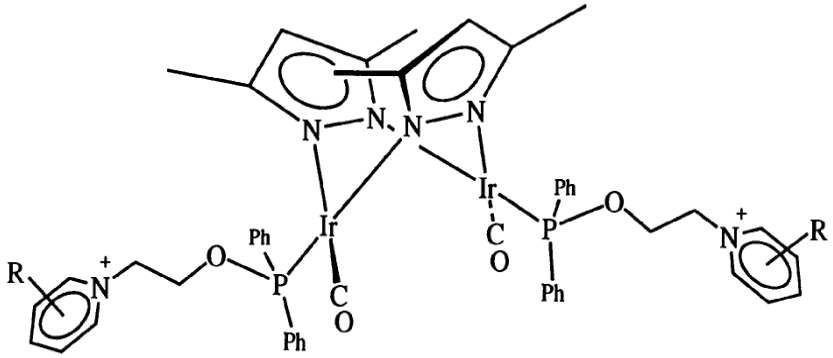
Chemistry 153a
Winter 2020
Due 21 February, 2020

Problem Set 7

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.

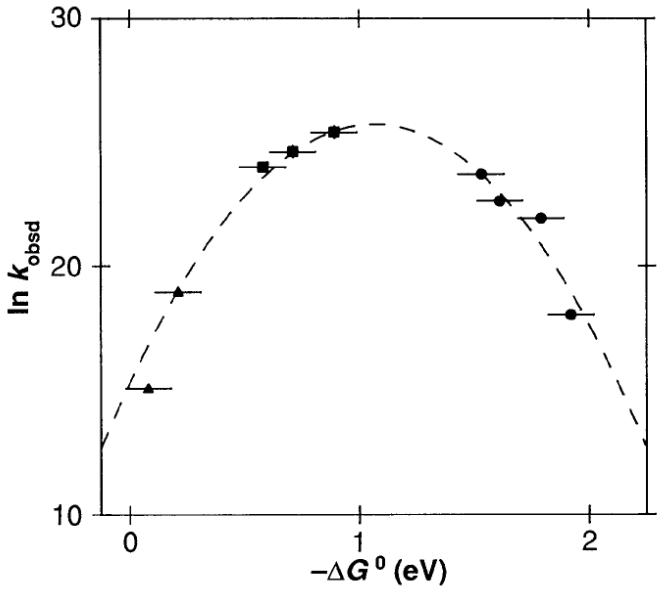


Table 2. Driving forces and rate constants for ET. Standard errors are 0.1 eV for $-\Delta G^\circ$ and ±10% for k_{ET}, except where noted.

Donor	Acceptor	$-\Delta G^\circ$ (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. The Ti(III) oxidation state is rare in terrestrial minerals due to the comparatively highly oxidizing environment on Earth. Trivalent titanium does occur in extraterrestrial materials; one example is a titanium pyroxene found in the Allende meteorite. The empirical formula for this mineral is $Ca_{1.01}Mg_{0.38}(Ti^{3+})_{0.34}(Ti^{4+})_{0.14}Al_{0.87}Si_{1.26}O_6$. The crystal structure reveals that this mineral contains chains of edge-shared distorted octahedra with $Ti^{3+/4+}$ ions at the center. The Ti-Ti distance is 3.15 Å. The polarized single-crystal absorption spectra of the Ti^{3+}-Ti^{4+} pyroxene from the Allende meteorite at different pressures are shown below (α and β refer to two different polarization directions).

   Propose assignments for the absorption bands at 14,000, 16,000, and 20,000 cm^{-1} (1 bar). On the basis of your assignments, offer explanations for the pressure dependent behavior of the three bands.