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Mechanism of the Quenching of the Emission of Substituted Polypyridineruthenium(II) Complexes by Iron(III), Chromium(III), and Europium(III) Ions

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Abstract: The series of complexes RuL_3^{2+}, where L is a bipyridine or phenanthroline derivative, has been used to investigate the mechanism of the quenching of $*RuL_3^{2+}$, the luminescent excited state of RuL_3^{2+}, by iron(III), chromium(III), and europium(III) in aqueous solutions at 25 °C. The quenching rate constants k_q were obtained from emission intensity and emission lifetime studies. In the iron(III)-$*RuL_3^{2+}$ systems flash-photolysis experiments showed that RuL_3^{3+} and iron(II) are produced in the quenching reaction. The steady-state levels of these products under continuous irradiation were determined as a function of iron(III) concentration and light intensity. In addition, the rate constants k_t for the thermal back-reaction of RuL_3^{3+} and iron(II) to re-form the starting species RuL_3^{2+} and iron(III) have been measured using flash-photolysis and stopped-flow techniques. The rate constants k_q and k_t are a function of excited state and ground state RuL_3^{3+}/RuL_3^{2+} potentials, respectively. Furthermore, the rate constants are, for the most part, in accord with the steady-state levels of RuL_3^{3+} and iron(II) produced under continuous illumination. Thus it is concluded that the mechanism of quenching by iron(III) is predominantly electron transfer in nature. The rate constants for the $*RuL_3^{2+}$-Eu(III) reactions vary more than two orders of magnitude on changing L. As the highest rate constants are observed for the ruthenium complexes with lowest reduction potentials, electron-transfer quenching is indicated and this hypothesis is supported by the results of flash-photolysis experiments. In sharp contrast, the lower than diffusion-controlled rate constants for the quenching of $*RuL_3^{2+}$ by chromium(III) are insensitive to the nature of L and do not follow the pattern expected from the redox potential of the ruthenium complex. In these systems, the quenching is ascribed to energy transfer in which ground state RuL_3^{2+} and the $^4T_{2g}$ and/or ^2E_g chromium(III) excited states are produced.

The quenching of the luminescence of tris(2,2′-bipyridine)ruthenium(II) by metal complexes is currently under active investigation.[1] Depending upon the system, the dynamic quenching of the ruthenium(II) emission may involve either oxidation (eq 1)[2-6] or reduction (eq 2)[7] of the excited state ($*Ru(bpy)_3^{2+}$) by the quencher (Q). Energy-transfer quenching also offers a pathway for deactivation of the excited state in some systems (eq 3).[8,9]

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{3+} + Q^- \qquad (1)$$

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{+} + Q^+ \qquad (2)$$

$$*Ru(bpy)_3^{2+} + Q \rightarrow Ru(bpy)_3^{2+} + Q^* \qquad (3)$$

Moreover, as has been pointed out,[1,10] energy transfer (eq 3) may also give rise to the electron-transfer products formed in eq 1 or 2. Conversely, the electron-transfer products generated in eq 1 or 2 may undergo subsequent reaction to yield the energy-transfer products of eq 3. Therefore the detection of electron-transfer products in flash-photolysis experiments[3] does not necessarily discriminate between primary electron-transfer and energy-transfer quenching mechanisms. In these instances, consideration of the relative reactivities of ground and excited donors and quenchers may make it possible to distinguish between the two mechanisms.

The series of luminescent polypyridineruthenium(II) complexes RuL_3^{2+} (L a 2,2′-bipyridine or 1,10-phenanthroline derivative) presents a useful probe for ascertaining the relative importance of electron-transfer and energy-transfer quenching mechanisms. The absorption and emission spectra of the complexes are nearly identical,[11,12] making it likely that the rates of energy-transfer quenching with a given acceptor Q will be constant for this series.[13] On the other hand, the redox potentials of the complexes in this series may be varied by changing the substituents on the ligands[11,14] and the rates of electron-transfer quenching reactions with a given oxidant or reductant Q should reflect the differences in driving force in a known manner.[15,16]

