PROBLEM SET #7: Reactions of Transition Metal Complexes

1. From Shriver + Atkins:
   Problems 7.10, 14.1, 14.6, 14.7 [Note: for 14.6, focus on a potential mechanism for the reaction, not the complications involving the activation enthalpy.]

2. Explain the following observations about square planar complexes (a, b, and c).

   (a) d⁶ Au(III) complexes typically react about 10⁴ times as fast as Pt(II) complexes. The following data (in aqueous solution) are representative:

   \[
   \text{[M(dien)Cl]}^{n+} + \text{Br}^- \rightarrow \text{[M(dien)Br]}^{n+} + \text{Cl}^-
   \]

<table>
<thead>
<tr>
<th>M</th>
<th>n</th>
<th>(k_1(\text{sec}^{-1}))</th>
<th>(k_2(M^{-1}\text{sec}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1</td>
<td>8.0x10⁻⁵</td>
<td>3.3x10⁻³</td>
</tr>
<tr>
<td>Au</td>
<td>2</td>
<td>0.5</td>
<td>154</td>
</tr>
</tbody>
</table>

   The Au and Pt complexes have the same square planar structure and the same d⁶ electron configuration. Why are their rates of ligand substitution so different?

   (b) The reactivity of [Au(dien)Cl]²⁺ and [Pt(dien)Cl]⁺ toward anions increases in the order OH⁻ << Br⁻ < SCN⁻ < I⁻. Explain these observations.

   (c) The replacement of chloride in [Au(Et₄dien)Cl]²⁺ by anions Y⁻ is independent of [Y⁻]. The rate constant (25 °C) increases with pH from \(k = 1.9x10^{-6}\) to a maximum of \(1.3x10^{-4}\) sec⁻¹. Explain these observations.

   Base hydrolysis is a well-known reaction of octahedral complexes and is generally about 10⁶ times faster than acid hydrolysis. From your answers to parts a-c, decide if a related base hydrolysis mechanism is also important for square planar complexes, and explain your answers.

3. Assign an outer-sphere or inner-sphere mechanism for each of the following reactions, and explain your answers.

   (a) The main product of reaction of [Cr(H₂O)₆]³²⁺ with [Cr(H₂O)₄(NCS)F]⁺ is [CrF(H₂O)₅]²⁺.

   (b) When [VO(edta)]³²⁻ reacts with [V(edta)]²⁻ a transient red color is observed. [Hint: this suggests formation of a short-lived intermediate.]

   (c) Rates of reduction of [Co(NH₃)₅(py)]³⁻ by [Fe(CN)₆]⁴⁺ are insensitive to substituents on the pyridine (py) ligand. In particular, when the pyridine ring contains potentially bridging substituents like an amide group, the reduction rate does not change significantly.

   (d) [Co(NH₃)₅(NCS)]²⁺ is reduced by [Ti(H₂O)₆]³⁺ 36,000 times slower than is [Co(NH₃)₅(N₃)]²⁺.

   (e) Activation parameters for reduction of [Co(NH₃)₅Br]²⁺ by [V(H₂O)₆]²⁺ are \(\Delta H^\ddagger = 30.1\) kJ/mol and \(\Delta S^\ddagger = -115\) J/Kmol.
4. Assign an inner-sphere or outer-sphere mechanism for the following reactions, and draw out the details of the reaction sequence:

(a) Note that the Co(III) starting material is substitution inert, while the Fe(II) reactant is substitution labile, and the Co(II) product is substitution labile, while the Fe product is substitution inert.

\[
\begin{align*}
&\text{[Co(NH}_3\text{)_6\text{]}^{3+} + [\text{Fe(CN)}_5(\text{OH}_2)]^{3-} \rightarrow [\text{Co(OH}_2\text{)}_6^{2+} + [\text{Fe(CN)}_5(\text{OH}_2)]^{2-}},
\end{align*}
\]

(b) Note that the Co starting material is substitution inert, while the Fe(II) reactant is substitution labile.

\[
\begin{align*}
&\text{[Co(NH}_3\text{)_6\text{]}^{3+} + [\text{Fe(CN)}_5(\text{OH}_2)]^{3-} \rightarrow [\text{Co(OH}_2\text{)}_6^{2+} + [\text{Fe(CN)}_5(\text{OH}_2)]^{2-}},
\end{align*}
\]