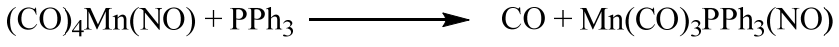
Recommended Reading: 23, **29** (3rd edition); **22**, **29** (4th edition)

Ch 102 – Problem Set 7
Due: Thursday, June 1 – *Before Class*

Problem 1 (1 points)

Part A

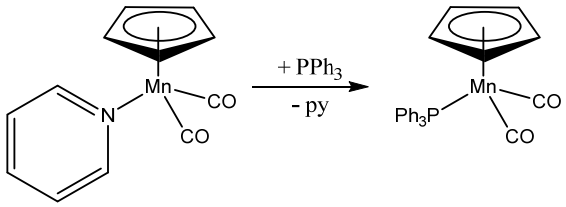


Kinetics experiments studying the above reaction determined that the rate law was second order overall and first order in both [PPh_3] and [$(CO)_4Mn(NO)$]. Additionally, an intermediate species was observed during the course of the reaction that was characterized as $(CO)_4Mn(NO)PPh_4$. Using this information, propose a mechanism for above reaction and predict the sign and magnitude of the entropy of activation ($\Delta S^{\ddagger}$).

In writing your mechanism be sure to assign formal oxidation states, d-electron counts and valence electron counts for all transition metal species and identify the rate limiting step. Describe the nature of Mn-NO bonding for the reactant, product and intermediate Mn species.

Part B

The following ligand substitution reaction where PPh_3 replaces the pyridine ligand on (η^5-Cp)Mn(py)$(CO)_2$ proceeds slowly even in the presence of large excesses of PPh_3 in refluxing toluene (110 °C). However, if a catalytic amount of the one electron oxidized compound [(η^5-Cp)Mn(py)$(CO)_2$]$^+$ is added to the reaction mixture, the rate of ligand substitution increases dramatically.



1. Assign oxidation states, d-electron counts and valence electron counts for (η^5-Cp)Mn(py)$(CO)_2$, [(η^5-Cp)Mn(py)$(CO)_2$]$^+$, and (η^5-Cp)Mn$(PPh_3)(CO)_2$.
2. Propose mechanisms for both the uncatalyzed and catalyzed reactions. Be sure to include how the catalyst interacts with the starting material and how it is regenerated in your mechanism.
3. Use your answers to 1 and 2 to explain how/why the addition of the catalyst leads to rate enhancement.
4. Draw a reaction energy diagram for the catalyzed and uncatalyzed reactions based on the mechanisms you have proposed. Be sure to indicate ΔG^{o} and $\Delta G^{\ddagger}$ for each reaction and how they relate to each other.

Problem 2 (3 points)

The 1950's was the golden age of radiochemistry. Access to radioactive isotopes synthesized in particle accelerators allowed chemists to track the progress of a reaction. The Calvin cycle was deduced from data obtained using ^{14}C radiolabeling! The kinetics of the chemical reaction below was also followed using isotopes.

For this problem, consider the self-exchange reaction of $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$ (* =radiolabel). The counter-anion in all cases is the non-coordinating perchlorate $[ClO_4]^-$ anion.

$$[V(H_2O)_6]^{2+} + [V^*(H_2O)_6]^{3+} \rightarrow [V(H_2O)_6]^{3+} + [V^*(H_2O)_6]^{2+}$$

a) Determine the d-electron count of each species. Assign each species as inert or labile with respect to ligand substitution.

b) From the two limiting mechanisms of electron transfer presented in class, which mechanism would you expect to be operative? Why?

The experimental rate law that could be consistent with either mechanism is shown below.

$$\text{Rate} = k_{obs}[V^{II}][V^{III}]$$

c) The rate is not affected by variation of proton concentration above 0.5 M $[H^+]$. Below 0.5 M $[H^+]$, the rate of the reaction was shown to depend on $[H^+]$. Using the data shown below, derive a rate expression that incorporates the effect of $[H^+]$.

Hint: $\text{Rate} = (k_1 + k_2[H+]^n)[V^{II}][V^{III}]$

$[H^+]$ (M)	k_{obs}, (M^{-1} min^{-1})
0.500	1.03
0.400	1.14
0.300	1.31
0.250	1.45
0.200	1.66
0.150	2.01
0.125	2.29
0.100	2.71

d) Providing an appropriate plot of the data shown above, determine the values of k_1 and k_2.

e) The temperature dependence of the rate was studied at 1 M [H^+]. From the data shown below, deduce the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Determine the standard Gibbs free energy of activation $\Delta G^{\ddagger}$. Estimate the value of λ.