In the present work, this series of complexes has been used to further probe the mechanism of the quenching of RuL_3^{2+} by Fe^{3+} ions. In this system it was observed that relatively high steady-state levels of $Ru(bpy)_3^{3+}$ and Fe^{2+} accumulate when solutions of $Ru(bpy)_3^{2+}$ and Fe^{3+} are continuously illuminated. Recently it was shown that the quenching of the $Ru(bpy)_3^{2+}$ emission by Fe^{3+} ions can be interpreted in terms of the electron-transfer scheme shown in eq 4-6.[3,17]

$$Ru(bpy)_3^{2+} \underset{k_0}{\overset{h\nu}{\rightleftharpoons}} *Ru(bpy)_3^{2+} \qquad (4)$$

$$*Ru(bpy)_3^{2+} + Fe^{3+} \xrightarrow{k_{el}} Ru(bpy)_3^{3+} + Fe^{2+} \qquad (5)$$

$$Ru(bpy)_3^{3+} + Fe^{2+} \xrightarrow{k_t} Ru(bpy)_3^{2+} + Fe^{3+} \qquad (6)$$

Here k_{el} is the second-order rate constant for the production of free $Ru(bpy)_3^{3+}$ and Fe^{2+} from the reaction of $*Ru(bpy)_3^{2+}$ with Fe^{3+} and k_t is the second-order rate constant for the back (thermal) electron transfer between $Ru(bpy)_3^{3+}$ and Fe^{2+}. In this interpretation, the steady-state levels of $Ru(bpy)_3^{3+}$ and

Fe^{2+} depend upon the relative rates of the excited state and thermal electron-transfer reactions. In the present study the steady-state concentrations and the relevant rate constants have been determined for a variety of polypyridineruthenium complexes and compared to theoretical predictions based on the above scheme. The quenching of the RuL_3^{2+} excited states by europium(III) and chromium(III) has also been investigated. The yields of electron-transfer products may be understood by considering the reactivities expected for the various excited states ($*RuL_3^{2+}$ or excited quencher formed by energy transfer) with respect to electron transfer. In addition the syntheses, spectral characteristics, emission lifetimes, and reduction potentials of a number of polypyridineruthenium complexes are reported.

Experimental Section

Materials. Hydrated ruthenium trichloride was purchased from Alfa. Tris(2,2′-bipyridine)ruthenium(II) chloride as obtained from G. F. Smith was used without purification. Potassium aquopentachlororuthenate(III) was prepared according to the procedure of Mercer and Buckley.[18] The bipyridine and phenanthroline derivatives were obtained from G. F. Smith and used without further purification. Europium trichloride (99.9% pure) was purchased from Ventron and 99.99% europium trioxide was obtained from Alfa. Acetonitrile used in the cyclic voltammetry studies was purchased from Matheson, Coleman and Bell (bp 80.5–82.5 °C) and passed three times through a column of acid alumina (Fisher, Brockman Activity 1, 80–200 mesh) which had been activated by heating to 350 °C overnight. The tetra-*n*-propylammonium hexafluorophosphate used in these experiments was made by mixing aqueous solutions of potassium hexafluorophosphate (Ozark-Mahoning Co.) and tetra-*n*-propylammonium iodide (Eastman Kodak). The crude product was recrystallized twice as follows: The solid was dissolved in a mixture (~10:1) of hot ethanol and acetone, then water was added until the solution became cloudy. The solution was warmed until clear, filtered, and cooled. The recrystallized material was dried at 50 °C in vacuo. The iron(II) complexes of bipyridine and phenanthroline derivatives were made as follows: A stoichiometric amount of ligand was added gradually to ferrous sulfate dissolved in water. The solution was filtered and the product was precipitated by the addition of sodium perchlorate and recrystallized from warm water.

Preparation of the Polypyridineruthenium(II) Complexes.[19,20] 1. RuL_3Cl_2: L = 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (5-Cl(phen)); 5-bromo-1,10-phenanthroline (5-Br(phen)); 5-methyl-1,10-phenanthroline (5-CH_3phen); 5,6-dimethyl-1,10-phenanthroline (5,6-$(CH_3)_2$phen); 4,7-dimethyl-1,10-phenanthroline (4,7-$(CH_3)_2$phen); 5-nitro-1,10-phenanthroline (5-NO_2phen); 3,4,7,8-tetramethyl-1,10-phenanthroline (3,4,7,8-$(CH_3)_4$phen); 3,5,6,8-tetramethyl-1,10-phenanthroline (3,5,6,8-$(CH_3)_4$phen); 5-phenyl-1,10-phenanthroline (5-C_6H_5phen); 4,4′-dimethyl-2,2′-bipyridine (4,4′-$(CH_3)_2$bpy). Potassium aquopentachlororuthenate(III) (0.5 g) was dissolved in 50 ml of hot water containing one drop of 6 N hydrochloric acid and a stoichiometric amount of the ligand was added slowly with stirring. The mixture was boiled 10–20 min until a deep green solution resulted. Hypophosphorous acid (1.2 ml of a 30% solution) neutralized with sodium hydroxide (~3.5 ml of a 2 N solution) was added and the mixture was refluxed 15–30 min until the color had changed to a deep orange red. The mixture was filtered and 10 ml of 6 N hydrochloric acid was added dropwise with stirring to the hot filtered solution. If no solid had formed at this point, the volume of the solution was reduced by evaporation until crystals formed. The crude product was recrystallized from hot water.

