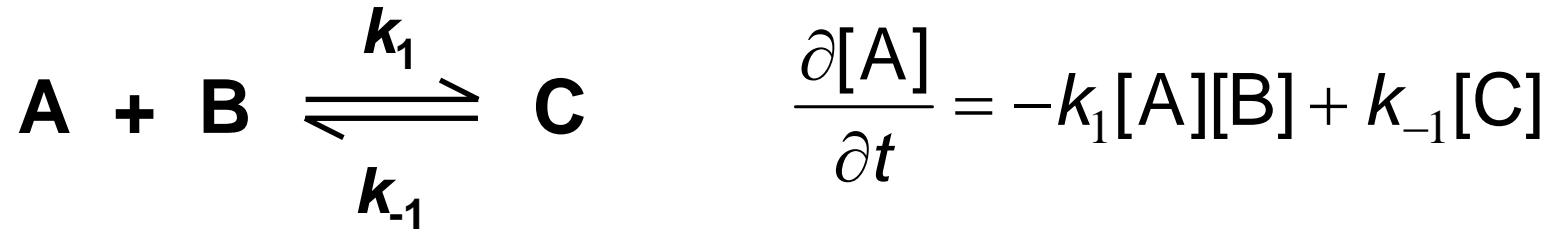


Approximations in Complex Kinetics



$$\frac{\partial[\text{C}]}{\partial t} = k_1[\text{A}][\text{B}] - k_{-1}[\text{C}] - k_2[\text{C}]$$

All of these expressions contain [C], which is often transient and unmeasurable.

How do we deal with [C]?

The Steady-State Approximation

A simplification:

$$[\text{Int}]_{\text{ss}} = \frac{\Sigma \text{ rates that create Int}}{\Sigma \text{ rates (omitting [Int]) that consume Int}}$$

so, for previous problem,

$$[\text{Tr}^+]_{\text{ss}} = \frac{k_1[\text{TrCl}]}{k_{-1}[\text{Cl}^-] + k_2[\text{EtS}^-]}$$

Steady-State and Pre-Equilibrium Assumptions

Steady-State:

$$\frac{\partial[\text{P}]}{\partial t} = \frac{k_1 k_2 [\text{A}][\text{B}]}{k_{-1} + k_2}$$

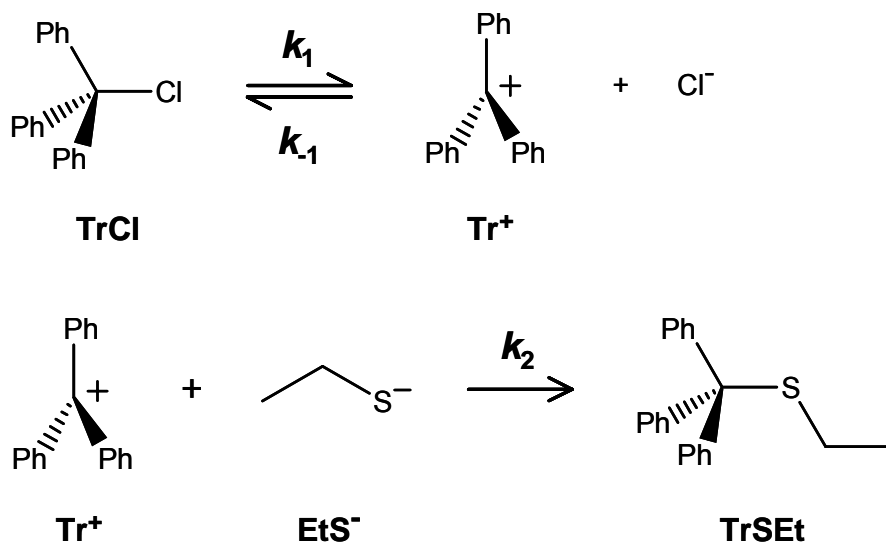
Pre-Equilibrium:

$$\frac{\partial[\text{P}]}{\partial t} = \frac{k_1 k_2 [\text{A}][\text{B}]}{k_{-1}}$$

Differ only in the way second step is treated.

Discussion Question

The nucleophilic conversion of trityl chloride (TrCl) to trityl ethyl thioether (TrSEt) occurs by a dissociative, S_N1 mechanism:



In this problem, we'll construct an integrated rate law for $\partial[\text{TrCl}]/\partial t$.

- a. Write basic (non-integrated) rate expressions for both $\partial[\text{TrCl}]/\partial t$ and $\partial[\text{Tr}^+]/\partial t$, in terms of any variables you want. (I.e., don't worry about integrating yet.) Make sure you include both processes that consume the species as well as those that create it.

$$\frac{\partial[\text{TrCl}]}{\partial t} =$$

$$\frac{\partial[\text{Tr}^+]}{\partial t} =$$

- b. Both of your expressions should contain $[\text{Tr}^+]$; trityl cation is a reactive intermediate, and its concentration can't be characterized, so we'll have to eliminate this term. We'll assume it's a steady-state intermediate, and that $\partial[\text{Tr}^+]/\partial t = 0$. Given this, use your answer to part (a) to solve for $[\text{Tr}^+]_{\text{ss}}$.

