Mechanisms of Inorganic Reactions   HS -26

A. Ligand Substitution Reactions
   Octahedral Co(III), Cr(III)  Dissociative mechanism
   Square Planar Pt(II)       Associative mechanism
   trans effect in Pt(II) complexes

B. Electron Transfer Reactions
   inner sphere (Taube 1952)
   outer sphere (Marcus theory)
   electron transfer proteins

* review of kinetics, rate laws, transition state theory
Mechanism of Inorganic Reactions

1. Octahedral Substitution

Water exchange rates correlate with charge/size and cfse

All $M_{aq}^{+2/+3}$ except Co(III) and Cr(III) are labile, $t_{1/2} < 1$ minute

$Al^{3+} < Fe^{3+} < V^{2+} Ni^{2+} < Co^{2+}, Fe^{2+} < Mn^{2+} < Cr^{2+}Cu^{2+}$

\[
\begin{align*}
d^n & \quad 0 \quad 5 \quad 3 \quad 8 \quad 7 \quad 6 \quad 5 \quad 4 \quad 9 \\
\log k & \quad 0.3 \quad 2 \quad 4 \quad 4 \quad 5.5 \quad 6 \quad 6.5 \quad 8.2 \quad 8.5
\end{align*}
\]

Inert Co$^{3+}$ is d$^6$ log k = -6 cfse = 24Dq

Cr$^{3+}$ d$^3$ log k = -5.5 cfse = 12Dq

Ir$^{3+}$ is low spin d$^6$ $k = 10^{-10}$ s$^{-1}$ $t_{1/2}$ water exchange 200 yrs
Trends in lability
1. charge/size ratio
2. CFSE

Co$^{3+}$ not shown as the aqua species is unstable and oxidizes water.

Co(NH$_3$)$_5$(H$_2$O)$_3^{3+}$ $k = 10^{-6}$ s$^{-1}$

d$^3$ and ls d$^6$ complexes inert
square d$^8$ Pt(II) inert

Richens, Chem Rev. 2005
Figure 3. Correlation of log $k_{\text{H}_2\text{O}}$ (s$^{-1}$) with LFSE (kJ mol$^{-1}$) for the first row transition metal $[\text{M(H}_2\text{O)}_6]^{2+}$ cations. (J–T is the apparent rate acceleration resulting from the Jahn–Teller distortion away from regular octahedral geometry).
Figure 4. Hydrogen-bonded localized water structure surrounding a metal cation in aqueous solution (here the metal ion is assumed to have a primary hydration number of 6).
OCTAHEDRAL SUBSTITUTION

Dissociative mechanism predominant (bond breaking)

**acid hydrolysis**

\[ L_5CoX^{2+} \rightarrow L_5Co \rightarrow L_5Co(H_2O)^{3+} \]

\[ Co(NH_3)_5X^{2+} + H_2O \rightarrow Co(NH_3)_5(H_2O)^{3+} + X^- \]

rate = \( k_x [Co] \)  
first order rate law

- steric effects \( L = NMe_3 \gg \gg NH_3 \)

- leaving group \( k \ (\text{s}^{-1}) \) decreases with strength of Co-X
  
  \( I^- > Br^- > Cl^- \)

**Anation**

\[ L_5Co(H_2O)^{3+} + X^- \rightarrow L_5CoX^{2+} + H_2O \]

rate = \( k_2 [Co] [X^-] \)  
second order rate law

\( k_2 \) is relatively independent of the nature of \( X^- \) except \( OH^- \)
Eigen Wilkins Mechanism

Rapid outer sphere association to form an encounter complex followed by slow interchange to give product.

\[ K_E \quad \quad \quad k_i \]

\[ ML_6 + Y \Leftrightarrow \{ML_6,Y\} \rightarrow ML_5Y + L \]

\[
\text{rate} = k_i K_E [ML_6]_{\text{total}} [Y] / (1 + K_E Y) = k_i K_E [ML_6]
\]

\[
[ML_6]_{\text{total}} = ML_6 + \{ML_6,Y\} \quad \text{fraction } ML_6 = 1 / (1 + K_E Y)
\]

\[
\text{fraction } \{ML_6,Y\} = K_E Y / (1 + K_E Y)
\]

for \( 1 >> K_E Y \) we have only \( ML_6 \): rate is second order

for \( K_E Y >> 1 \) we have only \( \{ML_6,Y\} \): rate is independent of \( Y \)

when \( ML_6 \) is a cation and \( Y \) an anion \( \{ML_6,Y\} \) is an ion-pair
anation (reverse of aquation)  rate = k [Co][X]  

Does 2\textsuperscript{nd} order kinetics mean Sn\textsuperscript{2} or A mechanism? NO