$RuL_2(ClO_4)_2$: L = 2,2′,2″-terpyridine (terpy). The above procedure was followed except that the hydrochloric acid was replaced by 5 ml of 70% perchloric acid. $RuL_2(ClO_4)_2$, L = 2,4,6-tri(2-pyridyl)-*s*-triazine (TPTZ). Following the above procedure a purple solution was produced. To the hot purple filtrate was added 10 ml of 5 M sodium perchlorate. The solid resulting was washed twice with water and dried, then extracted two times with boiling 1,4-dioxane.

RuL_3Cl_2: L = 4,7-diphenyl-1,10-phenanthroline (4,7-$(C_6H_5)_2$-phen). The above procedure was followed except that the ligand was dissolved in 30 ml of *N,N*-dimethylformamide (DMF), added gradually to the aqueous ruthenium solution and the mixture filtered before adding hypophosphorous acid. The crude chloride salt was washed with water, but was not recrystallized.

2. RuL_3Cl_2: L = 4,4′-diphenyl-2,2′-bipyridine (4,4′-$(C_6H_5)_2$bpy). Ruthenium trichloride (0.3 g) was dissolved in 25 ml of hot water containing 1 drop of 6 N hydrochloric acid. A solution containing the stoichiometric amount of ligand in 25 ml of DMF was added dropwise to the ruthenium solution. This solution was refluxed for 3 h, then the solvent was evaporated to give a final volume of 10 ml. This concentrate was diluted to 100 ml with water and 10 ml of 6 N hydrochloric acid was added dropwise to give the chloride salt. This product was recrystallized from hot water.

For the cyclic voltammetry studies all the complexes were used as perchlorate salts. Those obtained initially as the chloride salt were dissolved in water and filtered, and dilute perchloric acid was added to precipitate the perchlorate salt. All the solids were dried several days in vacuo before use.

Lifetime Measurements. The lifetimes of the excited states were measured by monitoring the decay in emission intensity of deaerated solutions 0.5 to 2.0×10^{-5} M in ruthenium complex after excitation with a ~30 ns pulse of 530-nm light. The excitation source was a frequency-doubled neodymium laser. The neodymium laser, which lases at 1060 nm, is described elsewhere.[21] The frequency doubling was accomplished by a potassium deuterated dihydrogen phosphate crystal (Korad Model KM2-901). Excitation intensities (530 nm) were typically $\sim10^{-1}$ einstein $cm^{-2}\,s^{-1}$ (0.03 J per flash). The emission (filtered with Corning Filter No. 2424 to exclude light below 580 nm) was detected with a photomultiplier (RCA 1P28) and preamplifier having a combined bandwidth in excess of 30 MHz. The signals from the preamplifier were displayed and photographed on a Tektronix 7633 oscilloscope equipped with Tektronix 7B71 time base and 7A13 amplifier. Values of I_t, the emission intensity at time t, were read from the photographs, and plots of log I_t vs. time were constructed. The lifetimes were obtained from the slopes of the semilog plots which were linear for at least two lifetimes. The lifetime values reported are averages obtained from five or six shots; the error limits given are standard deviations.

Cyclic Voltammetry Measurements. A Princeton Applied Research Corp. electrochemistry system consisting of a Model 173 potentiostat and a Model 175 universal programmer was employed in these studies. The cyclic voltammograms were recorded on an X-Y recorder (BBN Model 850A) with a sweep rate of 50 to 500 mV s^{-1}. The determinations were carried out in a cell containing two platinum wires as the working and counter electrodes and a Luggin capillary with a saturated calomel electrode as the reference electrode. The solutions used were 1–2 $\times 10^{-4}$ M in the ruthenium(II) or iron(II) complex as the perchlorate salt and were deaerated using an argon stream.

Emission Intensity Measurements. The emission from the polypyridine–ruthenium(II) complexes was monitored on a Perkin-Elmer Model MPF-4 fluorescence spectrophotometer equipped with a 150-W xenon lamp. Incident light intensity was measured using ferrioxalate actinometry,[22] and neutral density filters were used to reduce the light intensity. Solutions containing ruthenium(II) and quencher were excited at the absorbance maximum of the complex around 450 nm. The emission intensities were monitored at the wavelength of maximum emission (around 600 nm in the energy mode). In some cases, the emission intensities of the samples were measured against the reference solution as a function of wavelength.

