

Electron Transfer Quenching of Nonemitting Excited States of Ru(TPP)(py)₂ and Ru(trpy)₂²⁺

Roger C. Young, Jeffrey K. Nagle, Thomas J. Meyer,* and David G. Whitten

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. Received September 1, 1977

Abstract: Neither Ru(TPP)(py)₂ (TPP is tetraphenylporphine; py is pyridine) in DMF nor Ru(trpy)₂²⁺ (trpy is 2,2',2''-terpyridine) emits measurably at room temperature in solution using conventional detection methods. However, evidence for short-lived excited states has been obtained in both cases by flash photolysis experiments in the presence of high concentrations of redox quenchers. Flash photolysis of DMF solutions of Ru(TPP)(py)₂ in the presence of Ru(NH₃)₆³⁺ gives Ru(TPP)(py)₂⁺ and Ru(NH₃)₆²⁺ during the flash and their back reaction was followed directly, k_b (22 ± 2 °C) = 1.2 × 10⁹ M⁻¹ s⁻¹ at $I = 0.3$. Similarly, Ru(trpy)₃³⁺ and Fe(H₂O)₆²⁺ are produced by flash photolysis of solutions containing Ru(trpy)₂²⁺ and Fe(H₂O)₆³⁺. Excited state lifetimes have been estimated by a flash photolysis technique in which the concentrations of redox products generated during the flash are measured as a function of quencher concentration. The experiment gives the Stern-Volmer constant for the quenching step, K_{sv} , and if quenching rate constants are known or can be estimated, estimates for excited state lifetimes can be made. The lifetime of Ru(bpy)₃^{2+*} in 1.0 M HClO₄-H₂O at 26 °C obtained using this technique (565 ± 43 ns) is in good agreement with the value in the same medium obtained by luminescence decay measurements (620 ± 20 ns). The estimated lifetime for the excited state of Ru(trpy)₂²⁺ which undergoes electron transfer quenching is $\tau_0 \geq 1.2 \pm 0.2$ ns at 26 °C in HClO₄-H₂O. The observations reported here suggest that the redox chemistry of metal complex excited states may be far more extensive than previously thought. They also suggest that there may be some interesting features in the excited state structures of Ru(TPP)(py)₂ and Ru(trpy)₂²⁺.

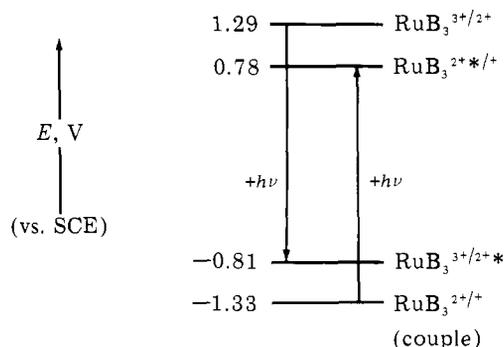
All molecular electronic excited states are potential redox reagents. Light absorption leads to excitation of an electron to a higher level where it is more weakly bound, and at the same time to an electron hole in a lower level. Following the lead of Weller and of Mataga and their co-workers, it is now accepted that a readily available reaction pathway for many organic excited states is electron transfer quenching.^{1,2} The quenching of metal complex excited states by bimolecular electron transfer to an acceptor or from a donor has also been demonstrated and exploited to a number of ends.³⁻¹⁵ The most notable example is the use of the strongly luminescent charge transfer (CT) excited state of Ru(bpy)₃^{2+*} (bpy is 2,2'-bipyridine).

Ru(bpy)₃^{2+*} has been shown to undergo both oxidative and reductive quenching by a combination of luminescence quenching and flash photolysis experiments.³⁻¹⁵ The formal reduction potential for the excited state couple, Ru(bpy)₃^{3+/2+*}, has been estimated to be -0.81 V (vs. the saturated sodium chloride calomel electrode in 0.1 M [N(C₂H₅)₄](ClO₄) at 22 ± 2 °C) by a quenching study using a series of nitroaromatic compounds.¹⁶ Potentials for the ground state couples Ru(bpy)₃^{3+/2+} and Ru(bpy)₃^{2+/+} are also known.^{5,17} Ru(bpy)₃⁺ can be generated by constant-potential electrolysis, and its properties are consistent with the added electron being in a π^* (bpy) level.^{5,17b}

The effects of optical excitation on the redox properties of Ru(bpy)₃²⁺ are shown in the redox potential diagram in Scheme I. From the diagram, both the oxidizing (RuB₃^{2+*} + e⁻ → RuB₃³⁺) and reducing (RuB₃^{2+*} - e⁻ → RuB₃³⁺) properties of the system are enhanced in the excited state by the excited state energy (2.10 V). Reduction potential diagrams such as the one in Scheme I provide a convenient summary of the thermodynamic properties of excited states as redox reagents and clearly suggest the possible use of excited states in energy conversion processes based on light-driven electron transfer reactions.

It is obviously desirable to see if the redox chemistry found for Ru(bpy)₃^{2+*} can be extended to new types of chemical systems. Electron transfer quenching has been shown to occur for a series of CT excited states involving polypyridine complexes,^{8,12} for f-f excited states,⁸ and for π - π^* excited states of porphyrins.^{8,18} The work in this areas has so far relied on emitting excited states, which is reasonable since the observation of luminescence gives direct evidence for the existence

Scheme I. Formal Reduction Potentials in Acetonitrile ($I = 0.1$ M; 22 ± 2 °C)



of the excited state and provides a convenient means for measuring rates and excited state lifetimes. However, the absence of a detectable emission does not preclude the possibility of observing electron transfer to or from an excited state. As shown by the properties of many organic triplet states in solution, even in the absence of an easily detectable emission, excited state lifetimes can be relatively long.¹⁹ At high quencher concentrations it should be possible to quench even short-lived excited states if they are capable of undergoing facile electron transfer.

