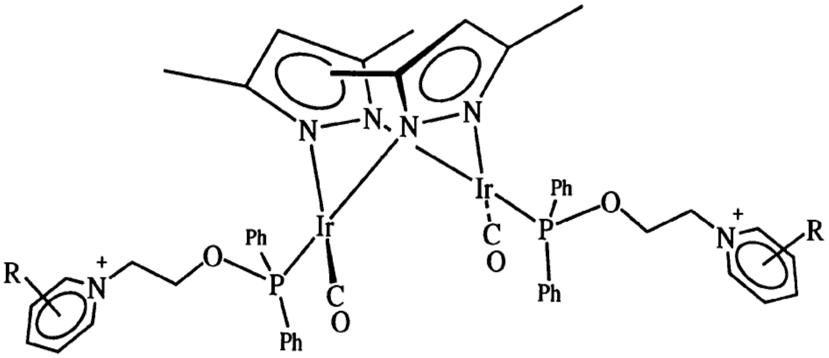
Chemistry 153a
Winter 2019
Due 13 March, 2019

Problem Set 9

1. Fox and coworkers (*Science* **1990**, *247*, 1069-1071) reported the kinetics of electron transfer in a series of Ir dimers of the following type:

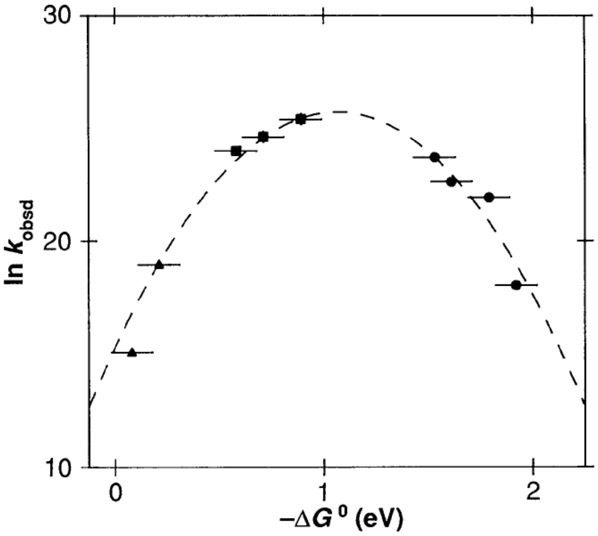


A plot of the driving force dependence of the rates is shown below, and a data table is shown on the following page.

Semiclassical electron-transfer theory predicts that intramolecular rates can be described by the following equation:

$$k_{ET} = \sqrt{\frac{4\pi^3}{h^2\lambda RT}} H_{AB}^2 \exp\left\{-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda RT}\right\}$$

On the basis of the electron transfer rate data, determine the value of H_{AB} for this series of complexes. Predict the positions, extinction coefficients, and widths of the Ir→(R–py)$^+$ charge transfer absorption bands for the four Ir compounds used in this study.



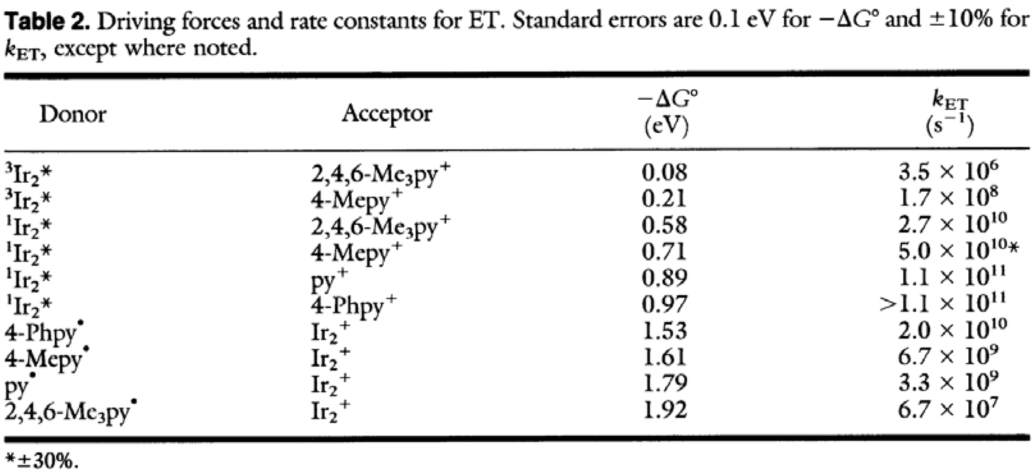
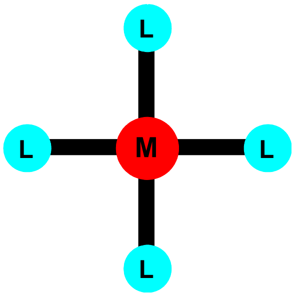


Table 2. Driving forces and rate constants for ET. Standard errors are 0.1 eV for $-\Delta G°$ and ±10% for k_{ET}, except where noted.

Donor	Acceptor	$-\Delta G°$ (eV)	k_{ET} (s^{-1})
$^3Ir_2$*	2,4,6-Me_3py^+	0.08	3.5×10^6
$^3Ir_2$*	4-$Mepy^+$	0.21	1.7×10^8
$^1Ir_2$*	2,4,6-Me_3py^+	0.58	2.7×10^{10}
$^1Ir_2$*	4-$Mepy^+$	0.71	5.0×10^{10}*
$^1Ir_2$*	py^+	0.89	1.1×10^{11}
$^1Ir_2$*	4-$Phpy^+$	0.97	$>1.1 \times 10^{11}$
4-$Phpy^{\bullet}$	Ir_2^+	1.53	2.0×10^{10}
4-$Mepy^{\bullet}$	Ir_2^+	1.61	6.7×10^9
$py^{\bullet}$	Ir_2^+	1.79	3.3×10^9
2,4,6-$Me_3py^{\bullet}$	Ir_2^+	1.92	6.7×10^7

*±30%.