For the samples containing Cr^{3+} as quencher, the excitation wavelength was set at 470 nm where Cr^{3+} has a very low absorbance (ϵ 3.7 $M^{-1}\,cm^{-1}$) and the emission was measured at 700 nm. The emission intensities were corrected for the absorption of the incident light by Cr^{3+} as previously described,[23] whereas absorption by Cr^{3+} at the emitting wavelength was neglected. These solutions were freshly prepared each time by dissolving solid chromium potassium sulfate in 0.25 M sulfuric acid.

The absorption spectra of the solutions containing the donor and various amounts of quenchers were equal within experimental error to the combined spectra of donor and quencher. Although some of the complexes are oxygen sensitive in the light in acid solution, they are fairly stable when oxygen is excluded.

All of the measurements were made with 1-cm^2 cells. The samples were bubbled with argon prior to use to remove oxygen.

Stopped-Flow Measurements. The reduction of the polypyridine-ruthenium(III) complexes by ferrous ion was studied using a Durrum stopped-flow spectrophotometer which has been modified as follows: The output from the photomultiplier tube was dropped across a 1 MΩ resistor offset by a constant voltage, and amplified. The amplified

Table I. Charge-Transfer Absorption and Emission Spectra and Emission Lifetimes (τ_0) of Polypyridineruthenium(II) Complexes in Water at 25 °C

Complex	Absorption λ_{max}, nm	Absorption $10^{-4}\epsilon$, $M^{-1}\ cm^{-1}$	Emission λ_{max}, nm Uncorr[a]	Emission λ_{max}, nm Corr	τ_0, μs[c]
$Ru[4,4'\text{-}(CH_3)_2bpy]_3[ClO_4]_2\cdot 3H_2O$	(~430),[b] 460	1.43	628	633	0.33 ± 0.01
$Ru]4,4'\text{-}(C_6H_5)_2bpy]_3Cl_2\cdot 6H_2O$	(~445),[b] 474	3.27	632	638 (653)[b]	0.67 ± 0.03
$Ru[bpy]_3Cl_2\cdot 6H_2O$	(~423),[b] 452	1.46	607	613, 627	0.60 ± 0.02
$Ru[3,4,7,8\text{-}(CH_3)_4phen]_3Cl_2\cdot 6H_2O$	438	2.45	597	605, 625	1.39 ± 0.10
$Ru[3,5,6,8\text{-}(CH_3)_4phen]_3[ClO_4]_2\cdot 2H_2O$	417, 440	1.96, 1.98	594	605, 625	2.22 ± 0.10[d]
$Ru[4,7\text{-}(CH_3)_2phen]_3Cl_2\cdot 6H_2O$	425, 445	2.53, 2.53	607	613, 626	1.74 ± 0.04
$Ru[5,6\text{-}(CH_3)_2phen]_3Cl_2\cdot 6H_2O$	425, 453	1.84, 2.04	602	608, 625	1.81 ± 0.05
$Ru[4,7\text{-}(C_6H_5)_2phen]_3Cl_2\cdot 3H_2O$	460	2.95	610	613, 627	4.68 ± 0.19
$Ru[5\text{-}(CH_3)phen]_3Cl_2\cdot 6H_2O$	420, 450	1.79, 1.94	597	605, 625	1.33 ± 0.03
$Ru[5\text{-}(C_6H_5)phen]_3Cl_2\cdot 5H_2O$	420, 448	2.32, 2.46	595	605, 625	1.29 ± 0.02
$Ru[phen]_3[ClO_4]_2\cdot 3H_2O$	421, 447	1.83, 1.90	593	605, 625	0.92 ± 0.10
$Ru[5\text{-}Cl(phen)]_3[ClO_4]_2\cdot 3H_2O$	422, 447	1.78, 1.84	593	605, 625	0.94 ± 0.03
$Ru[5\text{-}Br(phen)]_3Cl_2\cdot 5H_2O$	420, 448	1.82, 1.88	593	605, 625	1.04 ± 0.02
$Ru[5\text{-}NO_2phen]_3I_2\cdot 3H_2O$	449	2.0	~595	~606	$\leqslant 5 \times 10^{-3}$
$Ru[terpy]_2[ClO_4]_2\cdot 3H_2O$	473	1.62	~610	~628	$\leqslant 5 \times 10^{-3}$
$Ru[TPTZ]_2[ClO_4]_2\cdot 3H_2O$	501	1.92	~600	~605	$\leqslant 5 \times 10^{-3}$

[a] These maxima refer to values obtained in the "ratio mode". The quenching measurements were generally made at the emission maximum in the "energy mode". [b] Shoulder. [c] Average of five–six determinations, with standard deviation. [d] Emission lifetime is 2.08 ± 0.10 μs in 0.5 M sulfuric acid.