Experimental Section

The salts [Ru(bpy)₃](ClO₄)₂ and [Ru(trpy)₂]Cl₂ (trpy is 2,2',2''-terpyridine) were prepared as described previously.^{20a} A sample of Ru(TPP)(py)₂ was kindly provided by Dr. Fred Hopf. [N(*n*-C₄H₉)₄](ClO₄) (TBAP) (G. F. Smith) was recrystallized from hot ethanol and dried in a vacuum desiccator. [Ru(NH₃)₆]Cl₃ (Matthey-Bishop, Inc.) was converted into the perchlorate salt by dissolving the chloride salt in 0.01 M HClO₄-H₂O and adding a fivefold excess of NaClO₄. The perchlorate salt, which precipitated immediately, was collected, recrystallized from 0.10 M HClO₄, washed with ethanol and then ether, and stored in a vacuum desiccator. (*Caution: Perchlorate ammine complexes of ruthenium are explosive.*) Water was distilled twice from alkaline permanganate. ACS certified DMF (Fisher Scientific), ferric and ferrous perchlorates (G. F. Smith), and 70% perchloric acid (J. T. Baker ACS reagent) were all used without further purification.

Flash Photolysis Measurements. The laser flash photolysis appa-

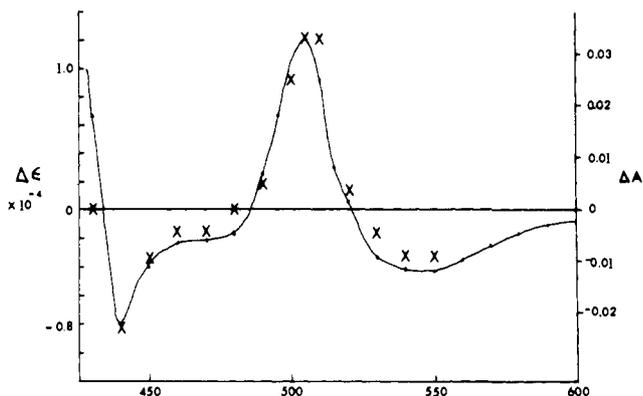


Figure 1. Difference spectrum (solid line) calculated from the absorbance spectra of $\text{Ru}(\text{TPP})(\text{py})_2$ and $\text{Ru}(\text{TPP})(\text{py})_2^+$ and (x) obtained from the differences in absorbance before flash photolysis and at 100 μs after the flash. $[\text{Ru}(\text{TPP})(\text{py})_2] = 2 \times 10^{-6} \text{ M}$, $[\text{Ru}(\text{NH}_3)_6]^{3+} = 0.05 \text{ M}$ in 0.01 M $[\text{N}(n\text{-C}_4\text{H}_9)_4](\text{ClO}_4)\text{-DMF}$ at $22 \pm 2^\circ \text{C}$.

ratus using a Moletron 400 nitrogen laser²¹ and the conventional microsecond flash photolysis apparatus^{21,22} have both been described in detail. For the conventional flash experiment, photolysis was limited to the visible region ($\lambda > 410 \text{ nm}$) using Corning 3-73 glass filters. A Xenon Corp. FP10 flash tube, a 10- μF capacitor, and a voltage of 3.5 or 4.0 kV were used in the experiments. The flash lamp pulse times (full width-half maximum) at these voltages were ~ 12 and 18 μs , respectively. Optical cells (12 cm) were used. Solutions were deaerated by bubble degassing using serum caps and syringe needles and solvent-saturated, purified nitrogen or argon. In experiments involving the short-lived excited states of $\text{Ru}(\text{trpy})_2^{2+}$ and $\text{Ru}(\text{TPP})(\text{py})_2$, the same results were obtained in deaerated or nondeaerated solutions.

Under the conditions of the flash photolysis experiments, excitation, e.g., $\text{Ru}(\text{bpy})_3^{3+} + h\nu \rightarrow \text{Ru}(\text{bpy})_3^{2+*}$, and quenching, e.g., $\text{Ru}(\text{bpy})_3^{2+*} + \text{Fe}^{3+} \rightarrow \text{Ru}(\text{bpy})_3^{3+} + \text{Fe}^{2+}$, occur during the flash giving redox products at low concentration levels. The subsequent, back thermal electron transfer reactions, e.g., $\text{Fe}^{2+} + \text{Ru}(\text{bpy})_3^{3+} \rightarrow \text{Fe}^{3+} + \text{Ru}(\text{bpy})_3^{2+}$, are observed after the flash but on a slower time scale (0.1–10 ms) with the exception described below. In experiments where rate constants for the back reactions were measured, intensity changes were followed at fixed wavelengths using Hewlett-Packard Model 184 or Tektronix Model 7514 storage oscilloscopes. Photographs of the oscilloscopic traces were taken and the data plotted assuming either second-order, equal concentration kinetics, $1/\Delta A$ vs. t , or first-order kinetics, $\ln(\Delta A)$ vs. t . ΔA is related to the measured intensity change ΔI at time t (in mV) by the Beer's law expression $\Delta A = \log(1 + \Delta I/I_0)$ where I_0 is the intensity prior to the flash (which is also the intensity at the end of the reaction since the system is photochromic). Kinetic plots from which rate data were taken were linear for at least 2–3 half-lives. Rate constants were calculated from the slopes of the plots where for a first-order reaction, slope = k , and for a second-order reaction, slope = $k/b\Delta\epsilon$. b is the cell path length and $\Delta\epsilon$ the molar extinction coefficient difference between reactants and products at the wavelength used. For the determination of rate constants, an average value from the results of at least three flashes was used.

