Foundations of Chemical Kinetics

Lecture 29:
Diffusion-influenced reactions, Part II

Marc R. Roussel

Department of Chemistry and Biochemistry
Diffusion-influenced reactions

- Consider an elementary reaction $A + B \xrightleftharpoons{\kD} \xrightarrow{k} \text{product(s)}$.
- If $\{AB\}$ is the encounter pair formed from the reactants $A$ and $B$, we can break down a reaction in solution into two steps:

  \[
  A + B \xrightleftharpoons{\kD \kM} \{AB\} \xrightarrow{k_2} \text{product(s)}
  \]

- An encounter pair is not
  - a chemical intermediate or
  - the transition state of a reaction.

- The encounter pair has a very short lifetime (to be estimated later).
  We should therefore be able to apply the steady-state approximation to the encounter pair.
Diffusion-influenced reactions (continued)

\[ A + B \xrightleftharpoons[k_D]{k_{-D}} \{AB\} \xrightarrow{k_2} \text{product(s)} \]

\[
\frac{d[\{AB\}]}{dt} = k_D[A][B] - (k_{-D} + k_2)[\{AB\}] \approx 0
\]

\[ \therefore [\{AB\}] \approx \frac{k_D}{k_{-D} + k_2} [A][B] \]

\[ \therefore v = k_2[\{AB\}] \approx \frac{k_D k_2}{k_{-D} + k_2} [A][B] \]

\[ \triangleright \text{Since } v = k[A][B], \]

\[
k = \frac{k_D k_2}{k_{-D} + k_2}
\]
Comparison of the two approaches

▶ In the last lecture, we derived the equation

\[ k = \frac{k_D k_R}{k_R + k_D \exp \left( \frac{U(R_{AB})}{k_B T} \right)} \]

for the case of weak intermolecular forces (hard-sphere potential), where \(k_R\) is the second-order rate constant for A reacting with B molecules that have already reached distance \(R_{AB}\).

▶ We now have

\[ k = \frac{k_D k_2}{k_{-D} + k_2} \]

where \(k_2\) is the first-order rate constant for the formation of products from the encounter pair.
Comparison of the two approaches (continued)

These are two different ways of describing the same thing, so the two $k$ expressions must be equal.

\[
\begin{align*}
\therefore \quad \frac{k_D k_R}{k_R + k_D \exp \left( \frac{U(R_{AB})}{k_B T} \right)} &= \frac{k_D k_2}{k_D + k_2} \\
\therefore \quad \frac{1}{1 + \frac{k_D}{k_R} \exp \left( \frac{U(R_{AB})}{k_B T} \right)} &= \frac{1}{1 + k_D / k_2} \\
\therefore \quad k_R &= \frac{k_D}{k_D} \exp \left( \frac{U(R_{AB})}{k_B T} \right) k_2 \\
\therefore \quad k_2 &= k_R \frac{1}{K_D} \exp \left( -\frac{U(R_{AB})}{k_B T} \right)
\end{align*}
\]

or

where $K_D = k_D / k_{-D}$ is the equilibrium constant for formation of the encounter pair.
Comparison of the two approaches (continued)

\[ k_2 = k_R \frac{1}{K_D} \exp \left( -\frac{U(R_{AB})}{k_B T} \right) \]

- \( K_D^{-1} \) has units of concentration. It is a characteristic concentration scale for the equilibrium of the formation of the encounter pair. (If \([A], [B] \sim K_D^{-1}\), then \([\{AB}\] \sim K_D^{-1}\).)

- Thus, \( k_R \) is the second-order rate constant we would get if the encounter pair were in equilibrium with A and B at the characteristic concentration. (Compare the last equation in lecture 27:

\[ c_i(r) = c_i^0 \exp \left( -\frac{U(r)}{k_B T} \right). \]
Comparison of the two approaches (continued)

- $k_2$ ought in principle be evaluable from variational transition-state theory or other similar approaches.
- In either theory, the same equation for $k_D$ holds.
Encounter pair formation and breakup

- For the special case of molecules whose intermolecular forces with the solvent are about the same as those between each other, we can estimate $K_D$ by a statistical argument. This will also lead to an estimate of $k_{-D}$ since we know how to calculate $k_D$.

- Focus again on an A molecule.