T (K)	k ($M^{-1}min^{-1}$)
313	2.0
298	0.8
286	0.3
273	0.1

f) Propose a mechanistic scheme that accounts for the kinetics data described above (note that the rate law has both proton dependent and proton independent terms). For the proton dependent mechanism, discuss why neither of the two limiting mechanisms of electron transfer can be ruled out based on the kinetics alone. Use your chemical intuition to evaluate the mechanisms by answering the following questions. Which oxidation state metal center do you expect to be more likely to be involved in the proton transfer process (evaluate in the context of pK_a of coordinated water molecules)? For the species that you favor for deprotonation, do you expect the resulting deprotonated product to be thermodynamically more or less prone to undergo the redox reaction (by an outer sphere mechanism)? Based on the bridging abilities of various ligands, do you favor a particular electron transfer mechanism for the proton dependent path?

g) Rate constant k_2 is a composite of rate and/or equilibrium constants. Based on your proposed mechanism for the proton dependent process, provide an expression of k_2 in terms of those elementary steps. If this mechanism involves a ligand substitution, assume that the substitution proceeds via a dissociative mechanism, for simplicity.

h) Maintaining 1 M [H^+], further experiments show that the identity of the counter-anion affects the rate of the reaction. For example, addition of chloride results in an increase in the rate that depends linearly with [Cl^-]. Provide a new rate expression and propose a mechanism consistent with this observation.

i) At 1 M [H^+], the self-exchange reaction of $[Cr(H_2O)_6][ClO_4]_{(2 \text{ or } 3)}$ is [H^+] independent, and k_1 is three orders of magnitude slower than the V analog. Considering the electronic structure of both Cr species, explain the decrease in rate.

$$[Cr(H_2O)_6]^{2+} + [Cr^*(H_2O)_6]^{3+} \rightarrow [Cr(H_2O)_6]^{3+} + [Cr^*(H_2O)_6]^{2+}$$

j) At lower [H^+] concentrations, the self-exchange reaction of $[Fe(H_2O)_6][ClO_4]_{(2 \text{ or } 3)}$ is [H^+] dependent in a similar manner to part c), but k_2 is three orders of magnitude faster than the V analog. Considering the electronic structure of both Fe species, explain the increase in rate. Assume that mechanism of the Fe complex is the same as for V, as derived in parts f) and g).

$$[Fe(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+}$$

Problem 3 (1 point)

A key result of Marcus theory is that the reaction barrier can increase when the reaction becomes too highly exergonic. One of the first experimental studies to test this was carried out in the 80s by Miller, Calcaterra, and Closs. They synthesized a class of organic compounds consisting of a biphenyl electron donor and variable acceptor tethered by a rigid aliphatic steroid scaffold (Figure 1).