For product yield studies and for the determination of difference spectra, I_0 before and ΔI after the flash were measured and ΔA_{max} ($= A_0 - A_\infty$) was calculated from $\Delta A_{\text{max}} = \log(1 + \Delta I_{\text{max}}/I_0)$. The back reactions are relatively slow and ΔI_{max} was found to be constant for the interval 100–1000 μs following the flash. On time scales much longer than 1 ms, the back reactions could be followed directly. An exception occurred in the quenching of $\text{Ru}(\text{trpy})_2^{2+*}$ at high Fe^{3+} concentrations. It had been reported earlier that the presence of small amounts of Fe^{2+} in Fe^{3+} stock solutions was sufficient so that following quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ by Fe^{3+} , the back reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and Fe^{2+} did not follow second-order, equal-concentration kinetics.⁴ At the high concentrations of Fe^{3+} (0.1–0.01 M) used in the quenching of $\text{Ru}(\text{trpy})_2^{2+*}$, the apparent ΔI value was observed to decrease following the flash because of the high concentrations of Fe^{2+} present in the Fe^{3+} stock solutions. The true time-independent value of (ΔI_{max}) arising from quenching during the flash could be determined by measuring ΔI immediately following completion of the flash ($\sim 100 \mu\text{s}$) since the observed decay during this time was

insignificant. However, the decay was significant over periods of a few hundred microseconds, and the pseudo-first-order rate constants calculated were of the expected relative magnitudes based on the amount of Fe^{3+} (and hence Fe^{2+}) present in the solutions. The amount of Fe^{2+} present, calculated from $k' = k[\text{Fe}^{2+}]$ where k' is the pseudo-first-order rate constant and k is the equal concentration, second-order rate constant ($= 9.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) was less than 1% of the concentration of Fe^{3+} , but was still in excess by about 350 times the concentration of $\text{Ru}(\text{trpy})_2^{3+}$ present.

The output of the flash lamp was found to be constant to within $\pm 20\%$ for a series of flashes. In order to minimize changes from experiment to experiment, the results obtained following several flashes were averaged and the same flash lamp was used throughout. Since it is necessary to measure and compare absorbance changes for a series of solutions it is also essential that the arrangement of the flash cell in the optical train be held fixed from experiment to experiment.

ΔI values were read directly from the oscilloscope, and the values used were the averages of at least six flashes. As shown in the Results section, the kinetic analysis used for the determination of K_{sv} requires a plot of $1/(\ln(D_{\text{T}}/D_{\text{a}}))$ vs. $1/[\text{Fe}^{3+}]$ where D_{T} is the total concentration of D before the flash, D_{a} is the concentration of D immediately after the flash, and D refers to the light absorber. Since $D_{\text{a}} = D_{\text{T}} - C$ where C ($= \Delta A_{\text{max}}/\Delta\epsilon b$) is the maximum concentration of the redox intermediates, it follows that $\ln(D_{\text{T}}/D_{\text{a}}) = -\ln(1 - (\epsilon\Delta A_{\text{max}}/\Delta\epsilon A_0))$. The ratios $\epsilon/\Delta\epsilon$ for $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{trpy})_2^{2+}$ were calculated from the known spectra of the $\text{Ru}(\text{II})$ and $\text{Ru}(\text{III})$ complexes.²⁰ A_0 is the absorbance at the observed wavelength before the flash and was measured in 10-cm optically matched cells in a Bausch and Lomb Model 210 UV spectrophotometer. Both $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ are essentially transparent in the visible where the absorbance changes were measured. The concentration of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ was determined spectrophotometrically using known extinction coefficients at 240 and 260 nm.²³

Emission Measurements. Solutions of $\text{Ru}(\text{TPP})(\text{py})_2$ in DMF and $\text{Ru}(\text{trpy})_2^{2+}$ in water (both at $1.0 \times 10^{-5} \text{ M}$) were bubble degassed in 1-cm square fluorescence cells. Neither excitation at 400 nm for $\text{Ru}(\text{TPP})(\text{py})_2$ (λ_{max} for the Soret band) nor at 476 nm for $\text{Ru}(\text{trpy})_2^{2+}$ (λ_{max} for CT absorption) gave rise to a detectable emission. An Hitachi Perkin-Elmer MPF-2A spectrofluorimeter was used with a 150-W xenon arc lamp as excitation source and a Hamamatsu R446 photomultiplier tube operated at 750 V as detector. A 20-nm band-pass was used for both excitation and emission.

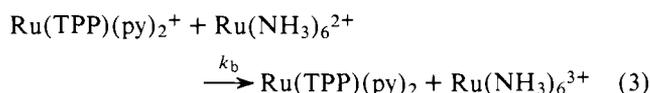
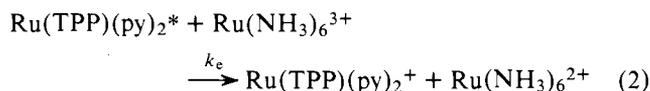
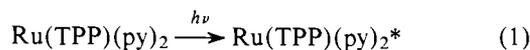
Results

