Topic IX

Reactions and Mechanisms

IX.1 Module 46: Ligand Substitution in Octahedral Complexes

3/8:
- Suggested reading: Chapter 12.

- Having learned about structure, isomerism, and electronic structure, let's now talk about reactivity.

- What makes transition metals unique is the reactions of the metal center (i.e., the first coordination sphere).

- **Substitution reaction**: A reaction where a ligand in the first coordination sphere is exchanged.

- Factors that affect the rate of substitution:

    - Role of the entering group.
    - Role of the leaving group.
    - Nature of the other ligands in the complex.
    - Effect of the metal center.

- Stable/unstable are thermodynamic terms, and labile/inert are kinetic terms.

    - $[Co(NH_3)_6]^{3+}$ is unstable but inert wrt. aquation (large K_{eq}, but slow to react).
    - $[Ni(CN)_4]^{2-}$ is stable but labile wrt. exchange (small K_{eq}, but equilibrium is established quickly).

- **Potential energy landscape**: A thermodynamic representation of a reaction by a (potentially multidimensional) potential energy surface along its reaction coordinate.

- Thermodynamics and kinetics are two different things, but they can be related.

- Potential energy landscapes with small ΔG and large ΔE_A are slow to react.

    - Increasing ΔG (perhaps by destabilizing the reactant) can speed up the reaction.
    - Increasing ΔG often occurs at the expense of ΔE_A (the activation energy literally decreases as the free energy change increases).

- Consider the reaction $[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$.

    - The more bulky/less electronegative the X-type ligand, the higher the equilibrium constant and reaction rate.

- But how do we adequately compare different reactions when so many parameters are entangled together?

- One good way to compare kinetics of transition metals is with water exchange rate constants (light/heavy water being exchanged in metal coordination spheres), since this eliminates thermodynamic consternation.

  - There is massive variation among the metals.
  - The fastest (the alkali metals) run up against the **diffusion limit**.
  - Metals with larger atomic radii react more quickly (the alkali and alkaline earth metals follow this pattern nicely, but the transition metals are all over the place).
    - Group 1A: As we go down the group, the cations are getting larger and the charge density decreases, so the $M^+ - OH_2$ bond is getting weaker and more easily broken.
    - Group 2A: The charge density is larger (doubly charged) so the strength of the bond is greater so the rate of exchange is slower.
  - We define such a reaction as having a labile half life if the half life is less than 1 minute; otherwise, it is inert.

- **Diffusion limit**: At most, one molecular collision can result in one successful reaction; thus, reaction rate is bounded above by how many molecular collisions can physically occur in a given period of time at a given temperature.

- You cannot prove mechanisms; you can only disprove other plausible scenarios.

- Possible mechanisms for $ML_5X + Y \longrightarrow ML_5Y + X$ where $X = H_2O$ and $Y =$ anion or vice versa:

- Associative (A): Via a 7-coordinate intermediate.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5XY \qquad \text{(slow)}$$

$$ML_5XY \xrightarrow{k_2} ML_5Y + X \qquad \text{(fast)}$$

  - Corresponds to organic S_N2.
  - First step (RDS) is slow since the incoming Y causes steric hindrance.
  - The transition state is either a monocapped octahedron or pentagonal bipyramidal, depending on how the Y attacks.
  - Applying a steady-state approximation for $[ML_5XY]$, we have

$$\frac{d[ML_5XY]}{dt} = 0 = k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY]$$

  - We can solve the above equation for $[ML_5XY]$:

$$[ML_5XY] = \frac{k_1[ML_5X][Y]}{k_{-1} + k_2}$$

  - Substituting the above into the rate constant equation for the fast step will give us the rate law in terms of the reactants (where $k = \frac{k_1 k_2}{k_{-1}+k_2}$):

$$\text{Rate} = k_2[ML_5XY]$$
$$= \frac{k_1 k_2[ML_5X][Y]}{k_{-1} + k_2}$$
$$= k[ML_5X][Y]$$

  - Thus, the S_N2 mechanism is second-order overall, but first-order in both reactants.

- Dissociative (D): Via a 5-coordiinate intermediate.

$$\mathrm{ML_5X} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{ML_5} + \mathrm{X} \qquad \text{(Slow)}$$

$$\mathrm{ML_5} + \mathrm{Y} \xrightarrow{k_2} \mathrm{ML_5Y} \qquad \text{(Fast)}$$

  - Corresponds to organic $\mathrm{S_N}1$.
  - First step (RDS) is slow since its spontaneous elimination of a ligand.
  - The transition state is generally square pyramidal, but if it is sufficiently long-lived, it can reorganize itself into the trigonal bipyramidal state.
  - The dissociative mechanism predicts that the rate of the overall substitution reaction depends on only the concentration of the original complex $[\mathrm{ML_5X}]$, and is independent of the concentration of the incoming ligand $[\mathrm{Y}]$.
  - Thus, the overall rate law is
  $$\mathrm{Rate} = k_1[\mathrm{ML_5X}]$$

  - We can also derive this with an analogous kinetic analysis to that used for the A mechanism, the only difference being that we simplify $\frac{k_1 k_2[\mathrm{ML_5X}][\mathrm{Y}]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$ to the rate law by noting that $k_2 >> k_{-1}$ or $[\mathrm{Y}] >> [\mathrm{X}]$.

