

**Chem 315, Fall 2001**  
**Answers to Problem Set #8**

**14.3.** The collapse of the triplet corresponds to the exchange of the  $\text{PEt}_3$  ligand with excess  $\text{PEt}_3$ . When the exchange of the ligand is quick the Hydride doesn't distinguish between the cis and trans ligands and the signal collapses. The mechanism is dissociate. If the other ligand was attached before losing one, there would be a more complex signal in the NMR.

**14.7.** Mechanism looks like the base hydrolysis (check p.483 of your textbook). The reaction of the complex  $\text{Co}(\text{NH}_3)_5\text{OH}]^{2+}$  is much faster because it is accelerated by  $\text{OH}^-$  ligands with acidic protons present. In the case of Co complexes the entering group is  $\text{H}_2\text{O}$  molecule and not an  $\text{OH}^-$  ion (the latter acts as a Brønsted acid, and not as an entering group). As for the Ru complexes, they most likely to have an outer-sphere mechanism. *Since the explanation in the book is not great, points were not taken off.*

**14.9.** Use the Markus equation to calculate the constants:

$k^2 = f k_1 k_2 K$  where  $K = e^{-EF/RT}$ , The following answers are calculated with  $T = 298\text{K}$ , if you used  $273\text{K}$  you answers will still be counted right.

- $k = 8.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ , differs greatly from the experimentally observed rate constant;
- $k = 1.72 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ , matches fairly well to the observed;
- $k = 7.36 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ , fair matching;
- $k = 1.26 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ , calculated number is larger than the observed one.

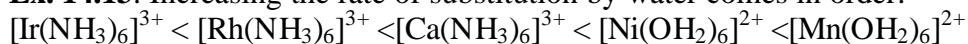
**Ex. 14.1.**

- $\text{NH}_3$  – nucleophile;
- $\text{Cl}^-$  - nucleophile;
- $\text{Ag}^+$  + electrophile;
- $\text{S}^{2-}$  - nucleophile;
- $\text{Al}^{3+}$  - nucleophile.

**Ex. 14.3.**

- cis? trans – addition of  $^{36}\text{Cl}^-$ . Stoichiometric mechanism;
- D replaces H in amine ligands, also causing the reducing of rate of displacement of NCS-by  $\text{H}_2\text{O}$ . Intimate mechanism.

**Ex. 14.13.** Increasing the rate of substitution by water comes in order:



Since  $\text{NH}_3$  gives the stronger than water ligand field, and  $\Delta_o$  increases on descending a group in a d-block.

**Ex. 16.3.**

- $\text{Fe(III)}$ ;
- $\text{Fe(0)}$ ;
- $\text{Fe(-II)}$ ;
- $\text{Co(0)}$ .

**Ex. 16.4**

16.1 a)  $18e^-$  b)  $18e^-$  c)  $18e^-$  d)  $18e^-$  e)  $17e^-$  f)  $16e^-$

16.3 a)  $17e^-$  b)  $18e^-$  c)  $18e^-$  d)  $18e^-$