A  \( L_5Co(H_2O)^{3+} + X^- \rightarrow 7 \text{ Coordinate} \rightarrow L_5CoX^{2+} + H_2O \)

rate = \( k_2 \) [Co][X]  \( X \) attacks giving 7 CN intermediate

D  \( L_5Co(H_2O)^{3+} \rightleftharpoons L_5Co \rightarrow L_5CoX^{2+} \)  \( W \) and \( X \) compete for I

rate = \( k_{-w} k_{+x} \) [Co][X] / \{ \( k_{+w} \) [W] + \( k_{+x} \) [X] \}

Ion Pair  \( L_5Co(H_2O)^{3+} + X^- \rightleftharpoons IP \rightarrow L_5CoX^{2+} + H_2O \)

rate = \( K_{IP} \) [Co][X] / \{ 1 + \( K_{IP} \) [X] \}  \( \) fast preEq followed by interchange step

All 3 mechanisms could give second order kinetics. The D mechanism explains why k is only slightly dependent on nature of entering nucleophile.
pH Effects (involve conjugate acid and conjugate base)

A. Base Hydrolysis \( \text{SN}_1 \) CB

\[
\ce{Co(NH_3)_5Cl^2+ \rightleftharpoons Co(NH_3)_4(NH_2)Cl^+ + H^+} \\
\ce{Co(NH_3)_4(NH_2)Cl^+ \rightarrow Co(NH_3)_4(NH_2)^{2+} + Cl^-} \\
\ce{Co(NH_3)_4(NH_2)^{2+} + H_2O \rightarrow Co(NH_3)_5(OH)^{2+}}
\]

B. Acid Catalysis

\[
\ce{H^+ + Co(NH_3)_5F^{2+} \rightleftharpoons Co(NH_3)_5(HF)^{3+}} \\
\ce{Co(NH_3)_5(HF)^{3+} \rightarrow Co(NH_3)_5^{3+} + HF} \\
\ce{Co(NH_3)_5^{3+} + H_2O \rightarrow Co(NH_3)_5(H_2O)^{3+}}
\]

Example from PS #5 Basolo,
Chelation Effects

relative rate of hydrolysis

\[
\begin{align*}
[\text{Co(NH}_3\text{)}_5\text{Cl}^2+] & \quad 100 \\
[\text{Co(en)}_2(\text{NH}_3\text{)}\text{Cl}]^2+ & \quad 21 \\
[\text{Co(tetraen)}(\text{NH}_3\text{)}\text{Cl}]^2+ & \quad 10 \\
[\text{Co(dien)}(\text{en})\text{Cl}]^2+ & \quad 7.8 \\
[\text{Co(tetraethylenepentaamine)}\text{Cl}]^2+ & \quad 3.8 \\
\end{align*}
\]

\[
\text{trans-}[\text{Co(AA)}_2\text{Cl}_2]^+ + \text{H}_2\text{O} \rightarrow \text{trans-}[\text{Co(AA)}_2\text{Cl(}\text{H}_2\text{O})]^2+ \\
\text{AA} \quad \text{kobs s}^{-1} \\
\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \quad 3.2 \times 10^{-5} \\
\text{NH}_2\text{CH(Me)}\text{CH}_2\text{NH}_2 \quad 6.2 \times 10^{-5} \\
\text{NH}_2\text{CH(Me)}\text{CH(Me)}\text{NH}_2 \quad 42 \times 10^{-5} \\
\text{NH}_2\text{C(Me)}_2\text{C(Me)}_2\text{NH}_2 \quad \text{over on mixing}
\]

Rate Coefficients $k_{n+(n-1)}$ (sec$^{-1}$) for the Aquation of $[\text{Cr(NH}_3\text{nW}_{6-n}]^{3+}$ in Nitrate and Perchlorate Media at 40$^\circ$.

<table>
<thead>
<tr>
<th></th>
<th>&gt;0.1 M HNO$_3$</th>
<th>1.0 M HClO$_4$</th>
<th>ratio</th>
</tr>
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<tr>
<td>$k_{6-5}$</td>
<td>1.4E-6</td>
<td>1.4 E-6</td>
<td>1</td>
</tr>
<tr>
<td>$k_{5-4}$</td>
<td>2.5 E-5</td>
<td>1.3 E-5</td>
<td>19</td>
</tr>
<tr>
<td>$k_{4c-3}$</td>
<td>2.8 E-5</td>
<td>6.1E-7</td>
<td>~ 46</td>
</tr>
<tr>
<td>$k_{4t-3}$</td>
<td>2.8 E-4</td>
<td>1.2 E-6</td>
<td>233</td>
</tr>
<tr>
<td>$k_{1-0}$</td>
<td>2.5 E-6</td>
<td>7.6 E-9</td>
<td>330</td>
</tr>
</tbody>
</table>

Data in HNO$_3$ make no sense because something fishy is going on.

Nitrate exchanges with water - reduced + charge labilizes NH$_3$.

