. With increasing resonance stabilization of the non-bonding electrons in the conjugate base anion (BUT, "quality" of resonance contributors over quantity!)

Rule #2. Left to right across the periodic table, since increasing electronegativity of the atom

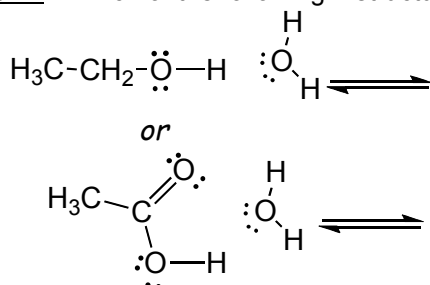
carrying the negative charge in the conjugate base anion "wins" over increasing bond strength

Rule #3. With increasing atomic size going down a group in the periodic table. Here, decreasing

bond strength in the A-H "wins" over decreasing electronegativity of the conjugate base anion

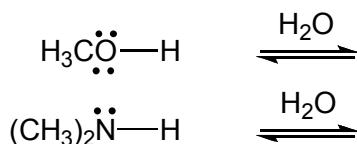
Rule #4. With increasing s character of the hybridization of the atomic orbital in the conjugate base atom that holds the non-bonding electrons, since increased stability of the electrons in the smaller A.O. in the anion "wins" over the increasing bond strength

Example of Rule #1: Which of the following 2 structures is the stronger acid (has the lower pKa)?



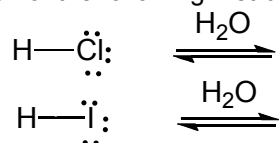
- in each case, break an O–H bond and make an O–H bond
- the energies of the electrons in the two O–H bonds in the acids are basically the same
- the energies of the electrons in the conjugate base anions are different, resonance in the second anion lowers the energies, making formation of the anion more favorable in this case

Example of Rule #2: Which of the following 2 structures is the stronger acid (has the lower pKa)?



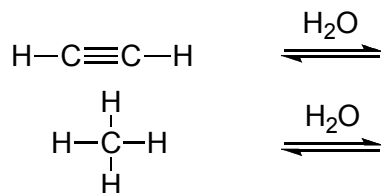
- here, the electrons in both the bonds in the acids and also in the anion conjugate bases are different
- the O–H bond is slightly stronger than the N–H bond, which would suggest that the top structure would be a weaker acid, BUT, the non-bonding electrons in the anions are MUCH more stabilized on O compared to N due to electronegativity
- going across the periodic table increases acidity, more electronegative elements stabilizes anions

Example of Rule #3: Which of the following 2 structures is the stronger acid (has the lower pKa)?



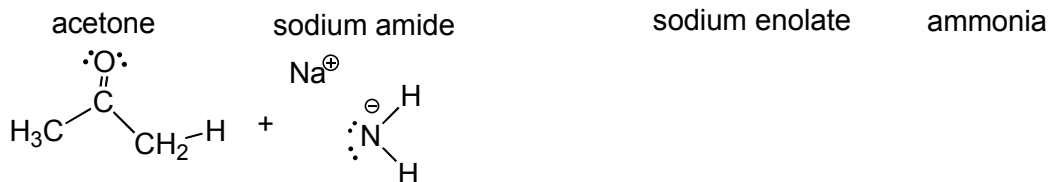
- in each case, break a X–H bond, make an O–H bond and a halide anion
- the electrons on chloride are lower in energy (Cl more electronegative), BUT, iodine is much larger than chlorine, orbital overlap with H poorer, MUCH weaker bond, electrons "begin" higher in energy in the weaker iodine–H bond
- going down the periodic table increases acidity, larger elements have weaker bonds

Example of Rule #4: Which of the following 2 structures is the stronger acid (has the lower pKa)?



- stronger C-H bond in alkyne, weaker in alkane (sp versus sp³)
- BUT, MUCH more stable anion from alkyne (electrons in sp A.O.) compared to alkane (electrons in sp³ A.O.), "wins" over bond strength (similar to going across the periodic table, above)

7 Predicting Bronsted Acid/Base Reactions



- proton transfer from the stronger acid is faster, thus equilibrium lies to the right
- "deprotonation" of acetone (the stronger acid) using sodium amide is exothermic and faster
- "deprotonation of ammonia (the weaker acid) using sodium enolate is endothermic and slower
- the reaction "goes" from left to right

Example: will water protonate methyl lithium?

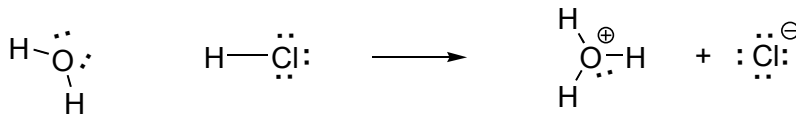


- the stronger acid reacts with the stronger base faster
- the weaker acid reacts with the weaker base slower
- Equilibrium lies to the RIGHT, the reaction "goes" to the right
- so, the answer to the question above is YES, water will protonate CH₃Li (explosively!!!!!!!!!!)

