

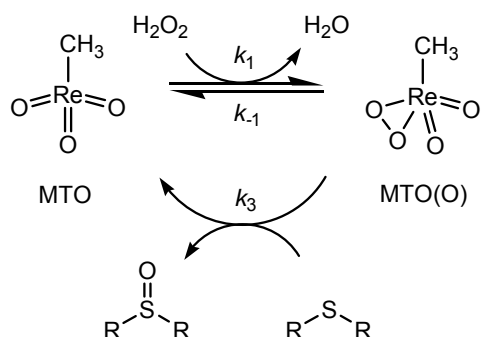
**Problem Set 4****Due:** *In class, Friday, October 20*

1. The *order* of the decomposition of  $(\text{H}_2\text{O})_5\text{CrO}_2^{2+}$  ion in water appears to depend on the concentration of the ion. At low concentration, the rate of decomposition is first-order in  $[(\text{H}_2\text{O})_5\text{CrO}_2^{2+}]$ , but at high concentration, the rate appears to be second-order in  $[(\text{H}_2\text{O})_5\text{CrO}_2^{2+}]$ .
- a) Three kinetics runs, in which the concentration of  $(\text{H}_2\text{O})_5\text{CrO}_2^{2+}$  was measured with respect to time, are included in a datafile posted on the web. (For these runs,  $[(\text{H}_2\text{O})_5\text{CrO}_2^{2+}]_0 = 1 \times 10^{-6} \text{ M}$ ,  $1 \times 10^{-4} \text{ M}$ , and  $1 \times 10^{-2} \text{ M}$ .) Fit each graph to the integrated rate expression for first- and second-order kinetics. Which graphs fit which model best, and what rate constants  $k_{1\text{st}}$  and  $k_{2\text{nd}}$  are returned by the fits? (Your second-order rate constant may or may not include a factor of 2, depending on how you wrote your second-order rate law. Make sure this is clear in your answer.)
- b) The kinetics of this process should be expressible in terms of a single rate law. Write a single differential rate law for  $-\partial[(\text{H}_2\text{O})_5\text{CrO}_2^{2+}]/\partial t$  that describes the reaction in terms of both first- and second-order kinetics (and two different rate constants  $k$ ). Then, integrate this into an integrated rate law. It may help you to use the following standard integral form:

$$\int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln \frac{a+bx}{x}$$

- c) Fit your single integrated rate expression to the three kinetics runs to obtain values for  $k_{1\text{st}}$  and  $k_{2\text{nd}}$ .

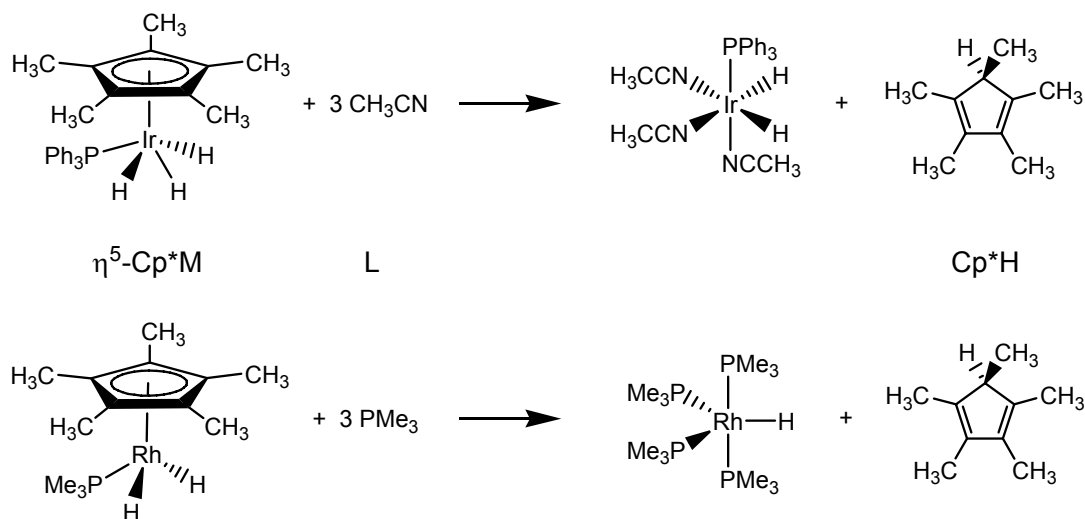
2. The complex methyltrioxorhenium (MTO) catalyzes the oxidation of sulfides to sulfoxides by  $\text{H}_2\text{O}_2$  according to the mechanism shown below.



This reaction is run in  $\text{H}_2\text{O}$ , so  $[\text{H}_2\text{O}]$  can be considered constant (55.6 M, in significant excess) for any rate expression that contains it.

