

Mechanism of Chemical Reactions

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- Given a mechanism to apply the SSA to the reactive intermediates
- Derive the expected rate law when the SSA applies
- Predict the rate law when the mechanism has a RDS
- Show how fractional powers appear in the rate expression
- Exemplify the concentration dependence in a catalytic mechanism

- Collection of individual kinetic steps (elementary reactions) involved
- Rate law expression entirely dependent on the mechanism
- Valid mechanism consistent with experimental data (stoichiometry, rate expression, temperature dependence etc.)
- More than one mechanism could explain the experimental observations
- Mechanism prediction is “educated guessing.” No universal rules.

A reactive intermediate implies $d[\text{I}]/dt = 0$

- Consider the consecutive reaction



- Imagine a reactive intermediate I
- Concentration of I is small relative to A and P.
- This situation is common and is referred to as the steady state region.
- Set $\frac{d[\text{I}]}{dt} = 0 = k_1[\text{A}] - k_2[\text{I}]$
- Steady state concentration of I is $[\text{I}]_{\text{ss}} = \frac{k_1[\text{A}]}{k_2}$
- Rate equations for reactant and product are

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{P}]}{dt} = k_1[\text{A}]$$

The SSA is accurate when $k_2 \gg k_1$

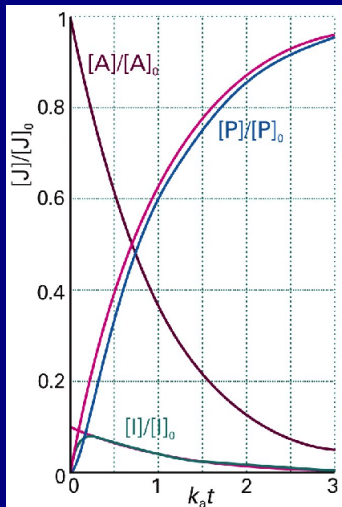


Figure 22-15
Atkins Physical Chemistry, Eighth Edition
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Comparison of exact result for the concentrations of a consecutive reaction and the concentrations obtained by using the steady state approximation ($k_2 = 20k_1$)

Is $d[\text{I}]/dt$ really zero at steady state?

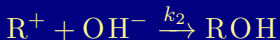
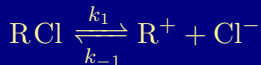
- Differentiating $[\text{I}]_{\text{ss}}$ we get

$$\frac{d[\text{I}]_{\text{ss}}}{dt} = \frac{k_1}{k_2} \frac{d[\text{A}]}{dt}$$

- The LHS is not zero BUT
- is small if $\frac{k_1}{k_2}$ is small or $k_1 \ll k_2$.
- In other words, $\frac{d[\text{I}]}{dt}$ is small relative to the overall rate
- SSA applies to the decreasing part of the $[\text{I}]$ vs. t graph

The SSA simplifies rate expressions

- The mechanism for the hydrolysis of *t*-butyl chloride is



- Suppose first step is not in equilibrium, $[\text{R}^+]$ is small, and $\frac{d[\text{R}^+]}{dt} \approx 0$.

$$\frac{d[\text{R}^+]}{dt} = k_1[\text{RCl}] - k_{-1}[\text{R}^+][\text{Cl}^-] - k_2[\text{R}^+][\text{OH}^-] = 0$$

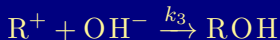
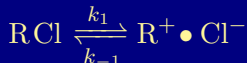
- Solve for the steady state concentration of $[\text{R}^+]$,

$$[\text{R}^+]_{\text{ss}} = \frac{k_1[\text{RCl}]}{k_{-1}[\text{Cl}^-] + k_2[\text{OH}^-]}$$

- The predicted rate equation becomes

$$\frac{d[\text{ROH}]}{dt} = k_2[\text{R}^+][\text{OH}^-] = \frac{k_1 k_2 [\text{RCl}][\text{OH}^-]}{k_{-1}[\text{Cl}^-] + k_2[\text{OH}^-]}$$

- Consider a second intermediate, the ion pair $R^+ \bullet Cl^-$, in the *t*-butyl chloride hydrolysis



- Assume that $\frac{d[R]}{dt}$ and $\frac{d[R^+ \bullet Cl^-]}{dt}$ are \approx zero
- Solve the two simultaneous equations for $[R^+]_{ss}$

$$[R^+]_{ss} = \frac{k_1 k_2 [RCl]}{k_2 k_3 + k_{-1} k_3 + k_{-1} k_{-2} [Cl^-]}$$



- The rate of the reaction is experimentally found to be

$$-\frac{d[\text{I}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$$

- Presence of $[\text{OH}^-]$ in rate law but not stoichiometry implies **Not a simple bimolecular reaction**
- Proposed mechanism:



Analysis of mechanisms with a RDS

- Second step is slow; HOI formed is immediately consumed in the third reaction
- First and third steps are in rapid equilibrium, the concentration of I^- hardly changes
- The rate of the reaction is

$$-\frac{d[I^-]}{dt} = k_2[HOCl][I^-]$$

- The first step is essentially at equilibrium, so

$$K_1 = \frac{[HOCl][OH^-]}{[OCl^-]}$$

Self-check: What further approximation to the SSA yields this result?

- The rate law is hence

$$-\frac{d[I^-]}{dt} = k_2 \frac{K_1[OCl^-]}{[OH^-]} [I^-]$$

Fast steps after a RDS do not figure in the rate law

- Rapid equilibrium steps after a RDS do not appear in the rate expression
- The appearance of a concentration in the denominator can result from a rapid equilibrium prior to the RDS
- If in a mechanism there is one RDS then the molecularity of that step is the molecularity of the reaction
- The predicted rate equation is obtained from the RDS
- There is no correspondence between the stoichiometry and the empirical rate law
- When the overall order exceeds three, then the presence of a rapid equilibrium before the RDS is likely