Quenching of $\text{Ru}(\text{TPP})(\text{py})_2^*$ by $\text{Ru}(\text{NH}_3)_6^{3+}$. We have been unable to observe room temperature emission following visible excitation of $\text{Ru}(\text{TPP})(\text{py})_2$ (TPP is tetraphenylporphine; py is pyridine). However, visible ($\lambda > 410 \text{ nm}$) flash photolysis of a solution containing $\text{Ru}(\text{TPP})(\text{py})_2$ ($2 \times 10^{-6} \text{ M}$) and $\text{Ru}(\text{NH}_3)_6^{3+}$ (0.05 M) in 0.01 M $[\text{N}(n\text{-C}_4\text{H}_9)_4](\text{ClO}_4)\text{-DMF}$ results in transient spectral changes on the millisecond time scale. The spectral changes were found to follow second-order equal concentration kinetics (plots of $1/\Delta A$ vs. t were linear) and to give back the absorbance of the original solution. In fact, the system is photochromic even after several flashes. However, upon standing for several hours, a solution containing only $\text{Ru}(\text{NH}_3)_6^{3+}$ in DMF turns deep purple. The resulting solution has λ_{max} at 550 nm and an absorbance that rises into the infrared. Consequently, the flash photolysis data reported here were obtained on fresh solutions before the decomposition reaction was appreciable.

In Figure 1 is shown a difference spectrum showing the differences in absorbance at various wavelengths before flash photolysis of a solution containing $\text{Ru}(\text{TPP})(\text{py})_2$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ and at 100 μs after the flash. Also shown in the figure is a difference spectrum calculated from the known spectra of $\text{Ru}(\text{TPP})(\text{py})_2$ and $\text{Ru}(\text{TPP})(\text{py})_2^+$ in 0.1 M $[\text{N}(n\text{-C}_4\text{H}_9)_4](\text{ClO}_4)\text{-DMF}$. $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ in DMF are transparent in the visible. The spectra of $\text{Ru}(\text{TPP})(\text{py})_2$ and $\text{Ru}(\text{TPP})(\text{py})_2^+$ in DMF are virtually identical with the spectra reported earlier in dichloromethane.²⁴ $\text{Ru}(\text{TPP})(\text{py})_2^+$ was generated in 0.1 M TBAH-DMF by exhaustive electrolysis of $\text{Ru}(\text{TPP})(\text{py})_2$ at 0.60 V ($n = 1.0$,

where n is the number of faradays of charge passed per Ru).

The observed spectral changes are consistent with excitation of Ru(TPP)(py)₂ to an excited state (or states) (eq 1) followed by oxidative quenching (eq 2), both of which occur during the flash. Following the quenching step, the redox products formed undergo back thermal electron transfer (eq 3).



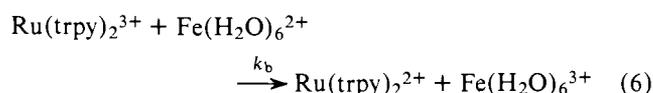
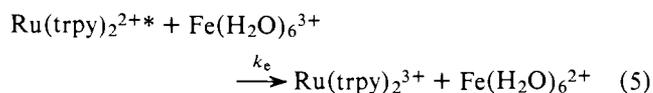
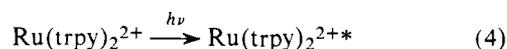
The back reaction returns the system to its initial prephotolysis state. The transient process observed by flash photolysis is reaction 3. Since the changes in absorbance vs. time follow the form expected for second-order, equal-concentration kinetics, reactions 2 and 3 are stoichiometric as written. The rate constant for the back reaction was calculated as described in the Experimental Section using $\Delta\epsilon(505 \text{ nm}) = 1.2 \times 10^4$, giving $k_b(22 \pm 2^\circ \text{C}) = 1.2 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 0.30 \text{ M}$. k_b was determined from the results of several flashes on a single sample solution.

Cyclic voltammetry experiments were carried out in 0.1 M [N(*n*-C₄H₉)₄](PF₆)-DMF in order to establish reduction potentials for the two Ru(III)/Ru(II) couples. At $22 \pm 2^\circ \text{C}$ vs. the saturated sodium calomel electrode, the values are

couple	$E_{1/2}, \text{V}$
Ru(TPP)(py) ₂ ^{+/0}	0.42
Ru(NH ₃) ₆ ^{3+/2+}	-0.20
Ru(TPP)(py) ₂ ^{0/-}	-1.63

The two Ru(III)-Ru(II) couples are reversible in DMF; $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials ($E_{1/2} = E_{p,a} - E_{p,c}/2$), and are essentially formal potentials for the two couples in the medium used. $E_{1/2}$ for the first porphyrin-based reduction in Ru(TPP)(py)₂ was also measured and is cited above.

Quenching of Ru(trpy)₂²⁺ by Fe³⁺. Again, as described in the Experimental Section, we were unable to observe a significant emission following visible excitation of aqueous solutions of Ru(trpy)₂²⁺ (trpy is 2,2',2''-terpyridine). However, transient spectral changes were observed following flash photolysis of solutions containing Ru(trpy)₂²⁺ ($2 \times 10^{-5} \text{ M}$), Fe(H₂O)₆³⁺ (0.03 M), and Fe(H₂O)₆²⁺ (2.8×10^{-4} to $1.12 \times 10^{-3} \text{ M}$) in 1.0 M HClO₄. Bleaching occurred at the absorbance maximum for Ru(trpy)₂²⁺ (476 nm) during the flash. The visible absorbance which is characteristic for Ru(trpy)₂²⁺ reappeared in a reaction which was first order and whose half-life depended directly on the concentration of added Fe(H₂O)₆²⁺. The observations made are consistent with reactions 4 and 5 occurring during the flash, followed by back electron transfer (reaction 6).