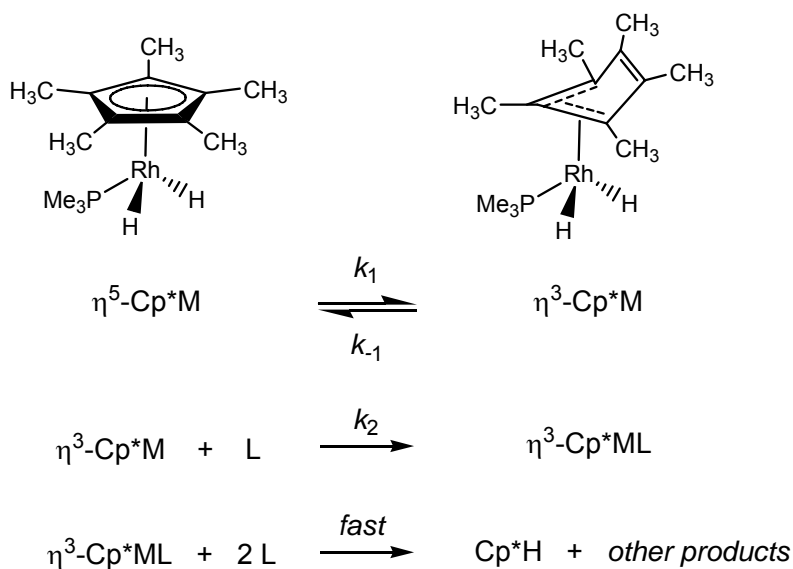
- Assuming that the complex MTO(O) is a *steady-state* intermediate, derive the rate law for sulfoxide formation via the mechanism above. Because the total concentration of rhenium catalyst species does not change over the course of the reaction, you should express your law in terms of  $[\text{Re}]_{\text{T}} = [\text{MTO}] + [\text{MTO(O)}]$ .
- Derive the rate law for sulfoxide formation in terms of  $[\text{Re}]_{\text{T}}$  assuming that  $k_3$  is rate-determining and that there is a rapid *pre-equilibrium* between MTO and MTO(O).
- The rate laws for situations (a) and (b) should be different. How would you experimentally determine which rate law is correct? What experiment(s) would you perform, and under what conditions? What would be the anticipated results, and how would you analyze them?

3. Cp\* (pentamethylcyclopentadienyl) ligands are displaced from both Cp\*Ir and Cp\*Rh hydride complexes in the presence of added, excess ligand:

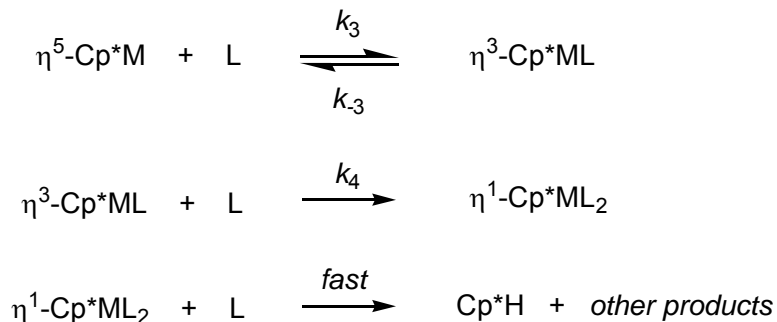


Both reactions follow pseudo-first-order kinetics with respect to the starting metal complex (excess CH<sub>3</sub>CN or PMe<sub>3</sub>, respectively). Two mechanisms can be envisioned for both reactions that involve ligand assisted "slippages" of the initially η<sup>5</sup>-Cp\* ligand to η<sup>3</sup>, η<sup>1</sup>, and ultimately η<sup>0</sup> (fully decomplexed) forms:

Mechanism I:



Mechanism II:



- a) Write full rate laws for these two reaction mechanisms. For Mechanism I, assume that  $\eta^3\text{-Cp}^*\text{M}$  is a steady state intermediate, and that every molecule of  $\eta^3\text{-Cp}^*\text{ML}$  is immediately converted to product (i.e., that  $\partial[\text{Cp}^*\text{H}]/\partial t = \partial[\eta^3\text{-Cp}^*\text{ML}]/\partial t$  from the second step). For Mechanism II, assume that  $\eta^3\text{-Cp}^*\text{ML}$  is a steady state intermediate, and that every molecule of  $\eta^1\text{-Cp}^*\text{ML}_2$  is immediately converted to product (i.e., that  $\partial[\text{Cp}^*\text{H}]/\partial t = \partial[\eta^1\text{-Cp}^*\text{ML}_2]/\partial t$  from the second step).
- b) What do these expressions reduce to when  $k_2[\text{L}] \gg k_1$  or  $k_4[\text{L}] \gg k_3$ ?
- c) The concentration of  $\eta^5\text{-Cp}^*\text{M}$  was monitored over time for a number of kinetics runs in which  $1.0 \times 10^{-4} \text{ M } \eta^5\text{-Cp}^*\text{Rh}$  or  $\eta^5\text{-Cp}^*\text{Ir}$  was mixed with different amounts of ligand (always in excess, such that  $[\text{L}]_t = [\text{L}]_0$ ). Data from these runs is posted on the course website. Based on your answers from parts (a) and (b), which of the two mechanisms above more appropriately describe the decomposition of  $\eta^5\text{-Cp}^*\text{Ir}$  and  $\eta^5\text{-Cp}^*\text{Rh}$ ? (The same or different mechanisms for each?)
- d) Calculate  $k_1$  and the ratio  $k_2/k_1$  for whichever reaction is described by Mechanism I.