Kinetics and Mechanisms

The field of inorganic reaction kinetics and mechanisms is not as developed as that of organic reactions (*systematization is rather difficult with some 80 or so elements*)

Even within a group, there can be differences in mechanism and reactivity (important to consider for synthetic approaches)

e.g., consider the following simple displacement reaction:

\[
[\text{CoCl}_4]^{2-} \xrightarrow{\text{NH}_3} [\text{Co(NH}_3)_6]^{2+} \xrightarrow{\text{oxidation}} \xrightarrow{\text{air, H}_2\text{O}_2} [\text{Co(NH}_3)_6]^{3+}
\]

- this reaction is easy to carry out in aqueous media when Co(II) is used as the starting complex
- it is not possible to use Co(III) as a starting material because Co(III) is not stable in water
Kinetics and Mechanisms

However, Rh\textsuperscript{3+} (for example) is stable in water!

Therefore, \([\text{Rh(NH}_3\text{)}_6]\text{Cl}^3+) can be prepared directly from \text{RhCl}_3

\textit{Note that the displacement of the last Cl}^\text{- ligand from \([\text{RhCl(NH}_3\text{)}_5]\text{Cl}^2+) is difficult, and requires higher temperatures and pressures!}
\textit{This is the old (19\textsuperscript{th} century) method of preparing hexaammine complexes!}

Today, with the knowledge of mechanisms of substitution reactions it is relatively easy to synthesize a variety of hexaammine complexes:

\[
[M(\text{NH}_3)_5\text{Cl}]^{2+} \xrightarrow{\text{CF}_3\text{SO}_3\text{H (triflic acid)}} [M(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)]^{2+} \xrightarrow{\text{NH}_3} [M(\text{NH}_3)_6]^{3+}
\]

\textbf{Triflic acid} (a superacid) removes the last chloro ligand by protonation (product is HCl). The conjugate base (triflate anion) is extremely weak, and therefore coordinates very weakly to the metal (hence: substitution with \text{NH}_3 is easy).
Substitutions in square-planar complexes

Important for $d^8$ TMs (e.g., Pt(II), Pd(II), Ni(II), Au(III), Rh(I))

In terms of kinetics and mechanisms, **Pt(II) complexes are the best studied** (many Russian laboratories investigated these complexes → vast Pt deposits in Russia)

Advantages of studying Pt(II) complexes:
- they are stable
- relatively easy to synthesize
- ligand exchange reactions are slow enough so that they can be followed (e.g., by spectroscopy)

Reaction rates: Pt : Pd : Ni 1 : $10^5$ : $10^7$
Substitutions in square-planar complexes

Three pathways by which one ligand can replace another:

1. Nucleophilic substitution
2. Electrophilic substitution
3. Oxidative addition / Reductive elimination

(familiar from Organic Chem)

(familiar from Organic Chem)

(this type of reaction is important in homogeneous catalysis; e.g., Monsanto process)
Nucleophilic substitutions in square planar complexes

Y: incoming ligand
X: leaving ligand

There are four types of mechanisms:

1. Dissociative (D): M-X bond is fully broken before M-Y bond is formed
2. Associative (A): M-Y bond is fully formed before M-X bond is broken
3. Interchange dissociative (I_d): M-Y bond begins to form before M-X is fully broken
4. Interchange associative (I_a): M-X bond begins to break before M-Y bond is fully formed

Note: most square-planar complexes undergo substitution according to an A or I_a-type mechanism!
1. **Dissociative (D):** M-X bond is fully broken before M-Y bond is formed

\[
\begin{align*}
\text{L} & \text{M} \text{X} \xrightarrow{\text{slow}} \text{L} \text{M} \xrightarrow{\text{fast}} + \text{Y} \\
& \text{L} \text{M} \text{Y} \\
\end{align*}
\]

Rate law:

\[v = - \frac{d[ML_3X]}{dt} = k \ [ML_3X]\]

