ELEMENTARY REACTIONS

The mechanism of a reaction is a series of steps leading from the starting materials to the products. After each step, an intermediate is formed. The intermediate is short-lived, because it quickly undergoes another step to form the next intermediate. These simple steps are called elementary reactions.

Because an overall reaction is composed of a series of elementary reaction, the overall rate of the reaction is somehow dependent on the rates of those smaller reactions. But how are the two related?

Let's look at two cases. We'll keep it simple and both cases will be two-step reactions.

The first case begins with a reaction having a pretty low activation barrier. Maybe there is a lot of bond-making involved at the beginning, so this reaction gets an easy start. However, after that, things get harder. The second step has a higher activation barrier.

Both of these reactions occur at particular rates. The first step has a low barrier, so it occurs quickly. The second step has a high barrier, so it happens only slowly.

In that case, the intermediate will be formed quickly and it will sit around for a while before the second step has a chance to happen. The second step is like a bottleneck or a traffic jam. No matter how quickly things were going in the first step, the reaction has to wait to get through the second step. The rate of the overall reaction really depends on the second step. We call this step the "rate-determining step".

Each step has its own rate constant associated with it. We'll call these constants k_1 and k_2. The lower the barrier, the faster the rate, and the larger the rate constant.

We can predict rate laws for elementary reactions (although the same thing isn't true for overall reactions). The rate law for an elementary reaction is simply its rate constant, times the concentrations of any species involved in that step.

The rate of formation of product will be determined by the rate of that second step, the rate-determining step. The rate of that second step is the rate constant, k_2, times the concentration of the intermediate.

$$d[\text{Product}]/dt = k_2[\text{Intermediate}]$$

But what is the concentration of the intermediate? The intermediate is produced in the first step, so its concentration depends on how quickly it is produced from the reactants. However, if the activation barrier is low, that first step may be reversible; it may really be an equilibrium reaction. So there is a third step in this reaction, and it goes backwards from the intermediate to the reactant. We'll call the rate constant for this step k_{-1}.

In terms of kinetics, an equilibrium is really just a ratio of forward and reverse steps. If the forward step is much faster, this ratio is bigger than one, and products are favoured. If the reverse step is much faster, the ratio is smaller than one, and reactants are favoured.

$$K_{eq} = k_1/k_{-1} = [Intermediate]/[Reactant]$$

Or, rearranging,

$$k_1/k_{-1}[Reactant] = [Intermediate]$$

Now we know the concentration of the intermediate. That means the rate of the overall reaction is

$$d[Product]/dt = k_2 k_1/k_{-1}[Reactant]$$

The take-home lesson is this: the second step is the rate determining step, so that step tells us how quickly the product forms. However, that step depends on an intermediate formed in an earlier step, so that earlier step also influences how quickly the product forms.

- The rate-determining step controls the rate of the reaction.
- The steps prior to the rate determining step influence the rate of the reaction by supplying intermediates needed for the rate determining step.

Now let's think about the opposite case. Suppose the first step has a very high barrier and the second step has a lower one. We have to wait and wait and wait for the intermediate to be produced, but once it's there, it reacts pretty quickly to give products.

In this case, the first step is the rate-determining step. That's the step that controls the rate of the reaction. As soon as that step proceeds, the rest of the reaction can occur quickly.

In this case,

d[Product]/dt = k$_1$[Reactant]

- Any steps after the rate-determining step don't influence the rate of the reaction.

In some cases, we can use our judgement to try to predict which transition states are highest in energy in a multi-step mechanism. However, much of the knowledge about what is happening between the reactant and the product would really come from computational chemistry. In computational chemistry, the energies of the intermediates and the transition states can be calculated using quantum mechanics. This task is not necessarily easy.

Source: http://employees.csbsju.edu/cschaller/Reactivity/kinetics/rkelementary.htm