Max effect is with nitrate cis to leaving group - chelation stabilizes intermediate.

In HClO$_4$ trend is that as the better donor NH$_3$ is replaced by water, the remaining NH$_3$’s are more tightly held.
$\Delta V^*$ + for D
-for A
solvation
effects may complicate matters for charged ions

similar for $\Delta S^*$

**Figure 7.** Volume changes accompanying ligand substitution reactions assuming a negligible change in volume of the first coordination sphere of the complex.
Square Planar Substitution in Pt(II)

Two term rate law

\[ \text{rate} = k_S \, [\text{Pt}] + k_Y \, [\text{Pt}] \, [Y] \]

Associative mechanism

- solvent attack path

\( k_S \) is independent of \( Y \)

\( k_Y \) depends on nucleophilicity of \( Y \), direct attack

*Figure 13. trans directing effect rationalized within the general accepted associative process on square-planar complexes.*
$k_{obs} = k_S + k_Y [Y]$

Intercept = $k_S$

slope = $k_Y$

Nucleophilicity

$\text{SCN}^- > I^- > \text{RSH} > \text{Br}^- > \text{N}_3^- > \text{NO}_2^-$

soft bases (polarizable) are the best nucleophiles.

$10^5 X$ $k_{obs}$ vs. $10^{-2}$ $[Y]$ for $\text{Pt(py)}_2\text{Cl}_2 + Y^-$ in methanol

Basolo JACS 87, 241 (1965).
A Bio-Inorganic Example. Myoglobin

While the pentacoordinate intermediate Co(NH$_3$)$_5$ cannot be detected in water, hemoproteins nicely illustrate the classic D mechanism, a pentacoordinate Fe(II) heme is seen in the X-ray structure of deoxy Myoglobin.

O$_2$ binds to the vacant coordination site on Fe in a bent geometry. CO binds to the same site in a linear geometry.
Kinetic data for O\(_2\) and CO binding is obtained by stopped-flow and flash methods. Equilibria can be computed from the rate data or independently by measuring the visible spectrum at various pressures of CO and O\(_2\).

\[
\text{Mb} + \text{CO} \rightleftharpoons \text{MbCO}
\]

\[
K_{\text{CO}} = \frac{[\text{MbCO}]}{[\text{Mb}] [\text{CO}]}
\]

rate \( f \) = \( k_{+\text{CO}} [\text{Mb}] [\text{CO}] \)

rate \( r \) = \( k_{-\text{CO}} [\text{MbCO}] \)

\[
k_{+\text{CO}} = 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}
\]

\[
k_{-\text{CO}} = 0.017 \text{ s}^{-1}
\]

\[
K_{\text{CO}} = 3 \times 10^7 \text{ M}^{-1}
\]

\[
K = k_{+}/k_{-}
\]

\[
\text{Mb} + \text{O}_2 \rightleftharpoons \text{MbO}_2
\]

\[
K_{\text{O}_2} = \frac{[\text{MbO}_2]}{[\text{Mb}] [\text{O}_2]}
\]

rate \( f \) = \( k_{+\text{O}_2} [\text{Mb}] [\text{O}_2] \)

rate \( r \) = \( k_{-\text{O}_2} [\text{MbO}_2] \)

\[
k_{+\text{O}_2} = 1.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}
\]

\[
k_{-\text{O}_2} = 11 \text{ s}^{-1}
\]

\[
K_{\text{O}_2} = 1.27 \times 10^6 \text{ M}^{-1}
\]
Flash Photolysis - Gibson technique for MbCO or FeN₄LCO

note that \( k_{+O_2} \) is 24 X larger than \( k_{+CO} \) while \( K_{CO} \) is 23 X larger than \( K_{O2} \)

pentacordinate intermediate

\[
\text{FeN}_4\text{L(CO)} \rightleftharpoons \text{FeN}_4\text{L} \rightleftharpoons \text{FeN}_4\text{L(O}_2)\]

hv

FeN₄L rapidly adds O₂ (microsec) and then slowly (millisecs) reverts back to the CO complex via a classic D mechanism. (steady state neglecting \( k_{-co} \))

\[
k_{obs} = k_{-O_2} k_{+CO} [CO] / \{k_{+O_2} [O_2] + k_{+CO} [CO] \}
\]

rate constants are obtained from plot of 1/kobs vs [O₂]/[CO].
Kinetics of CO Dissociation

$$\text{FeN}_4(\text{PY})(\text{CO}) + \text{PY} \rightarrow \text{FeN}_4(\text{PY})_2 + \text{CO}$$

$$k_{\text{obs}} = \frac{k_{-\text{CO}}k_{+\text{PY}}[\text{PY}]}{k_{+\text{PY}}[\text{PY}] k_{+\text{CO}}[\text{CO}]}$$