Reminiscent of \(S_N1\) in Organic Chemistry

2. **Associative (A):** M-Y bond is fully formed before M-X bond is broken

\[
\begin{align*}
\text{L} & \text{M} \text{X} \xrightarrow{\text{slow}} \text{L} \text{M} \text{X} \xrightarrow{\text{fast}} + \text{Y} \\
& \text{L} \text{M} \text{Y} \\
\end{align*}
\]

Rate law:

\[v = - \frac{d[ML_3X]}{dt} = k \ [ML_3X] [Y]\]

Reminiscent of \(S_N2\)

Differences in energy between TBP and square pyramid are typically small

\(k\) depends on the nature of the nucleophile

\(k\) depends on the nucleophile concentration
3. Interchange dissociative (I_d): M-Y bond begins to form before M-X is fully broken

4. Interchange associative (I_a): M-X bond begins to break before M-Y bond is fully formed

**Refined (observed) rate law:** \( v = k_1[ML_3X] + k_2[ML_3X][Y] \)

Why this term?

Substitution proceeds via solvolysis (formation of solvent complexes):

\[
ML_3X \rightarrow ML_3S \rightarrow ML_3Y \quad (S = \text{solvent})
\]

*Note: solvent molecules are nucleophiles (they compete with the Y ligand)*

rate law: \( v = k'[ML_3X][S] + k_2[ML_3X][Y] \)

Since solvent is in vast excess (and its concentration does not change during the reaction): \( k_1 = k'[S] \rightarrow \) this gives the refined rate law shown above
Trans effect (kinetic effect)

The **trans effect** is the best studied of all kinetic effects (introduced by Chernyaev, 1926)

Describes **the effect of a coordinated ligand on the rate of substitution of the ligand opposite to it**

Observed (and quite profound) in square-planar complexes

Either of the two circled ligands are substituted in the second step of the reaction

1. Replacement of one Cl⁻ ligand yields the amminetriclоро complex.
2. The displacement of another chloro ligand yields the **cis-isomer** of diamminedichloro complex

```
[Cl]₂Pt[Cl]₂⁻ + NH₃ → [Cl]₂Pt[Cl]⁻[NH₃]⁺
```

```
[Cl]₂Pt[Cl]₂⁻ + NH₃ → [Cl]₂Pt[Cl]⁺[NH₃]⁻
```

```
H₃N⁺PtCl⁻Cl⁺ NH₃
```

```
Cl⁻Pt⁺NH₃⁻Cl⁻ NH₃
```

```
trans-diamminedichloro-platinum(II) (Not found in this reaction)
```

```
cis-diamminedichloro-platinum(II) (Exclusive product)
```
1. Replacement of one \(\text{NH}_3\) ligand yields the triamminechloro complex.

2. The displacement of another \(\text{NH}_3\) ligand yields the \textit{trans}-isomer of the diamminedichloro complex

However: with the tetraammine complex as the starting material, the \textit{trans} isomer is obtained.

Interaction of cisplatin with DNA leads to kinking (bending) of the DNA duplex via an intrastrand cross-link. \textit{Note that in order to interact with DNA, the two chloro ligands need to be displaced.}
It is possible to establish the **trans-directing** ability of the ligands A and B in substitution reactions on square-planar Pt(II) complexes:

When such studies are performed with a variety of ligands, one can establish the **trans-directing series** of ligands:

\[
\text{CN}^-, \text{CO}, \text{NO}, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^- > \text{CH}_3^-, \text{C}_6\text{H}_5^-, \text{SC(NH}_2)_2, \text{SR}_2 > \text{SO}_3\text{H}^- > \text{NO}_2^-, \text{I}^-; \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{RNH}_2, \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}
\]

* L > L’ means that the reaction is faster when a ligand trans to L is lost (and slower when a ligand trans to L’ is lost
Relative *trans* and *cis* effects based on rates of substitution of H$_2$O for Cl$^-$ in [PtCl$_3$L]$^{n-}$