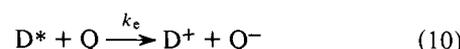
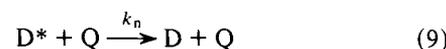
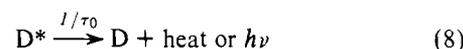


The flash experiments were carried out in the presence of added Fe(H₂O)₆²⁺ so that the rate constant for the back reaction could be obtained. As noted previously in the quenching of Ru(bpy)₃²⁺* by Fe(H₂O)₆³⁺, second-order, equal-concentration plots for the back reaction are not linear, apparently because of trace amounts of Fe(H₂O)₆²⁺ in the Fe(H₂O)₆³⁺ stock solutions.⁴ The equal concentration plots are very sensitive to slight concentration differences and since the redox products are formed in small amounts, even trace Fe²⁺ in the Fe³⁺ stock solutions could cause the observed deviations from linearity. For the experiments with added Fe(H₂O)₆²⁺, Fe²⁺ was present in pseudo-first-order excess. A plot of the observed first-order rate constants, k_{obsd} , vs. [Fe(H₂O)₆²⁺] gave a straight line consistent with the expected first-order dependence on Fe²⁺. From the slope of the plot, $k_b(20^\circ \text{C})$ was calculated to be $9.2 \pm 0.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 1.18$ ([HClO₄] = 1.0 M). The value is in reasonable agreement with the value found earlier using the stopped-flow technique ($7.2 \pm 0.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C in 1.0 M HClO₄).²⁵

Estimation of Excited State Lifetimes. For both Ru(TPP)(py)₂ in DMF and Ru(trpy)₂²⁺ in water the flash photolysis experiment provides evidence for the existence of excited states which are spectrally unobservable using conventional detection techniques. Attempts to observe the excited states directly using laser flash photolysis were unsuccessful and given the time resolution of the apparatus used ($\sim 30 \text{ ns}$),²¹ it can be estimated that both excited state lifetimes are considerably shorter than the duration of the flash.

We have developed an approach for the estimation of excited state lifetimes based on the generalized quenching scheme in reactions 7-10. It is a steady-state method in which the yield of separated redox intermediates (D⁺ and Q⁻) is measured as a function of added quencher after flash photolysis but before back electron transfer (reactions 3 and 6) can occur.

In reactions 7-10,



$1/\tau_0$ is the sum of the radiative and nonradiative rate constants for excited state decay and $k_n + k_e = k_q$ is the total bimolecular quenching rate constant. The meaning of k_n and k_e can be seen in Scheme II which uses the quenching of Ru(trpy)₂²⁺* by Fe³⁺ as the example. k_e is the rate constant for formation of separated redox products D⁺ and Q⁻ which form by redox quenching (k_1) followed by product separation (k_3). k_n includes the effects of collisional deactivation or energy transfer quenching (k_2), if they are of importance, and of back electron transfer between the redox products before they can separate in solution (k_4).

A kinetic analysis using the scheme in eq 7-10 and the steady-state assumption for [D*] gives eq 11 where the quencher [Q] is assumed to be present in large excess.²¹ The steady-state assumption for (D*) would seem to be reasonable as long as the solutions used are optically dilute (which is the

Scheme II

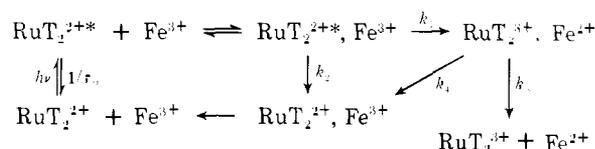


Table I. Redox Product Yields Following Flash Photolysis of Solutions Containing Ru(bpy)₃²⁺^a or Ru(trpy)₂²⁺^b and Fe(H₂O)₆³⁺ at 26 ± 1 °C

expt no.	[Fe ³⁺] × 10 ⁴	[Ru(bpy) ₃ ³⁺] × 10 ⁷ ^c	expt no.	[Fe ³⁺] × 10 ²	[Ru(trpy) ₂ ³⁺] × 10 ⁷ ^c
1	14.30	7.75	1	9.84	3.57
2	9.54	7.11	2	7.87	3.12
3	8.58	6.74	3	6.56	2.70
4	7.63	6.47	4	5.25	2.39
5	6.68	6.35	5	4.59	2.21
6	5.72	6.02	6	3.94	1.82
7	4.77	5.78	7	3.28	1.61
8	3.81	4.98	8	2.62	1.30
9	2.86	4.48	9	1.97	1.01
10	1.91	3.62	10	1.31	0.68

^a [Ru(bpy)₃²⁺] = 1.18 × 10⁻⁶ M in 1.0 M HClO₄. ^b [Ru(trpy)₂²⁺] = 1.54 × 10⁻⁶ M. The ionic strength was held constant at 0.97 by adding appropriate amounts of HClO₄. ^c [Ru(III)] observed following flash photolysis.

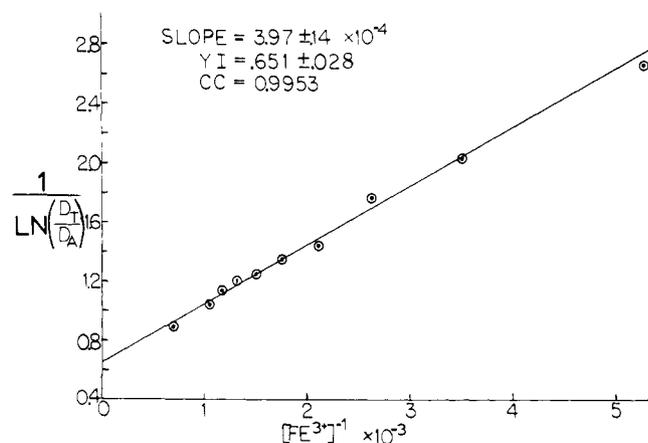


Figure 2. Plot of $(\ln [Ru(bpy)_3^{2+}]_T/[Ru(bpy)_3^{2+}]_A)^{-1}$ vs. $1/[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$ (eq 11) following flash photolysis of a series of solutions containing Ru(bpy)₃²⁺ (1.18×10^{-6} M) and varying amounts of Fe(H₂O)₆³⁺ in 1.0 M HClO₄ at 26 ± 1 °C. [Ru(bpy)₃²⁺]_T is the concentration of Ru(bpy)₃²⁺ before the flash and [Ru(bpy)₃²⁺]_A the concentration immediately following the flash. Each point represents the average of at least six flashes.

