

Consecutive Chemical Reactions

CHEM 361A: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
California State University, Fullerton

Lecture 18

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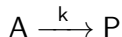
Learning Objective: Quantify integrated rate law expressions for multi-step reactions.

References:

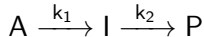
- Atkins and de Paula Focus 6F
- Chang §12.3 and §12.4

Multi-Step Reactions

The overall chemical reaction for a given process is typically written as



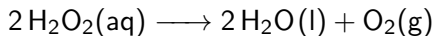
However, many chemical reactions occur in a series of steps. A **reaction mechanism** is a collection of individual steps that transform reactants to products. For example



is a reaction mechanism where reactant A decays to intermediate I_1 , which then decays to product P.

Multi-Step Reactions (cont.)

Since a reaction seldom takes place according to the balanced chemical reaction the challenge is to identify the steps. Consider the decomposition of H_2O_2 :



When the reaction is catalyzed by I^- , the rate law is found experimentally to be:

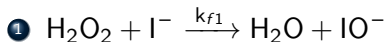
$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

The reaction mechanism potentially follows these two steps:

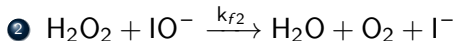
- 1 $\text{H}_2\text{O}_2 + \text{I}^- \xrightarrow{k_{f1}} \text{H}_2\text{O} + \text{IO}^-$
- 2 $\text{H}_2\text{O}_2 + \text{IO}^- \xrightarrow{k_{f2}} \text{H}_2\text{O} + \text{O}_2 + \text{I}^-$

Elementary Reactions

In the correct reaction mechanism, each step is an **elementary reaction**. An elementary reaction is one that follows what actually happens at the molecular level with no intermediates. For elementary reactions, **the order** of each component in the rate law expressions **follows the stoichiometry** of the balanced reactions. For example:



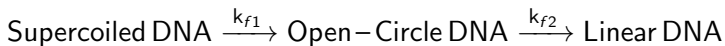
$$\text{rate}_1 = k_{f1}[\text{H}_2\text{O}_2][\text{I}^-]$$



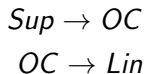
$$\text{rate}_2 = k_{f2}[\text{H}_2\text{O}_2][\text{IO}^-]$$

Multi-Step Reaction Example

The restriction enzyme EcoRI catalyses the cleavage of DNA and brings about the sequence of reactions:



Let us assume that each of these reactions are elementary reactions and that the reverse reaction is very slow (so that we can ignore it). In this case, the reaction mechanism can be broken down into two parts:



Integrated Rate Law Expressions

Assume that at $t = 0$, $[Sup] = [Sup]_0$ and $[OC] = [Lin] = 0$.
The decay of $[Sup]$ is

$$[Sup] = [Sup]_0 e^{-k_{f1}t}$$

The net rate of formation of OC is

$$\frac{d[OC]}{dt} = k_{f1}[Sup] - k_{f2}[OC]$$

and the integrated rate law for OC is

$$[OC] = \frac{k_{f1}}{k_{f2} - k_{f1}} \left(e^{-k_{f1}t} - e^{-k_{f2}t} \right) [Sup]_0$$

Integrated Rate Law Expressions

Now that we know $[Sup]$ and $[OC]$ then we can determine $[Lin]$.

Since

$$[Sup] + [OC] + [Lin] = [Sup]_0$$

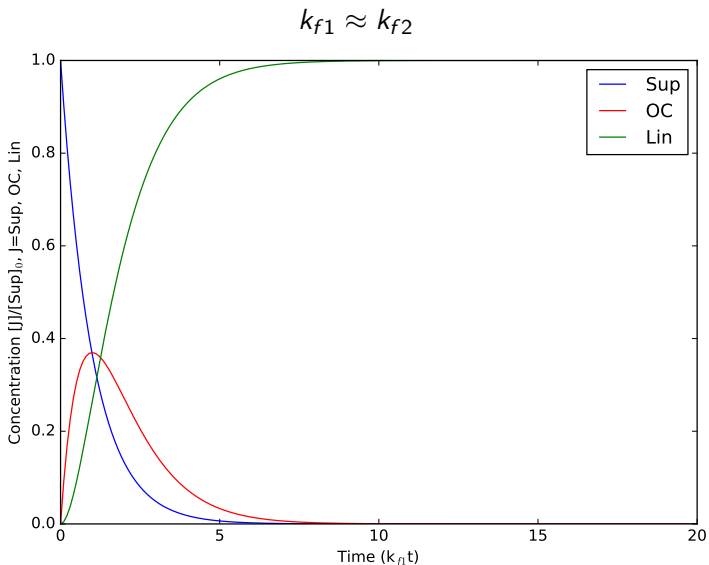
Then

$$[Lin] = [Sup]_0 - [Sup] - [OC]$$

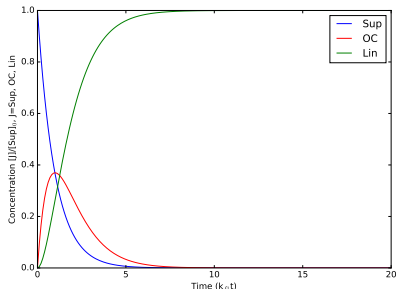
and

$$[Lin] = \left(1 + \frac{k_{f1}e^{-k_{f2}t} - k_{f2}e^{-k_{f1}t}}{k_{f2} - k_{f1}} \right) [Sup]_0$$

