

Experiment I.¹

Excited State Electron Transfer in Transition Metal Compounds

This experiment involves a study of the fate of molecules which are promoted to electronically excited states by the absorption of light. The excited state reactivity of ruthenium trisbipyridine, $\text{Ru}(\text{bpy})_3^{2+}$, is undoubtedly the most well studied transition metal compound in the world.² In this compound, a ruthenium metal center is chelated by three 2,2'-bipyridine ligands in an octahedral geometry, Figure 1. The orange color of this compound results from metal-to-ligand charge transfer, MLCT, transitions. Upon light absorption, an electron is formally transferred from the $\text{Ru}(\text{II})$ metal center to one of the bipyridine ligands, Equation I. The excited state can relax to the ground state non-radiatively or radiatively in the form of photoluminescence.

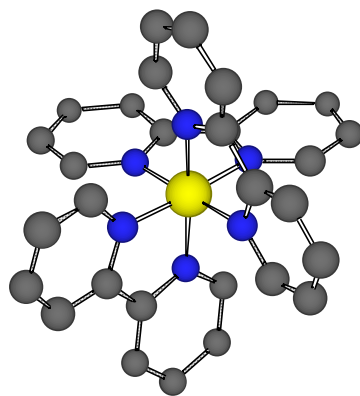


Figure 1.

The broad MLCT absorbance provide good overlap with the solar spectrum reaching our earth. A vast research effort around the world is devoted to exploring the photophysical properties of $\text{Ru}(\text{bpy})_3^{2+}$, it's derivatives, and related compounds based on $\text{Re}(\text{I})$ and $\text{Os}(\text{II})$. The excited states of $\text{Ru}(\text{bpy})_3^{2+}$ and it's derivatives undergo a wide variety of electron and energy transfer processes. Many of these processes involve important catalytic reactions like the splitting of water into hydrogen and oxygen.² There is also a

major theoretical impetus to understand excited state electron and energy transfer processes.³

In this experiment, you will explore the optical properties of ruthenium trisbipyridine by obtaining absorption, excitation and photoluminescence spectra in aqueous solution. You will then examine excited state electron transfer reactions to ions in solution. An electron transfer rate from $\text{Ru}(\text{bpy})_3^{2+*}$ excited states to Cu^{2+} will be calculated and compared to theory.

Hazards.

Sulfuric Acid (CAS No. 7664-93-9): Sulfuric acid is extremely corrosive. It is also a strong oxidizing and dehydrating agent.

Ruthenium (II) tris(2,2'-bipyridine) chloride (CAS No. 14898-67-0): This compound is harmful if swallowed, inhaled or absorbed through the skin. IPR-RAT LD50: 360 mg/kg.

Copper(II) sulfate pentahydrate (CAS No. 20919-8): This compound is not normally considered dangerous, but the usual precautions should be taken. ORL-RAT LD50: 300 mg/kg, ORL-HMN LDLo: 1088 mg/kg.

Avoid skin contact with the aqueous solutions, ruthenium and copper salts.

Experimental Procedure.

An aqueous stock solution of approximately 10^{-3} M $\text{Ru}(\text{bpy})_3(\text{Cl})_2$ in 0.5 M H_2SO_4 will be provided. The precise molarity and source will be provided.

Begin by preparing a series of 6 solutions which have a constant $\text{Ru}(\text{bpy})_3^{2+}$ concentration of $\sim 10^{-5}$ M, varying Cu^{2+} concentrations from 0.00 to 0.20 M in 0.5 M H_2SO_4 . For the 6 solutions the $[\text{Ru}(\text{bpy})_3^{2+}]$ must be constant. It is not important what the $[\text{Cu}^{2+}]$ concentrations are as long as you know them precisely and they fall within the above range. Once you analyze your data, you may want to repeat the measurements with a few other Cu^{2+} concentrations.

Place a ~ 3 mL aliquot of the $\sim 10^{-5}$ M $\text{Ru}(\text{bpy})_3(\text{Cl})_2$ solution you prepared in a polystyrene cuvette. In a separate cuvette place a 3 mL aliquot of 0.5 M H_2SO_4 . Obtain an absorption spectrum from 300 to 600 nm on a UV/Vis spectrometer. Assign the MLCT absorbance.

Hold the Ru(II) containing cuvette in front of a black light and observe the color of the photoluminescence. Place this sample in the fluorometer and record both a photoluminescence and excitation spectrum. The photoluminescence spectrum is obtained by setting the excitation monochromator to 450 nm and scanning the detection

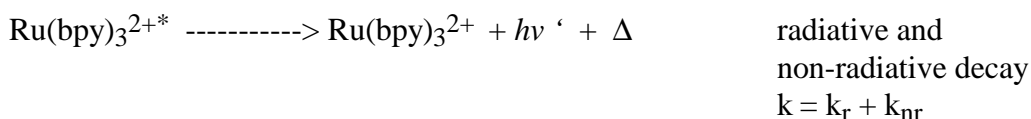
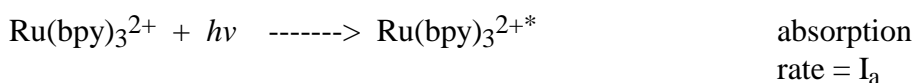
monochromator from 500 to 800 nm. The excitation spectrum is obtained by setting the detection monochromator at the wavelength of maximum photoluminescence intensity and scanning the excitation monochromator from 350 to 550 nm.