- Suppose that the coordination number of the reactive site of A is $N$, i.e. that the reactive site of A makes contacts with $N$ neighboring molecules in solution.

- Let $[S]$ be the mole density of the solvent. The probability that any given molecule of S has been replaced by a B in the first solvation sphere of A is $[B]/[S]$. 
Encounter pair formation and breakup

- If $[B] \ll [S]$, the probability that one of the $N$ solvent molecules around A has been replaced by a B is $N[B]/[S]$.
- Another way to think about it is that $N[B]/[S]$ is the fraction of A molecules that have a B molecule in their first solvation sphere.
- Therefore,

$$[{AB}] \approx N \frac{[B]}{[S]} [A]$$

- Since

$$K_D = \frac{[{AB}]}{[A][B]}$$

we get

$$K_D = \frac{N}{[S]}$$
Example:
Reaction of bromphenol blue with hydroxide ion

\[ \text{quinoid form (blue)} \quad + \text{OH}^- \xrightarrow{k} \text{carbinol form (colorless)} \]

\[ k = 9.30 \times 10^{-4} \text{ L mol}^{-1}\text{s}^{-1} \text{ in water at 25}^\circ\text{C}. \]

To do: Estimate \( k_2 \).
Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of $k_D$

- Given: $D_{\text{OH}^-} = 5.30 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, $D_{\text{BPB}} = 4.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, C-O bond length = 143 pm, $\kappa_{\text{H}_2\text{O}} = 78.37$ (all at 25 $^\circ\text{C}$)
- Take $R_{AB} \approx \text{C-O bond length}$.
- The two reactants are both anions with a single negative charge.

\[
\epsilon = \kappa \epsilon_0 = 6.939 \times 10^{-10} \text{ C}^2\text{J}^{-1}\text{m}^{-1}
\]

\[
\beta = \frac{z_A z_B e^2}{4 \pi \epsilon k_B T \left[ \exp \left( \frac{z_A z_B e^2}{4 \pi \epsilon k_B T R_{AB}} \right) - 1 \right]}
\]

\[
= 4.846 \times 10^{-12} \text{ m}.
\]
Example:
Reaction of bromphenol blue with hydroxide ion
Estimate of $k_D$ (continued)

.$$k_D = 4\pi LD_{AB} \beta$$

$$= 4\pi (6.022142 \times 10^{23} \text{ mol}^{-1})[(5.30 + 0.44) \times 10^{-9} \text{ m}^2\text{s}^{-1}]$$

$$\times (4.846 \times 10^{-12} \text{ m})$$

$$= 2.11 \times 10^5 \text{ m}^3\text{mol}^{-1}\text{s}^{-1} \equiv 2.11 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1}$$
Example:
Reaction of bromphenol blue with hydroxide ion
Estimate of $K_D$

- For this structure, $N = 2$ seems reasonable.
- The mole density of water at 25 °C is 55.33 mol L$^{-1}$.
- Therefore

$$K_D \approx \frac{N}{[H_2O]} = \frac{2}{55.33 \text{ mol L}^{-1}} = 4 \times 10^{-2} \text{ L mol}^{-1}$$
Example:
Reaction of bromphenol blue with hydroxide ion

Estimate of $k_{-D}$

Since $K_D = k_D/k_{-D}$, we have

$$k_{-D} = k_D/K_D = 6 \times 10^9 \text{s}^{-1}$$

Aside: This value of $k_{-D}$ implies a half-life of the encounter pair of

$$t_{1/2} = \ln 2/k_{-D} = 1 \times 10^{-10} \text{s} \equiv 100 \text{ps}$$
Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of $k_2$

- By rearranging:
  
  $$k = \frac{k_D k_2}{k_D - k}$$

  we get

  $$k_2 = \frac{kk_D}{k_D - k}$$

  $$= \frac{(9.30 \times 10^{-4} \text{ L mol}^{-1}\text{s}^{-1})(6 \times 10^9 \text{ s}^{-1})}{2.11 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1} - 9.30 \times 10^{-4} \text{ L mol}^{-1}\text{s}^{-1}}$$

  $$= 3 \times 10^{-2} \text{ s}^{-1}$$

- The very small value of this rate constant compared to $k_D$ means that many, many encounter pairs are formed and broken up for each one that reacts.