A Plot of these Rate Law Expressions



Determining the Maximum of an Intermediate

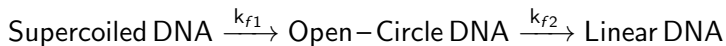


To determine the time at which the intermediate is at a maximum is found when

$$\left(\frac{d[I]}{dt} \right)_{t=t_{max}} = 0$$

Determining the Maximum for [OC]

Your experiment requires Open-Circle DNA which you know you can synthesize using the reaction

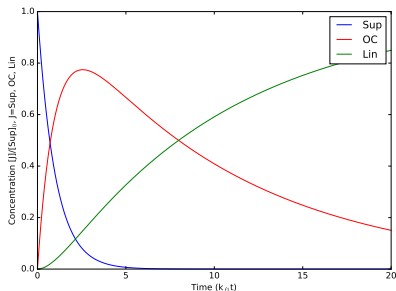


catalyzed by the restriction enzyme EcoRI. How long after initialization of the reaction should you extract the Open-Circle DNA to get the maximum amount?

Rate Determining Step

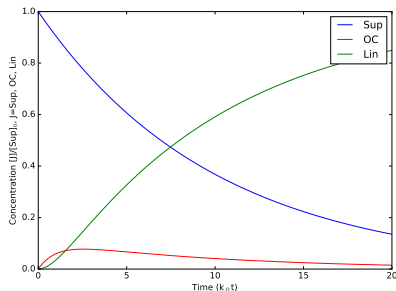
When the overall rate is determined by a single step, we call that the **rate determining step**. It is the slowest step that is critical to the formation of products.

$$k_{f1} = 10k_{f2}$$



Second Step is Rate Determining

$$10k_{f1} = k_{f2}$$



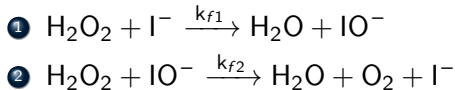
First Step is Rate Determining

Rate Determining Step - Decomposition of H_2O_2

For the decomposition of H_2O_2 the rate law expression is

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

Even though the reaction mechanism potentially follows these two steps:

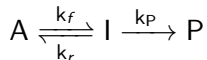


The overall rate law expression matches the first step and can be explained by the fact that $k_{f1} \ll k_{f2}$.

The first step is rate determining for this reaction.

The Preequilibrium Approximation

Consider the following reaction



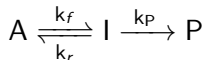
If the rate constants $k_f, k_r \gg k_p$ then the mechanism occurs in two distinct steps:

- 1 The equilibrium between the reactants and the intermediate is established and maintained during the course of the reaction
- 2 The intermediate undergoes decay to form the product

This description of events is called the **preequilibrium approximation**.

Preequilibrium Approximation Example

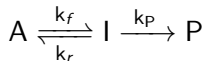
It is determined that the process under study uses the following mechanism:



where the rate constants $k_f, k_r \gg k_p$. If at $t=0$ $[A] = [A]_0$ and $[I] = [P] = 0$, use the preequilibrium approximation to determine the rate law expression and the integrated rate law expressions for $[A]$, $[I]$ and $[P]$.

The Steady State Approximation

Consider the following reaction scheme



The rate law expression for the intermediate is

$$\frac{d[I]}{dt} = \overbrace{k_f[A]}^{\text{Production}} - \overbrace{(k_r + k_p)[I]}^{\text{Consumption}}$$

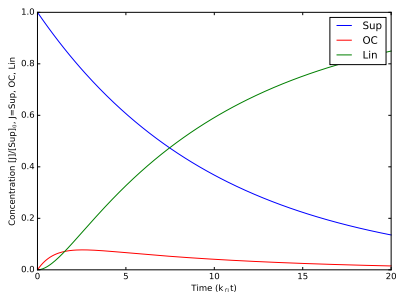
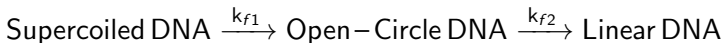
If $k_f \ll k_r + k_p$ then $[I]$ undergoes little change with respect to time. This typically means that the intermediate is consumed as soon as it is produced.

Under these conditions, the rate of change of the intermediate can be set to zero:

$$\frac{d[I]}{dt} = 0$$

The Steady State Approximation Example

Consider the following reaction:



You are interested in predicting the concentration of Linear DNA from Supercoiled DNA and you know that $k_{f2} \gg k_{f1}$. Use the steady state approximation to determine the concentration of Linear DNA as a function of time assuming that you start with only Supercoiled DNA.

Summary

- For consecutive reactions, rate laws are written as elementary reactions whose order is from the stoichiometric coefficients
- The time where the maximum amount of an intermediate is present is found by solving for t when $d[I]/dt = 0$.
- The rate determining step is the step which dictates the speed of the overall reaction
- When equilibria are present in a multi-step process, and the rate constants for the equilibrium reaction are much larger than the others involving the intermediate, it can be assumed that the system has a stable equilibrium.
- If the consumption of an intermediate is much larger than its production, the steady state approximation can be used to assume the concentration of an intermediate does not vary with time.