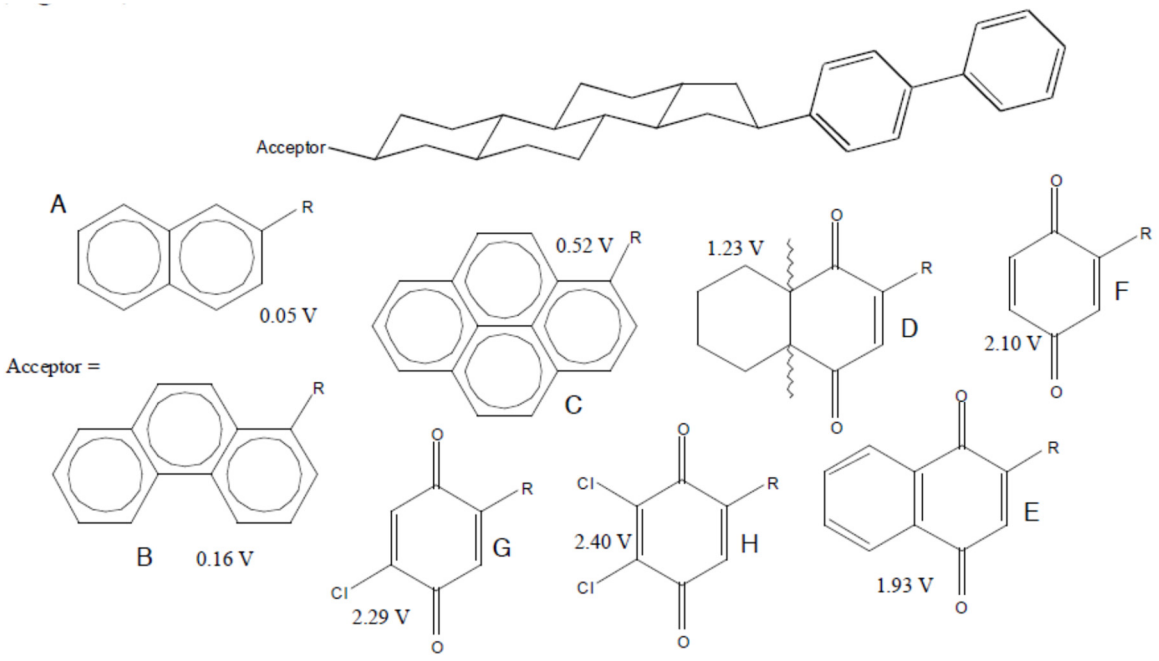
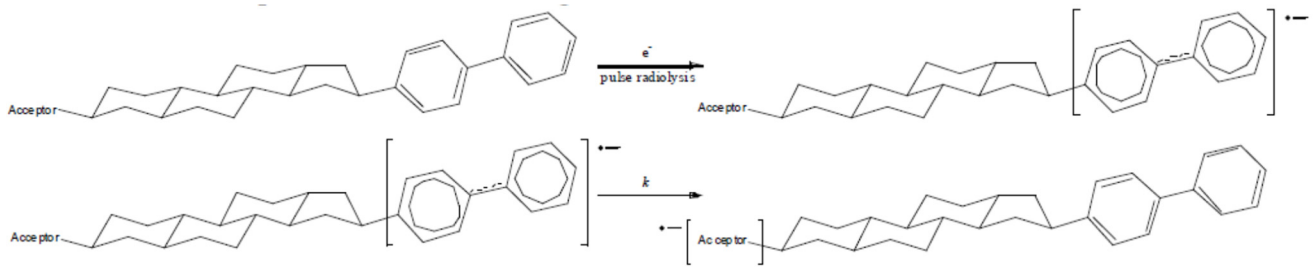


Figure 1. Donor-acceptor molecule, acceptor groups and standard reduction potentials (E°; A is hardest to reduce, H is easiest).

Pulse radiolysis generates a biphenyl radical anion in the donor region. The rate of electron transfer to the acceptor was measured (Figure 2).



Fgure 2. Electron transfer measurements.

A graph showing electron transfer rate versus thermodynamic favorability for each of the donor-acceptor pairs is given below. A trendline is also given, confirming the presence of an inverted region, as predicted by the Marcus theory.

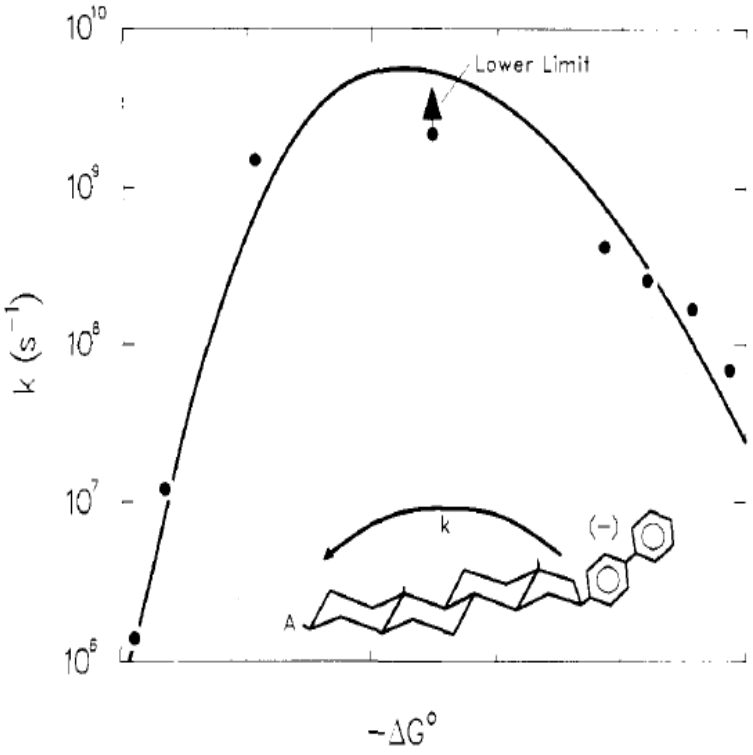
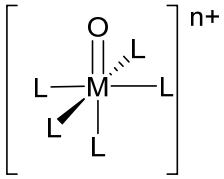


Figure 3. Marcus plot.

a) Assign each point on figure 3 to the corresponding acceptor.
b) Indicate clearly the location of the Marcus inverted region in figure 3.
c) Which acceptor gives an activation energy closest to zero?
d) Which acceptor gives the most thermodynamically favorable electron transfer? Does it lie in the Marcus Inverted Region?
e) Draw a qualitative plot of the activation energy versus -ΔG°.