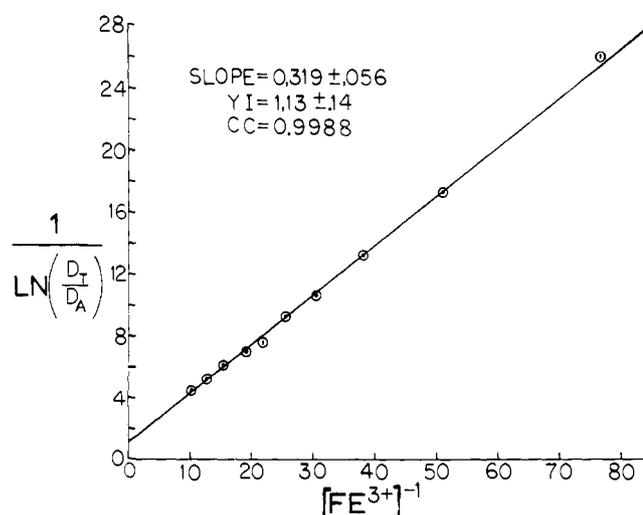


Figure 3. Plot of $(\ln [Ru(\text{trpy})_2^{2+}]_T/[Ru(\text{trpy})_2^{2+}]_A)^{-1}$ vs. $1/[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$ (see eq 11) following flash photolysis of a series of solutions containing Ru(trpy)₂²⁺ (1.54×10^{-6} M) and varying amounts of Fe(H₂O)₆³⁺ and HClO₄ (adjusted to maintain a constant ionic strength of 1.0) at 26 ± 1 °C. [Ru(trpy)₂²⁺]_T is the concentration of Ru(trpy)₂²⁺ before the flash and [Ru(trpy)₂²⁺]_A the concentration immediately following the flash. Each point represents the average of at least six flashes.

case for the experiments described here) and as long as the half-time for excited state decay ($\tau = \tau_0/(1 + k_q\tau_0[Q])$), eq 8–10) is short compared to the flash pulse width: $\sim 12 \mu\text{s}$ for the lamp used here. For example, for Ru(bpy)₃²⁺* at room temperature in 1.0 M HClO₄, $\tau_0 = 0.63 \mu\text{s}$.²¹ Even at low quencher levels where $k_q[Q]$ is small, τ is short compared to the flash lamp pulse width and the steady-state approximation remains valid.

In eq 11 D_T , the total concentration of D, is the concentration of D before the flash and D_A is the concentration of D immediately following the flash, before any back reaction between D⁺ and Q⁻ can occur. D_A can be determined experimentally by measuring the change in absorbance ΔA from before to just after the flash at a fixed wavelength. From eq 10, the redox products are formed in equal amounts, $[D^+] = [Q^-]$. If the extinction coefficient differences between D⁺ and D and Q⁻ and Q ($\Delta\epsilon$) are known, the concentration of redox products formed, C, can be calculated from the Beer's law expression $C = \Delta A/\Delta\epsilon b$ where b is the cell path length, and $D_A = D_T - C$.

$$\frac{1}{\ln\left(\frac{D_T}{D_A}\right)} = \frac{k_q}{k_e L} + \frac{1}{L k_e \tau_0 [Q]} \quad (11)$$

From eq 11, a plot of $(\ln(D_T/D_A))^{-1}$ vs. $1/[Q]$ should be linear and the intercept to slope ratio should equal the Stern-

Volmer constant, $K_{sv} = k_q\tau_0$, where k_q is the total rate constant for quenching ($= k_n + k_e$).

The constant L in eq 11 is proportional to the integrated flash lamp intensity. A single flash lamp was used for all experiments described here and its output was found to be constant to within $\pm 20\%$ during the course of our experiments. For each experiment at a given quencher concentration, an average value for D_A was calculated from the results of at least six flashes. The constant L appears in both the slope and intercept of plots of $(\ln(D_T/D_A))^{-1}$ vs. $1/[Q]$, and so data from different flash lamps could give results which appear different but give the same K_{sv} value.

In Table I are shown redox product yield data obtained following flash photolysis of solutions containing Ru(bpy)₃²⁺ and various concentrations of Fe(H₂O)₆³⁺. Similar data are also given for the extent of appearance of redox products following flash photolysis of solutions containing Ru(trpy)₂²⁺ at various concentrations of Fe(H₂O)₆³⁺. For Ru(bpy)₃²⁺, changes in absorbance were monitored at 451 nm. For Ru(trpy)₂²⁺, $\lambda = 476$ nm was the wavelength monitored.

The data in Table I for the two systems are shown plotted according to eq 11 in Figures 2 and 3. For the quenching of Ru(bpy)₃²⁺* by Fe³⁺, $K_{sv} = 1640 + 130 \text{ M}^{-1}$, which is in good agreement with the value $1810 \pm 60 \text{ M}^{-1}$ obtained earlier by emission quenching.⁸ For quenching of Ru(trpy)₂²⁺* by Fe³⁺,

$K_{sv} = 3.55 \pm 0.51 \text{ M}^{-1}$. The K_{sv} values reported for the flash photolysis experiments were determined by a weighted linear least-squares treatment of the data in Table I, which is also the origin of the estimated uncertainties.

