How to Think About Reactions

A good way to think about chemical reactions is that they are like crimes. Both crimes and chemical reactions need motive and opportunity to take place.

Motive

For reactions, the motive refers to the thermodynamic driving force. In other words, a reaction can be thought of as having a motive (thermodynamic driving force) if the products are more stable than the reactants. If the reaction does have a motive (thermodynamic driving force), it is said to be thermodynamically favorable and it will occur if given the opportunity. Reactions will have a favorable motive (thermodynamic driving force) if ΔG for the process is negative ($\Delta G = \Delta H - T\Delta S$). The $\Delta G = \Delta H - T\Delta S$ equation can be hard to apply to new situations, but the following rules of thumb can be helpful.

1. Reactions will usually have a motive (thermodynamic driving force) if stronger bonds are made than are broken in going from starting materials to products. This is primarily a ΔH effect.

2. In reactions involving proton transfers, the reaction will generally have a motive (thermodynamic driving force) if the products represent the weaker acid and/or weaker base. Recall that equilibrium favors formation of the weaker acid/weaker base in an acid-base reaction. This is primarily a ΔH effect.

3. Reactions will usually have a motive (thermodynamic driving force) if a greater number of smaller molecules are created from fewer larger molecules, especially if a small gaseous molecule such as CO_2, N_2 or HCl is produced as a product. This is primarily a ΔS effect.

Of course, the above rules of thumb also predict when reactions are not likely to have a favorable motive (thermodynamic driving force) as well. For example, reactions will usually not have a favorable motive (thermodynamic driving force) if weaker bonds are made than are broken in going from starting materials to products. This is primarily a ΔH effect.

Opportunity

Even if reactions have a motive (thermodynamic driving force), they can only occur if given the opportunity for the atoms and electrons to rearrange into the product. This rearrangement of atoms and electrons is what we refer to as the mechanism of the reaction. For a reaction to have an opportunity to react, the reaction cannot have an energy barrier that is too large. In other words, the mechanism cannot have any species (i.e. transition state) in it that is too high in energy (too unstable) to be formed at a given temperature. The Golden Rules of Chemistry are used to help predict the relative stabilities of proposed transition states. An obvious corollary to all of this is that reactions find the lowest energy opportunity (mechanism) to react out of all the possibilities, that is why reactions can usually be thought of as having a single mechanism. Thus, predicting mechanisms comes down to predicting the relative stabilities of potential transition states using the Golden Rules of Chemistry as a guide.* Great rule of thumb for most mechanisms: Each step involves a nucleophile attacking an electrophile, and when in doubt as to what to do, transfer a proton!

*The emphasis in this class is on qualitative thinking. Even though modern computers can usually calculate exact motives (thermodynamic driving forces) and exact transition state energies with a high degree of quantitative accuracy, that will not help you unless you have a suitable computer handy. The Golden Rules of Chemistry presented here are intended to give you the qualitative tools you need to think about chemistry without the aid of a computer calculation.