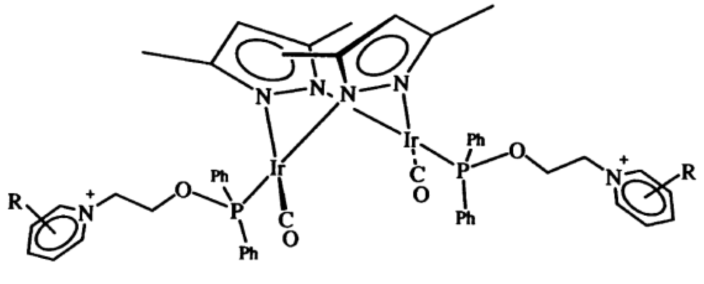
Problem Set 9
Ch 153a – Winter 2023
Due: 3 March, 2023

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 and a data table are show.

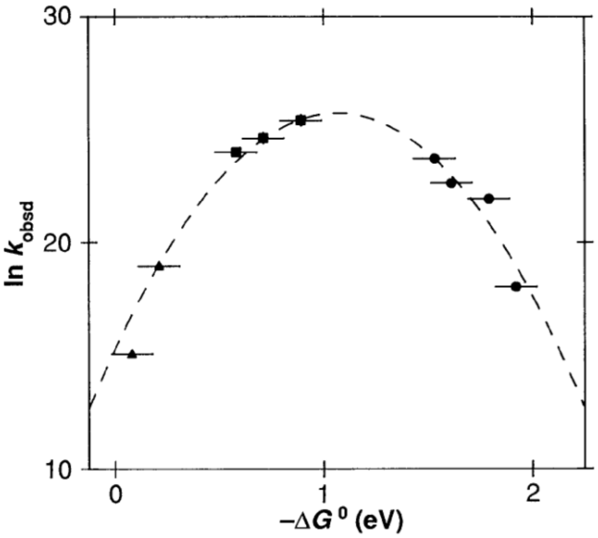


Table 2. Driving forces and rate constants for ET. Standard errors are 0.1 eV for $-\Delta G^\circ$ and ±10% for k_{ET}, except where noted.

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

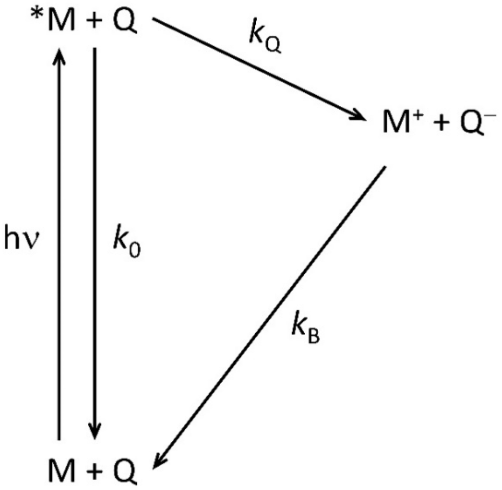
*±30%.

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, what is 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.

2. Photoinduced electron-transfer reactions that are relevant to photoredox catalysis are depicted in the following scheme:



Assume that immediately after excitation by a pulsed laser the concentration of the excited metal complex is $[{}^*M]_0$ and that $[{}^*M]_0 << [Q]$ for all quencher concentrations under consideration. In the absence of quencher *M decays back to M with rate constant k_0, and *M reacts with the quencher with a rate constant k_Q.

a. Derive a rate law for the time dependence of [*M].
b. Solve the rate law to give an expression describing the time dependence of [*M].
c. Derive an expression for the quantum yield of Q^- formation.
d. Assume that k_0 can take on the values: 1×10^9 s^{-1}; 1×10^8 s^{-1}; 1×10^7 s^{-1}; 1×10^6 s^{-1}. Assume also that k_Q can take on the values: 1×10^9 M^{-1}s^{-1}; 1×10^8 M^{-1}s^{-1}; 1×10^7 M^{-1}s^{-1}. Find the quencher concentration required to give 90% quantum yield of $[Q^-]$ for all twelve pairs of k_0 and k_Q rate constants.
e. If the quenching reaction yields a product concentration of $[Q^-]_\infty$, derive an expression for the half-time of the reaction to regenerate M and Q.