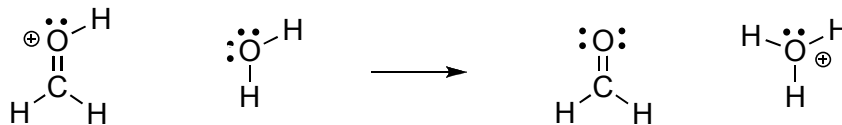
8 Curved Arrow-Pushing

- curved arrow pushing is an important part of the organic chemistry GRAPHICAL LANGUAGE
- curved arrows represent the movement of electrons (only)
- the arrow "starts" where the electrons come from, "ends" where they go to

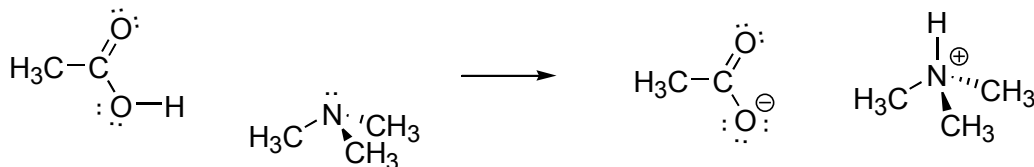
Examples:



- draw a dotted line to show the new bond if it helps you



- the arrow shows that how the electrons are used to make the bond, NOT how the atoms "move"

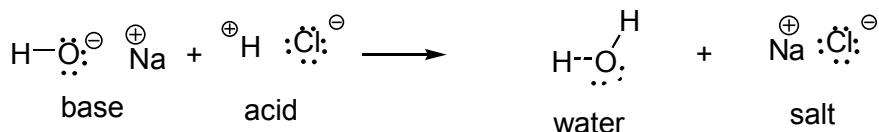


- The arrow starts at the electrons, and ends "in" the new bond, NOT at the H, since the electrons are not given to the H.

9 Lewis Acid/Base Reactions

EXTREMELY IMPORTANT SUBJECT

Question?: Why **does** acid + base give salt + water?



Answer: Because this gets TWO electrons into a bond, thus **lowering their energy**

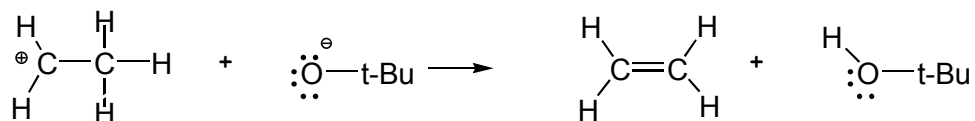
G. N. Lewis proposed that the most significant thing about the above reaction is NOT that a proton was transferred from the acid to the base, but:

- the BASE DONATED two electrons to make the new bond
- the ACID ACCEPTED two electrons to make the new bond

This is Lewis's (broader) definition of an acid and a base

Examples:

- this reaction "goes" from left to right because it gets 2 electrons into a bond, lowering their energy, the reaction is exothermic



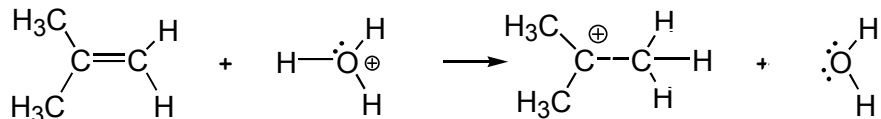
- this reaction "goes" because although 1 bond is broken, 2 are formed
- the acid transfers a proton to the base, this is thus BOTH a Lewis and a Brønsted acid/base reaction

IMPORTANT

- ALL Brønsted acids/bases are also Lewis acids/bases
- NOT all Lewis acids/bases are Brønsted acids/bases

not all acid/base reactions have to be exothermic:

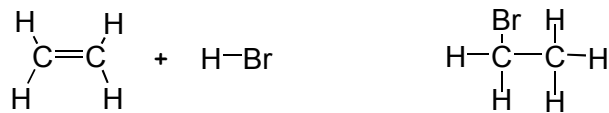
- this reaction is also a Brønsted acid/base reaction



- the products of this reaction are higher in energy than the reactants (the reaction is endothermic)
- nevertheless, we will see later that reactions such as these are **important**

• Lewis acid/base reactions can be "complete" single step reactions in their own right as in the examples above, or they can be "parts" of more complex reactions which have multiple steps (see later).