Discussion

The most important development to appear from the results described here is the demonstration that electron transfer chemistry can be observed even from excited states which are short lived and not observable spectrally. The results suggest that metal complex excited states may have a far more extensive and accessible redox chemistry than previously thought. The essential feature in observing electron transfer quenching may lie in the ability of the excited state to undergo facile electron transfer processes and not necessarily in a long excited state lifetime. In systems having intramolecular quencher sites, on attachment to semiconductor electrodes, or in the presence of high concentrations of quencher, electron transfer quenching may become competitive with decay processes even for very short-lived excited states, including upper excited states of the light acceptor. Obvious examples are photoredox reactions which involve the solvent as electron donor or acceptor. Such processes are probably far more common than suspected and probably the origin of many of the "photooxidations" or "photoreductions" reported in the chemical literature.

Excited State Lifetimes by Redox Quenching. The appearance of redox products following flash photolysis provides a method for obtaining Stern-Volmer constants for electron transfer quenching reactions which cannot be observed by the usual luminescence or lifetime quenching techniques. With certain assumptions, the technique can be used to obtain estimates for excited state lifetimes which are far shorter than the duration of the flash. Application of the technique was "calibrated" by studying the quenching of Ru(bpy)₃²⁺* by Fe(H₂O)₆³⁺ which had been studied previously by luminescence quenching.^{4,6,8,9,12} Using the measured rate constant for quenching of Ru(bpy)₃²⁺* by Fe³⁺ in 1.0 M HClO₄ ($2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)⁸ and $K_{sv} = k_q \tau_0$ gives for the excited state lifetime $\tau_0 = 565 \pm 43 \text{ ns}$, which is in good agreement with $\tau_0 = 620 \text{ ns}$ obtained by luminescence decay measurements in the same medium.²¹

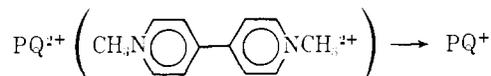
The more important point is the observation of redox products following flash photolysis of Ru(trpy)₂²⁺ in the presence of Fe³⁺. In the experiment using Ru(trpy)₂²⁺, it was necessary to use higher concentrations of Fe³⁺ than for Ru(bpy)₃²⁺ because of the shorter excited state lifetime. Even at the highest concentrations of Fe³⁺ used (0.0984 M), there is no suggestion of deviation from linearity in the plot of $(\ln(D_T/D_a))^{-1}$ vs. $1/[Q]$ in Figure 3 and quenching must be solely by diffusional quenching. The observed linearity rules out a significant contribution from quenching within a contact ion pair, eq 12, since as in the luminescence quenching Stern-Volmer experiment, a curvature in the plot would have been observed at high Fe³⁺ concentrations.



The quenching of Ru(bpy)₃²⁺* by Fe³⁺ in 1.0 M HClO₄ is at or very near the diffusion-controlled limit.^{26,27} The rate constant for quenching of Ru(trpy)₂²⁺* by Fe³⁺ must be less than or equal to this value of $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. From K_{sv} for the reaction, the lifetime of the bis-trpy excited state at $26 \pm 1 \text{ }^\circ\text{C}$ in HClO₄ must then be $\tau_0 \geq 1.2 \text{ ns}$, which is consistent with an earlier value of $\tau_0 \leq 5 \text{ ns}$ estimated by Lin et al.¹²

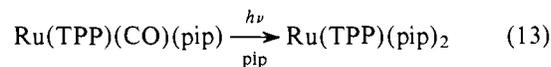
It could be argued that the experiment described here for the estimation of excited state lifetimes is superfluous given the existence of what are becoming established techniques for the direct observation of short-lived transients even on the picosecond time scale. However, the technique has the advantage

that neither significant changes in absorbance nor the appearance of an emitting excited state need exist. The necessary absorbance change can be introduced by choosing an appropriate quencher system where one of the forms is highly colored, e.g.,



and the technique may be of general value in obtaining evidence for the existence of nonemitting excited states.

The Excited States Ru(trpy)₂²⁺* and Ru(TPP)(py)₂*. Earlier work with ruthenium porphyrins has shown that complexes like Ru(TPP)(CO)(pip) (pip = piperidine) which contain an axially bound CO are luminescent and undergo simultaneous loss of CO:^{28,29}

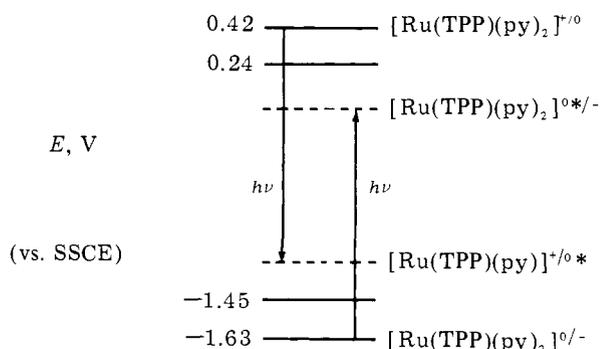


Vogler and Kunkely have studied the loss of CO quantitatively and have suggested that the luminescence observed is a typical porphyrin-based phosphorescence and that photosubstitution occurs from a higher ligand field (LF or d-d) or CT state based on the metal.³⁰ In the related iron complex Fe(TPP)(CO)(pip) and other iron-CO porphyrin complexes containing an axial base, phosphorescence is not observed, but CO is lost with high efficiency. The excited state structure may be similar to that for the Ru-CO case but with a metal-based d-d or CT state lying lower than the lowest porphyrin triplet.³⁰