2. Consider a binuclear metal complex constructed from two square-planar ML_4 fragments where the L ligands are σ-donors. There are two limiting conformations in the resulting M_2L_8 complex: in one the ligands are eclipsed and in the other they are staggered.



   a) Draw the two conformations of the binuclear metal complex and assign each to a symmetry point group.

   b) Construct an MO diagram for each conformation using the following orbitals: five M *d* orbitals and four L σ orbitals. Assume that M-L σ-bonding is quite strong.

   c) Assume that ML_4 has a d^4 electron configuration, and that each ligand L contributes two σ electrons.

      i. Predict the preferred ground-state conformation of the corresponding M_2L_8 complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

      ii. Identify the spin-allowed electronic transitions involving the *d*-orbitals, determine the term symbols for the excited states, and predict the relative energy ordering of these states.

      iii. Predict the lowest-energy electric-dipole-allowed transition. Also, predict the polarization of light that will induce the transition.

   d) Assume that ML_4 has a d^6 electron configuration, and that each ligand L contributes two σ electrons. Predict the preferred ground-state conformation of the corresponding M_2L_8 complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

   e) Assume that ML_4 has a d^7 electron configuration, and that each ligand L contributes two σ electrons.

      i. Predict the preferred ground-state conformation of the corresponding M_2L_8 complex, and give the electronic configuration and term symbol for the ground electronic state. Determine the metal-metal bond order.

ii. Identify the spin-allowed electronic transitions involving the *d*-orbitals, determine the term symbols for the excited states, and predict the relative energy ordering of these states.

iii. Predict the lowest-energy electric-dipole-allowed transition that should be M—M axis polarized.

3. The absorption spectrum of $Mn_2(CO)_{10}$ exhibits an intense absorption band at 30,000 cm^{-1}, and a lower-energy feature at 27,000 cm^{-1}. The 30,000-cm^{-1} absorption band is polarized parallel to the Mn-Mn axis, and the 27,000 cm^{-1} band is polarized perpendicular to this axis. Propose assignments for these bands based on a MO diagram for binuclear d^7-d^7 complexes.

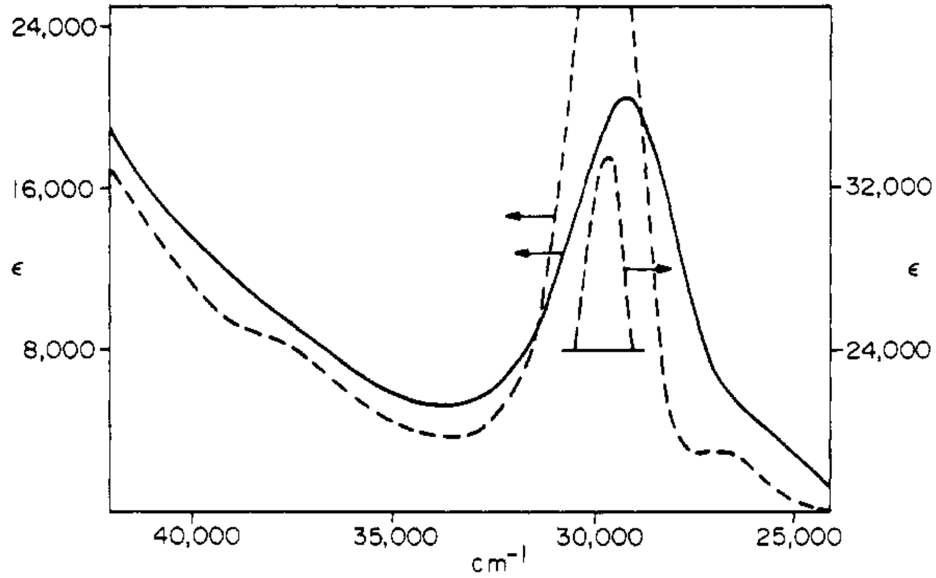


Figure 2. Electronic spectra of $Mn_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

4. Consider an oxo-bridged $[L_5MOML_5]^n$ metal complex in which each L_5MO fragment has C_{4v} symmetry.

   a) Construct MO diagrams for two likely conformations of $[L_5MOML_5]^n$ assuming $\angle$(M-O-M) = 180° using the following orbitals: two sets of five metal *d*-orbitals, ten ligand σ-orbitals, and the oxo 2*s*, 2*p*σ, and two 2*p*π orbitals.

   b) How will your MO diagrams change if $\angle$(M-O-M) $<$ 180° ?

   c) On the basis of your MO diagrams, predict the geometry of the $[Cl_5RuORuCl_5]^{4-}$ anion. Do you expect this anion to be diamagnetic or paramagnetic? What is the formal Ru-O bond order?

d) The "blue-dimer" water oxidation catalyst ($[(bpy)_2(H_2O)RuORu(OH_2)(bpy)_2]^{4+}$) can be considered a low-symmetry version of $[L_5MOML_5]^n$. Do you expect ∠(Ru-O-Ru) in the blue dimer to be less than or equal to 180° (provide an explanation for your answer)? What is the formal Ru-(μ-O) bond order?

e) The temperature dependence of the magnetic susceptibility and magnetic moment of the blue dimer are shown below. Does the magnetic behavior of this molecule agree with the prediction based on your MO model? Provide a qualitative explanation for the magnetic behavior.