10 How and Why Chemical Reactions "Go"?



- In principle, ALL chemical reactions are reversible (not just acid/base)
- Equilibria defined by equilibrium constant, K_{eq}

- thus, this reaction "GOES" from left to right, not the other way round, because the GIBBS FREE ENERGY of products **lower** than reactants - thus exothermic
- this reaction (left to right) is **exothermic** by ~ 11 kcal/mol
- the reaction right to left would be **endothermic** by ~ 11 kcal/mol

in general, reaction "goes" if $> 99.9\%$ on one side of equilibrium
i.e. $K_{\text{eq}} > 1000$, i.e. $\Delta G_{\text{rxn}} \sim -4$ kcal/mol or more negative

What determines reaction (Gibbs) free energy? **enthalpy and entropy**

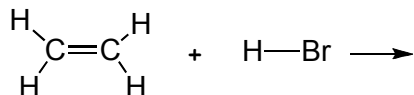
- **enthalpy** term usually dominates
- enthalpy term determined mainly by **energy of electrons in bonds** (sometimes solvation)
- when enthalpy term is small, sometimes **entropy** determines

11 Reaction Mechanisms

The Mechanism:

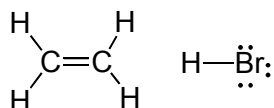
- describes how a reaction occurs
- describes which intermediates are involved
- which bonds are made/broken and in what order
- is the key to minimizing memorization in organic chemistry!

the reaction



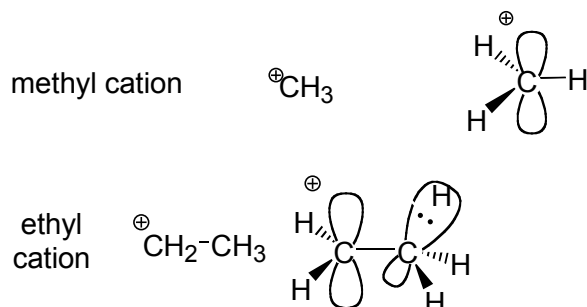
- This reaction is EXOTHERMIC, 1 sigma bond and 1 pi-bond are broken, but 2 sigma-bonds are made

the mechanism

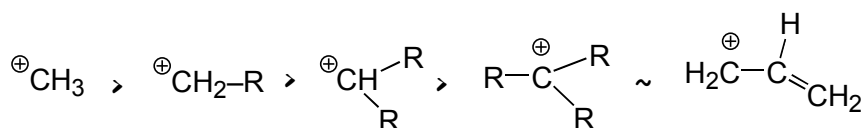


- **this** mechanism consists of two consecutive Lewis acid/base reactions
- the first step forms intermediates from the reactants, the second the final product
- we will use the abbreviations LA and LB to represent Lewis Acid and Lewis Base

More On Carbocation Intermediates (more correctly, carbenium ions)

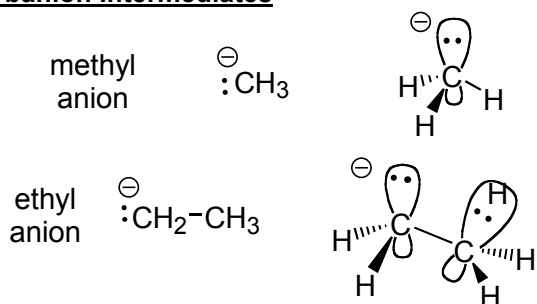


- hyperconjugation "donates" electrons from the methyl group to the positively charge carbon, which delocalizes electrons, they "see" more nuclei, lowers electron energy, also "spreads out" the positive charge, thus the ethyl cation is more stable (less reactive) than the methyl cation.

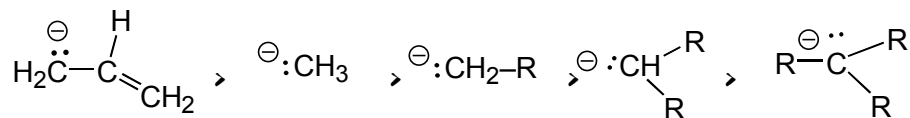


- increasing stability from left to right as the cation is increasingly stabilized by hyperconjugation, and ultimately, true resonance

Carbanion Intermediates



- this time hyperconjugation INCREASES the energy of the non-bonding electrons on the negatively charged carbon, actually results in an ANTI-BONDING interaction



- decreasing stability from left to right as the radical is LESS DESTABILIZED by hyperconjugation, however true resonance in the ally anion still "wins", since it delocalizes the electrons without an ANTI-BONDING interaction