- Interchange (I): As Y begins to bond, X begins to leave, i.e., the bond making to Y and bond breaking to X occur simultaneously.

$$\mathrm{ML_5X} + \mathrm{Y} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{ML_5X \cdot Y} \qquad \text{(Slow)}$$

$$\mathrm{ML_5X \cdot Y} \xrightarrow{k_2} \mathrm{ML_5Y} + \mathrm{X} \qquad \text{(Fast)}$$

  - Corresponds to organic $\mathrm{SN_2}$.
  - This is how the majority of ligand substitutions occur.
  - It is too simplistic to assume that a first-order rate law implies D and a second-order rate law implies A. Indeed, most substitution reactions probably involve a mechanism like this, i.e., one that is intermediate between these two extremes.
  - In an interchange mechanism, the intermediate involves an association between the original $\mathrm{ML_5X}$ complex and the attacking Y ligand. The Y ligand remains outside the coordination sphere of $\mathrm{ML_5X}$, unlike the $\mathrm{S_N}2$ mechanism, so the intermediate is not seven coordinate. However, it can help weaken the $\mathrm{M-X}$ bond.
  - Assuming high $[\mathrm{Y}] \approx [\mathrm{Y}]_0$, it can be shown that the rate is given by

  $$\mathrm{Rate} = \frac{k_2 K_1 [\mathrm{M}]_0 [\mathrm{Y}]_0}{1 + K_1 [\mathrm{Y}]_0}$$

  where $[\mathrm{M}]_0 = [\mathrm{ML_5X}]_0 + [\mathrm{ML_5X \cdot Y}]$ and $[\mathrm{Y}]_0$ are initial conditions and $K_1 = \frac{k_1}{k_{-1}}$ is the equilibrium constant for the RDS reaction.

    - At high $[\mathrm{Y}]$ and $K_1[\mathrm{Y}]_0 >> 1$, the rate is first-order in $[\mathrm{M}]_0 \approx [\mathrm{ML_5X}]$.
    - At lower $[\mathrm{Y}]$, the rate is second order.

- At some point, the kinetic analysis becomes essentially worthless. Indeed, although we speak generally about associative and disassociative reaction mechanisms, the terms A and D are reserved for situations where 7- and 5-coordinate intermediates have actually been isolated and positively identified. If no intermediates have been isolated or identified, the designations I_d and I_a are more appropriate.

  - Two minor variations on the I mechanism are I_d (dissociative interchange) and I_a (associative interchange).

- If breaking the $M-X$ bond is more important, the mechanism is I_d.
- If bond formation between ML_5X and Y is significant, the mechanism is I_a.
- The difference between I_d and I_a is subtle and does not necessarily correspond to whether the observed rate law is first or second order.
- If the rates of a series of comparable substitution reactions are most sensitive to the identity of X, the leaving ligand, then the mechanism is more probably I_d, and vice versa for I_a.
- For example, the rate constants for the anation of $[Cr(NH_3)_5(H_2O)]^{3+}$ by various ligands vary very little. Thus, it is probably I_d. However, the rate constants for the anation of $[Cr(H_2O)_6]^{3+}$ by various ligands vary by three orders of magnitude. Thus, it is probably I_a.

- Solvent (e.g., water) effects in substitution reactions:

  - Many substitution reactions occurring in solvent water may have first-order kinetics regardless of whether their initial steps are primarily D or A.
  - For example, this occurs if aquation is a precursor RDS.
  - If D, Rate $= k[ML_5X]$.
  - If A, Rate $= k[ML_5X][H_2O] = k'[ML_5X]$.
    - The latter equality is valid since water has constant concentration[1].
  - Both mechanisms lead to apparent first-order kinetics.

- Steric factors favoring D or I_d:

  - For most octahedral complexes, steric factors inhibit formation of a CN7 intermediate, which suggests a dissociative mechanism (D or I_d) is more plausible.
    - Even cases showing second-order kinetics may not be A for this reason.
  - For example, aquation of ammine-halides is second order with a first-order dependence on [OH$-$].
  - If $k_2 >> k_1$, the rate is approximately Rate $= k_2[Co(NH_3)_5X]^{2+}[OH-]$.
  - Calls for an alternate mechanism called S_N1CB, where ligands with lower energy bond as <u>c</u>onjugate <u>b</u>ases and those with higher Δ_0 (hence CB).

- Kinetically analyzes S_N1CB.

---

[1]Is this what we meant when we said in Labalme (2020) that liquids and solids don't have active mass? In other words, the species should be included in the mass-action expression; they just simply get lumped in with the rate constant generally.