<table>
<thead>
<tr>
<th><em>Trans</em> ligand</th>
<th><em>Trans</em> effect</th>
<th><em>Cis</em> ligand</th>
<th><em>Cis</em> effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>1</td>
<td>H$_2$O</td>
<td>1</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>200</td>
<td>NH$_3$</td>
<td>1</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>330</td>
<td>Cl$^-$</td>
<td>0.4</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>3000</td>
<td>Br$^-$</td>
<td>0.3</td>
</tr>
<tr>
<td>DMSO</td>
<td>2,000,000</td>
<td>DMSO</td>
<td>5</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>$10^{11}$</td>
<td>C$_2$H$_4$</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*Note: the cis effect is very small compared to the trans effect*
Mechanism of nucleophilic substitution in square-planar complexes

$T =$ trans-directing ligand, $Y =$ incoming ligand, $X =$ leaving ligand

- $Y$ experiences repulsion from filled $d$ orbitals and from bonding electrons (slow step)
- When approaching the metal ion, $Y$ may coordinate through an empty $p_z$ orbital of the metal
- Note that in the trigonal-bipyramidal intermediate, $X$, $Y$, and $T$ occupy the equatorial positions!
Explanation of the *trans* effect

Two factors need to be considered (both determine the order of the *trans*-directing series):
1. Weakening of the M-X bond
2. Stabilization of the TBP intermediate

**Reaction coordinates and activation energy**

A: poor *trans* effect (low ground state, high transition state)
B: **σ**-bonding effect (high ground state, high transition state) → *trans influence*
C: **π**-bonding effect (low ground state, low transition state)

* Thermodynamic effect
**σ-bonding effects:**

- In square-planar complexes, the bond strength of the M-X bond is influenced by the M-T bond because the orbitals of T and X overlap with the same metal atomic orbitals ($p_x$ and $d(x^2-y^2)$)

- The stronger the M-T $σ$-bond, the weaker the M-X $σ$-bond (i.e., ground state has a high energy)

- This ground state effect is called **trans influence**, and is a **thermodynamic effect**

- The **trans influence** correlates well with the order of $σ$ **donor strength:**
  - $H^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$

$T =$ **trans-directing ligand**, $X =$ **leaving ligand**
\[ \pi \text{-bonding effects:} \]

*The \( \sigma \)-bonding effect does not explain the position of CO, CN\(^{-}\), PR\(_{3}\), etc. in the trans-directing series of ligands!*  

- A strong \( \pi \)-bonding (accepting) ligand T can remove charge from the metal centre (this makes the entrance of the incoming ligand energetically more favorable)

- In the TBP geometry: \( d_{xz}, d_{yz}, \) and \( d(x^2-y^2) \) (!) participate in \( \pi \)-bonding!
  - results in lowering of the energy of the transition state (see panel C in the figure on page 13)!

In the end, the trans-directing series of ligands comes from a combination of \( \sigma \) and \( \pi \) effects. Nonetheless, there is still some debate as to whether the \( \sigma \) or \( \pi \) effect contributes more in some cases.
Nucleophilic substitution reactions on octahedral complexes

- Can in principle occur via D, I_d, A, or I_a-type mechanisms
- Most common type in octahedral complexes is D or I_d
- Reactions of octahedral complexes are more complex than those of square-planar complexes because there are more possibilities for reaction products
**Dissociative mechanism** with *cis*-complexes

1. If intermediate (square-pyramidal) is **configurationally ‘stable’**, *cis*-\([ZL_4AX]\) is obtained.

2. If intermediate (square-pyramidal) is **configurationally ‘unstable’**, *cis*-\([ZL_4AX]\) and *trans*-\([ZL_4AX]\) are obtained.
**Dissociative mechanism** with *trans*-complexes

*trans*-[^{ZL_4AB}]