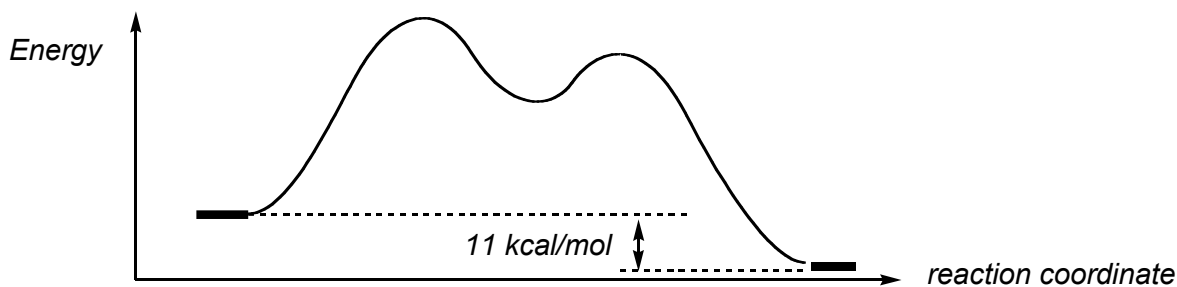
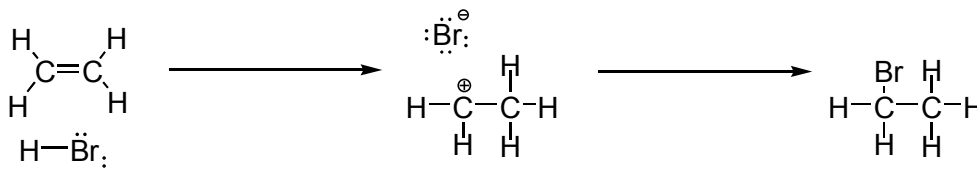
12 Kinetics and Energy Diagrams

- The thermodynamic description of a reaction indicates whether a reaction is possible, but says nothing about how FAST it might occur

Critical connection between kinetics and thermodynamics

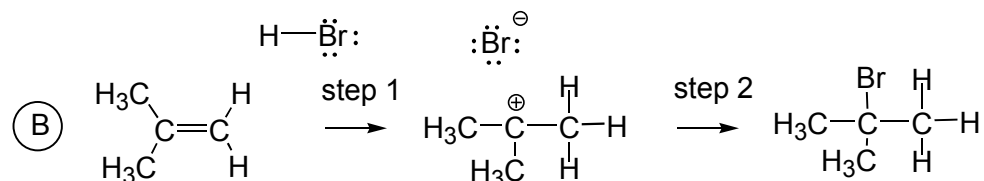
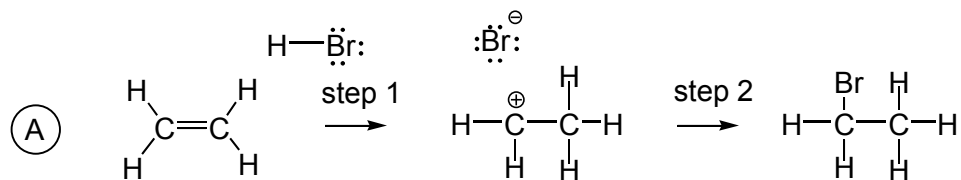
$$\text{rate} = k = A \exp(-E_a/RT)$$

- thus, a **smaller E_a** results in a **larger k** , i.e. a **faster rate**
- a **larger E_a** results in a **smaller k** , i.e. a **slower rate**



- Each step (1 and 2) has its own energy barrier, E_a
- $E_a(\text{step 1}) > E_a(\text{step 2})$
- step 1 is thus slower than step 2
- step 1 is the **RATE DETERMINING STEP**, i.e. the **slowest step**

Example, which of the following two reactions A or B is faster??



- the rate determining step in A involves formation of a higher energy, less stable primary cation
- the rate determining step in B involves formation of a lower energy, more stable tertiary cation
- the rate determining step in B is faster than that in A, thus reaction B is overall faster than reaction A

The Hammond postulate:

all other things being equal (i.e. for similar or related reactions.....)

- **More endothermic** reactions have **later, higher energy transition states** (\ddagger)
- **More exothermic** reactions have **earlier, lower energy transition states** (\ddagger)



- The rate determining step, step 1, for reaction (A) is **more endothermic** than the same step for reaction (B)
- The more endothermic step has the LARGER E_a and the LATER transition state, $E_{a1}(A) > E_{a1}(B)$
- The more endothermic step also has a LATER transition state
- The first step in reaction A is SLOWER, because the intermediate cation is less stable
- The second step for reaction (A) is **more exothermic** than the second step for reaction (B)

- The more exothermic step has a SMALLER E_a , $E_{a2}(A) < E_{a2}(B)$, and an earlier transition state
- The second step in reaction (A) is faster because the intermediate is less stable

- Reactions that FORM less stable intermediates are SLOWER
- Reactions OF less stable intermediates are fa