An axial CO group is known to have a significant effect on the electronic structures of Fe, Ru, and Os metalloporphyrins.³¹⁻³³ Reduction potentials for couples like [Ru(TPP)(CO)(py)]^{+ / 0} are shifted positively by 0.6-0.8 V compared to couples like [Ru(TPP)(py)₂]^{+ / 0} and in the Ru complexes, the site of oxidation actually changes from Ru, Ru(TPP)(py)₂ - e⁻ → [Ru^{III}(TPP)(py)₂]⁺, to the porphyrin π system, Ru(TPP)(CO)(py) - e⁻ → [Ru^{II}(TPP⁺)(CO)(py)]⁺, when CO is present. The effect of CO has been attributed to stabilization of the largely dπ(Ru) levels by Ru → CO back-bonding. Back-bonding appears to stabilize dπ levels in the ground state to such an extent that π(porphyrin) orbitals become the lowest filled levels of the system. A greater stabilization of the ground state by back-bonding compared to stabilization of the excited state would also increase the energies of excited d-d or CT states relative to the lowest π(porphyrin) triplet and explain a porphyrin-based luminescence in Ru(TPP)(CO)(pip). Greater back-bonding in the ground state is reasonable given the t₂⁶ configuration for the ground state and the t₂⁵e and d⁵π*(L) configurations for the d-d and MLCT excited states, respectively.

The ground-state electronic structure of Ru(TPP)(py)₂ is similar to that of the Fe-CO complexes in that the lowest levels are mainly dπ(metal) in character. If the similarity is carried over into the excited state electronic structures, the lack of emission from Ru(TPP)(py)₂ may arise from the same cause, a d-d or CT state lying lower than the lowest porphyrin triplet.

The results of the redox quenching experiment using Ru(TPP)(py)₂ and Ru(NH₃)₆³⁺ only show that an excited state exists which undergoes electron transfer. K_{sv} for the quenching step was not measured by flash photolysis, so that an estimate for the lifetime of the excited state quenched is not available. It may be an upper, relatively long-lived excited state, perhaps metal or metal-pyridine (CT) in origin, which undergoes inefficient conversion to the low-lying porphyrin triplet, or, less likely, it could be an upper triplet state of the porphyrin. It seems more reasonable that the state is the lower lying d-d or CT state suggested by Vogler and Kunkely for Fe(TPP)(CO)(piperidine). If so, it is possible to estimate the

Scheme III. In DMF ($I = 0.1$ M)

thermodynamic properties of the excited state as a redox reagent as shown in Scheme III.

Vogler and Kunkely give 652 nm for the 0-0 energy of the emitting π (porphyrin) triplet state of Ru(TPP)(CO)(pip)*. Adding the small contribution from the difference in the electronic entropy between a triplet excited state and a singlet ground state, gives ~ -1.87 V for the free-energy content of the excited state above the ground state. Assuming that the porphyrin triplet excited state is at the same energy in Ru(TPP)(py)₂ as in Ru(TPP)(CO)(pip) allows upper limits for reduction potentials to be given for the excited state acting as either oxidant or reductant.

The ground-state reduction potentials for the Ru(III)-Ru(II) and ligand-localized Ru^{II}(TPP)(CO)(py)₂- [Ru^{II}(TPP)(py)₂]⁻ couples are at 0.42 and -1.63 V (Scheme II). Assuming that the excited state quenched is beneath the porphyrin triplet means that, for the excited state acting as an oxidant (Ru(TPP)(py)₂^{0*} + e⁻ → Ru(TPP)(py)₂⁻), the formal potential is $E < 0.24$ V and, for the excited state as reductant (Ru(TPP)(py)₂^{0*} - e⁻ → Ru(TPP)(py)₂⁺), it is $E > -1.45$ V.

The lack of room temperature emission for Ru(trpy)₂²⁺ and the short excited state lifetime (≥ 1.2 ns) estimated here are extraordinary when compared to closely related polypyridine complexes of Ru(II) such as Ru(bpy)₃²⁺ and Ru(phen)₃²⁺ (phen is 1,10-phenanthroline). Absorption spectra³⁴ and redox properties of Ru(trpy)₂²⁺ are similar to those of Ru(bpy)₃²⁺, although λ_{\max} for the CT band energy is slightly red shifted (475 nm compared to 454 nm).³⁵ In an ethanol-methanol glass at 77 K, a strong emission is observed when Ru(trpy)₂²⁺ is irradiated and both the quantum efficiency for emission (0.48 vs. 0.38) and excited state lifetime (10.7 vs. 5.2 μ s) for Ru(trpy)₂^{2+*} are noticeably larger than for Ru(bpy)₃^{2+*}.³⁴ Yet at room temperature in acidic aqueous solution the lifetime of Ru(bpy)₃^{2+*} is 620 ns, and only ~ 1.2 ns for Ru(trpy)₂^{2+*}. As mentioned in the Experimental Section, we have been unable to observe a significant luminescence when aqueous solutions of Ru(trpy)₂²⁺ are irradiated in the visible.

Given the similarity in optical spectra and redox properties between Ru(trpy)₂²⁺ and other polypyridine complexes of Ru(II),¹² it seems reasonable that the lowest excited state, which emits strongly at low temperature, is basically MLCT in nature. If so, the luminescence and lifetime properties of the excited state suggest that it may be strongly medium and/or temperature dependent. One possible explanation is that compared to Ru(bpy)₃²⁺, Ru(trpy)₂²⁺ has a more open structure. The mixing of solvent redox properties into the CT excited state, which has been suggested by Van Houten and

Watts for Ru(bpy)₃^{2+*},³⁶ may be more feasible structurally and of more importance in describing the excited state of the trpy complex.

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