Finally, record the photoluminescence spectrum of each of the seven solutions on the same relative scale. It may be worthwhile to record the spectra on top of each other by rewinding the plotter paper.

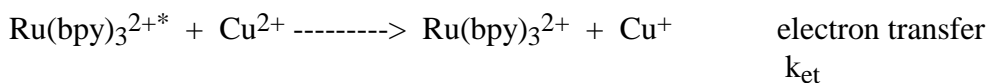
Data Analysis.

A. Calculation of Electron Transfer Rate by Stern-Volmer Analysis.

The excitation and photoluminescence may be written as:



If an electron transfer quencher is present, such as Cu^{2+} , another deactivation path exists:



We can then write:

$$d[\text{Ru}(\text{bpy})_3^{2+*}]/dt = I_a - k[\text{Ru}(\text{bpy})_3^{2+*}] - k_{et}[\text{Ru}(\text{bpy})_3^{2+*}][\text{Cu}^{2+}]$$

Applying the steady-state approximation to $[\text{Ru}(\text{bpy})_3^{2+*}]$ so that $d[\text{Ru}(\text{bpy})_3^{2+*}]/dt = 0$, we have:

$$[\text{Ru}(\text{bpy})_3^{2+*}] = I_a / (k + k_{et}[\text{Cu}^{2+}])$$

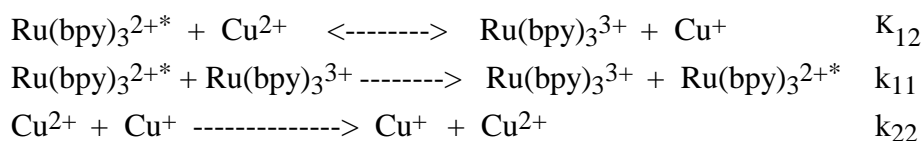
The photoluminescence intensity I is proportional to $[\text{Ru}(\text{bpy})_3^{2+*}]$. Let I_0 be the photoluminescence intensity when no Cu^{2+} is present, $[\text{Cu}^{2+}] = 0$. Under the conditions of the experiment $[\text{Cu}^{2+}] \gg [\text{Ru}(\text{bpy})_3^{2+*}]$ so that $[\text{Cu}^{2+}]$ is approximately constant throughout the experiment. Therefore,

$$I_0/I = (k + k_{et}[\text{Cu}^{2+}]) / k = 1 + [\text{Cu}^{2+}] (k_{et}/k), \quad \text{II}$$

and a plot of I_0/I versus $[Cu^{2+}]$ yields a straight line of slope k_{et}/k . This is known as a Stern-Volmer plot. Under the conditions of your experiment $k \sim 2 \times 10^6 \text{ s}^{-1}$.

B. Calculation of Electron Transfer Rate by Marcus Theory.

The electron transfer process studied in this experiment is an example of an outer-sphere reaction, one in which there is little interaction between the oxidant and the reductant at the moment of electron transfer. Dr. R. Marcus, who one the 1992 Nobel prize in chemistry, developed a theory by which the electron transfer rate constant, k_{et} (k_{12}) may be calculated from the equilibrium constant K_{12} of the overall reaction, and the self-exchange coefficients k_{11} and k_{22} which relate to the transfer of an electron between the oxidized and reduced forms of the same species:



The required relation is then:

$$k_{et} = k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad \text{III}$$

K_{12} may be calculated from the electrode potentials using the relation:

$$\Delta E^{\circ} = -\Delta G/nF = (RT/nF) \ln K_{12} \quad \text{IV}$$

where n is the number of electrons transferred and F is Faraday's constant.

Marcus has shown that:^{3b,c}

$$\log f = (\log K_{12})^2 / 4 \log (k_{11}k_{22}/Z^2) \quad \text{V}$$

where the collision frequency factor Z may be taken as $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution at 25 C. Also for $Cu^{2+}(aq)/Cu^+(aq)$: $k_{22} = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and $E^{\circ} = 0.16 \text{ V}$; and for $Ru(bpy)_3^{2+*}/Ru(bpy)_3^{3+}$: $k_{11} = 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $E^{\circ} = -0.84 \text{ V}$.

Compare the experimental and calculated values of k_{et} . The rate constant for diffusion controlled electron transfer by Cu^{2+} is $\sim 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

Current Research Efforts

The goal of the Dr. Meyer's research is to efficiently harvest solar energy.⁴ Research toward this goal has focused on studying the excited state reactivity of charge

transfer compounds, similar to the one you studied today, in solution and in the solid state. Major research efforts exist throughout the world with the goal of mimicking photosynthesis and producing solar energy conversion devices. Many researchers have focused on charge transfer compounds related to $\text{Ru}(\text{bpy})_3^{2+}$,⁵ while many others have designed systems, more similar to nature based on porphyrins and quinones.⁶

Finally, the role of electron transfer is central to chemistry. There exists major research efforts to understand molecular level electron transfer from an experimental and theoretical point of view. The 1992 Nobel Prize in chemistry was awarded to Dr. R. Marcus at the California Institute of Technology for his work on the theory of electron transfer processes.

References

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