$$[\text{Tr}^+]_{\text{ss}} =$$

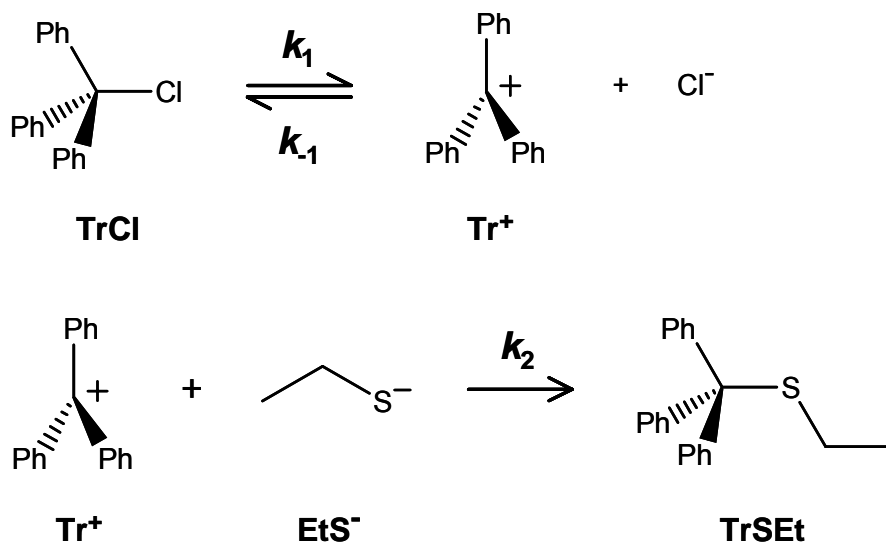
- c. Plug this into your expression for $\partial[\text{TrCl}]/\partial t$ from (a), and simplify as much as you can to end up with a new expressions for $\partial[\text{TrCl}]/\partial t$.

$$\frac{\partial[\text{TrCl}]}{\partial t} =$$

- d. EtS^- is a better nucleophile than Cl^- , so $k_2[\text{EtS}^-]$ should always be greater than $k_{-1}[\text{Cl}^-]$ if even a small excess of EtS^- is used. How does this affect your expression in (c)? What is the order of this reaction in $[\text{TrCl}]$ and $[\text{Cl}^-]$?
- e. On your own: How would the expression for $\partial[\text{TrSEt}]/\partial t$ compare to the one for $\partial[\text{TrCl}]/\partial t$ in (c)?
- f. On your own: How would the expressions be different if you made a pre-equilibrium assumption rather than a steady-state assumption?

Discussion Question—Solutions

The nucleophilic conversion of trityl chloride (TrCl) to trityl ethyl thioether (TrSEt) occurs by a dissociative, S_N1 mechanism:



In this problem, we'll construct an integrated rate law for $\partial[\text{TrCl}]/\partial t$.

- a. Write basic (non-integrated) rate expressions for both $\partial[\text{TrCl}]/\partial t$ and $\partial[\text{Tr}^+]/\partial t$, in terms of any variables you want. (I.e., don't worry about integrating yet.) Make sure you include both processes that consume the species as well as those that create it.

$$\frac{\partial[\text{TrCl}]}{\partial t} = -k_1[\text{TrCl}] + k_{-1}[\text{Tr}^+][\text{Cl}^-]$$

$$\frac{\partial[\text{Tr}^+]}{\partial t} = k_1[\text{TrCl}] - k_{-1}[\text{Tr}^+][\text{Cl}^-] - k_2[\text{Tr}^+][\text{EtS}^-]$$

- b. Both of your expressions should contain $[\text{Tr}^+]$; trityl cation is a reactive intermediate, and its concentration can't be characterized, so we'll have to eliminate this term. We'll assume it's a steady-state intermediate, and that $\partial[\text{Tr}^+]/\partial t = 0$. Given this, use your answer to part (a) to solve for $[\text{Tr}^+]_{\text{ss}}$.

$$[\text{Tr}^+]_{\text{ss}} = \frac{k_1[\text{TrCl}]}{k_{-1}[\text{Cl}^-] + k_2[\text{EtS}^-]}$$

- c. Plug this into your expression for $\partial[\text{TrCl}]/\partial t$ from (a), and simplify as much as you can to end up with a new expressions for $\partial[\text{TrCl}]/\partial t$.

$$\frac{\partial[\text{TrCl}]}{\partial t} = -k_1[\text{TrCl}] + k_{-1} \frac{k_1[\text{TrCl}]}{k_{-1}[\text{Cl}^-] + k_2[\text{EtS}^-]} [\text{Cl}^-]$$

$$\frac{\partial[\text{TrCl}]}{\partial t} = -\frac{k_1 k_2 [\text{TrCl}] [\text{EtS}^-]}{k_{-1} [\text{Cl}^-] + k_2 [\text{EtS}^-]}$$

- d. EtS^- is a better nucleophile than Cl^- , so $k_2[\text{EtS}^-]$ should always be greater than $k_{-1}[\text{Cl}^-]$ if even a small excess of EtS^- is used. How does this affect your expression in (c)? What is the order of this reaction in $[\text{TrCl}]$ and $[\text{EtS}^-]$?

$$\frac{\partial[\text{TrCl}]}{\partial t} = -k_1[\text{TrCl}]$$

- e. On your own: How would the expression for $\partial[\text{TrSEt}]/\partial t$ compare to the one for $\partial[\text{TrCl}]/\partial t$ in (c)?

$$\frac{\partial[\text{TrSEt}]}{\partial t} = \frac{k_1 k_2 [\text{TrCl}] [\text{EtS}^-]}{k_{-1} [\text{Cl}^-] + k_2 [\text{EtS}^-]}$$

- f. On your own: How would the expressions be different if you made a pre-equilibrium assumption rather than a steady-state assumption?

$$\frac{\partial[\text{TrCl}]}{\partial t} = -\frac{k_1 k_2 [\text{TrCl}][\text{EtS}^-]}{k_{-1}[\text{Cl}^-]}$$