Problem 4 (1 point)

Typically, transition metal ions in aqueous solutions are coordinated by water molecules. Binding to a Lewis acidic metal center increases the acidity of the water ligand such that one or two protons can be lost, producing hydroxo or oxo ligands. The metal−oxo motif is a common intermediate in the biological activation of dioxygen and subsequent oxidation of organic substrates. MO diagrams may help us elucidate the chemistry of metal−oxo species. Toward this end, provide the following:



a) Provide a full MO diagram of a generic metal−oxo complex shown above by taking into account only σ−interactions. Assume that L is a neutral σ−only donor of lower electronegativity than oxygen (z axis along the M−O bond, and x,y axes along equatorial M−L bonds). Label each MO with Mulliken symbols and assign them as σ, σ*, or nb. Populate the MO diagram for a Mo^{V}−oxo species. Draw a box around the orbitals of d−parentage.

b) Taking into account the π−*basicity* of oxo ligands, generate a partial MO diagram between the metal d−orbitals and the two oxygen p−orbitals. Label each resulting MO as σ, σ*, π, π*, or nb. Sketch all orbitals.

c) Predict the M−O bond order for $[VOL_5]^{3+}$, $[CrOL_5]^{3+}$, $[MnOL_5]^{3+}$, $[MnOL_5]^{2+}$, $[FeOL_5]^{2+}$.

d) Using your MO diagrams, explain why Fe^{IV}−oxo species are more reactive with respect to oxygen transfer reactions than the V^{IV} analog.

e) $[CoOL_5]^{2+}$ is not known. Provide an explanation.

Problem 5 (2 points)

The chemical reactivity of dioxygen with organic molecules at ambient temperatures is low and oxygen does not spontaneously oxidize most organic compounds in the absence of a catalyst (if this were not the case, we would have to worry about oxygen spontaneously oxidizing us). The low kinetic reactivity of dioxygen stems from its triplet ground state; that is, dioxygen has two unpaired electrons in two degenerate π* orbitals (draw the MO diagram if this is not clear). Most stable organic molecules, however, are in singlet states with all of their electrons paired, and hence display low reactivity toward dioxygen. Although singlet states of oxygen are known, the lowest energy singlet state is significantly higher in energy than the triplet state (22.5 kcal/mol) and is not easily accessible. Oxygenases are a class of enzymes that are able to bind and activate triplet oxygen leading to oxygenation of organic molecules. Cytochrome P450 is a well-studied type of oxygenase. The transition metal ion (Fe^{II}) in this protein is bound by a porphyrin and is able to bind triplet dioxygen and activate it toward incorporation into organic substrates.

Lewis dot structures of the Fe-heme complex and O_2 may help clarify the movement of electrons throughout the catalytic cycle for the oxidation of an organic substrate with dioxygen.

a) Draw the cytochrome P450 cycle for oxygen activation and insertion into R–H as was shown in class (NOTE: you do not need to draw rigorous Lewis dot structures for this part and the Fe complex may be abbreviated as in class)

b) Draw the Lewis dot structure for O_2

c) Draw a Lewis dot structure for the Fe-dioxygen adduct that forms upon coordination of O_2 to Fe-cytochrome P450 (NOTE: The Fe–O–O bond angle is ~120°). Draw "dots" only for oxygen.

d) Draw a resonance form of the Fe-O_2 complex that changes the oxidation state of Fe and puts a negative charge on an oxygen atom. This is an Fe-superoxide species.

e) The reaction mechanism for cytochrome P450 involves a one-electron reduction of the Fe-superoxide species. If this electron transfer were slow, what would be a possible competing side reaction, leading to a reactive and potentially detrimental side-product?

f) Draw a Lewis dot structure for the Fe-hydroperoxide complex resulting from the addition of a proton and an electron to the Fe-superoxide species.

g) Addition of a second proton to the Fe-hydroperoxide complex generates an Fe-oxo species upon loss of H_2O. If this proton delivery step were slow, what would be a possible competing side-reaction?

h) Based on what you learned in class, what is the ultimate electron source for the cytochrome P450 catalytic cycle?

Problem 6 (2 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, electron count, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, you are now expected to include some molecular orbital pictures / MO diagram analysis / IR/Raman analysis). Attach a printout of the slides to your solution of the problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as "FirstName_LastName_PSET#" and include your name on the first slide.