1. If intermediate (sq.-py.) is **configurationally ‘stable’**, *trans*-[^{ZL_4AX}] is obtained

2. If intermediate (square-pyramidal) is **configurationally ‘unstable’**, *cis*-[^{ZL_4AX}] and *trans*-[^{ZL_4AX}] are obtained
Associative mechanisms

1. *trans*-attack on *trans*-\([ZL_4AB]\) results in *cis*-\([ZL_4AX]\)

2. *cis*-attack on *trans*-\([ZL_4AB]\) results in *trans*-\([ZL_4AX]\)
3. trans-attack on cis-[ZL₄AB] results in cis-[ZL₄AX] or trans-[ZL₄AX]

4. cis-attack on cis-[ZL₄AB] results in cis-[ZL₄AX]
Example of substitution reactions with chelate complexes:

Note that nucleophilic attack can occur from two directions in the equatorial plane, resulting in two enantiomers.
Kinetic and thermodynamic stability of complexes

Thermodynamic terms: stable and unstable
Kinetic terms: inert and labile

Definition of labile (Taube):
Reaction half-time (i.e., the time of disappearance of half of the initial compound) of 1 minute or less

All of the following cyano-complexes are extremely stable!
(dissociation constant for the hydrolysis of $[\text{Ni(CN)}_4]^{2-}$ to $[\text{Ni(H}_2\text{O)}_6]^{2+}$ is $10^{-22}$ M$^{-2}$)

\[
[\text{Ni(CN)}_4]^{2-} + 4^{14}\text{CN}^{-} \rightarrow [\text{Ni}^{(14}\text{CN})_4]^{2-} + 4\text{CN}^{-} \\
\quad t_{1/2} \approx 30 \text{ s}
\]

\[
[\text{Mn(CN)}_6]^{3-} + 6^{14}\text{CN}^{-} \rightarrow [\text{Mn}^{(14}\text{CN})_6]^{3-} + 6\text{CN}^{-} \\
\quad t_{1/2} \approx 1 \text{ h}
\]

\[
[\text{Cr(CN)}_6]^{3-} + 6^{14}\text{CN}^{-} \rightarrow [\text{Cr}^{(14}\text{CN})_6]^{3-} + 6\text{CN}^{-} \\
\quad t_{1/2} \approx 24 \text{ days}
\]
Fig. 1. Water-exchange rate constants, $k_{H_2O}$, for a particular water molecule in the first coordination sphere of $[M(H_2O)_n]^{m+}$. Bold bars represent directly determined $k_{H_2O}$ values while hashed bars indicate $k_{H_2O}$ values estimated from ligand-substitution studies.
Rule-of-thumb for inert and labile structures:

Inert: \( d^3, d^4 \) (l.s.), \( d^5 \) (l.s.), \( d^6 \) (l.s.), strong-field \( d^8 \) (square planar)

High CFSE

Intermediate: weak-field \( d^8 \) (octahedral, tetrahedral)

Intermediate CFSE

Labile: \( d^1, d^2, d^4 \) (h.s.), \( d^5 \) (h.s.), \( d^6 \) (h.s.), \( d^7, d^9, d^{10} \)

Low CFSE

Note that the charge of the metal ion is also a contributing factor!
Example: CrCl₃ (d³)

- Pure CrCl₃ is insoluble in water
- Traces of Cr(II) or a reducing agent dissolve CrCl₃ in aqueous solution, leading to the violet hexaaquacomplex [Cr(H₂O)₆]Cl₃
- [Cr(H₂O)₆]³⁺ is inert to substitution

Because of the inertness of [Cr(H₂O)₆]³⁺, ligand substitution is a poor method of synthesis for Cr(III) complexes!

Better approach: Air oxidation of [Cr(H₂O)₆]²⁺ in the presence of ligand(s)
Reduction of Cr₂O₇²⁻ in the presence of ligand(s)