Table II. Formal Reduction Potentials of Polypyridineruthenium(III) and -iron(III) Complexes (ML_3^{3+}) in 1 M Sulfuric Acid at 25 °C (reported vs. hydrogen)

Ligand, L	E^0_{Ru}, V[a]	E^0_{Fe}, V	$^*E^0_{Ru}$, V[h]
$4,4'\text{-}(CH_3)_2bpy$	1.10	0.92[a]	−0.94
$4,4'\text{-}(C_6H_5)_2bpy$	1.17	1.00[a]	−0.85
bpy	1.26[b]	1.05[a]	−0.84
$3,4,7,8\text{-}(CH_3)_4phen$	1.02	0.81[d]	−1.11
$3,5,6,8\text{-}(CH_3)_4phen$	1.09	0.87[e]	−1.04
$4,7\text{-}(CH_3)_2phen$	1.09	0.87[d]	−1.01
$5,6\text{-}(CH_3)_2phen$	1.20	0.97[c]	−0.93
$4,7\text{-}(C_6H_5)_2phen$	1.20	0.99[a]	−0.90
$5\text{-}(CH_3)phen$	1.23	1.02[g]	−0.90
$5\text{-}(C_6H_5)phen$	1.26	1.06[a]	−0.87
phen	1.26[b]	1.06[g]	−0.87
5-Cl(phen)	1.36	1.11[g]	−0.77
5-Br(phen)	1.37	1.12[f]	−0.76
$5\text{-}NO_2phen$	1.46	1.25[g]	−0.67

[a] Calculated (see text) from results obtained by cyclic voltammetry in acetonitrile containing 0.1 M tetra-*n*-propylammonium hexafluorophosphate unless otherwise noted. [b] Determined from cyclic voltammetry on a platinum electrode in 1 M H_2SO_4. [c] G. F. Smith and W. W. Brandt, *Anal. Chem.*, **21,** 948 (1949). [d] Reference 30. [e] Estimated from E^0 = 0.93 V in 0.1 M H_2SO_4 according to the procedure described by Brandt and Smith (ref 30). [f] G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, **16,** 580 (1944). [g] G. F. Smith and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74,** 3532 (1952). [h] Potential for the reduction of ruthenium(III) to the emitting state of ruthenium(II).

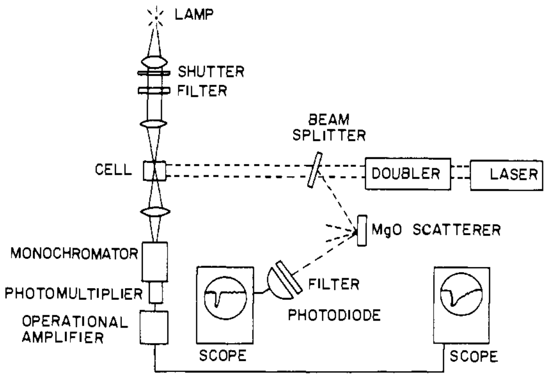


Figure 1. Schematic diagram of the laser flash-photolysis apparatus.

signal was digitized (resolution 1 part in 999) and stored in a 39 point memory with the last 10 points being channels 149–159. The digitized kinetic data were punched onto computer cards and the data were then fitted by a nonlinear least-squares program. All kinetic measurements were carried out under pseudo-first-order conditions with the iron(II) in excess. The iron(II) solutions were prepared from solid ferrous sulfate daily and analyzed as the phenanthroline complex.[24] Solutions 10^{-6} to 10^{-5} M in the ruthenium(III) complex were prepared in situ by lead(IV) dioxide oxidation of the ruthenium(II) complex in sulfuric acid. The oxidized solution was filtered prior to use.

Flash-Photolysis Studies. The absorbance changes resulting upon flash photolysis of deaerated solutions $\sim 10^{-3}$ M in Fe^{3+} and $\sim 10^{-4}$ M in ruthenium complex in 0.5 M sulfuric acid were studied using the frequency-doubled neodymium laser described above. In these experiments the light intensity was 10 to 10^2 einstein $cm^{-2}\ s^{-1}$. The probe beam source (positioned at 90° to the laser exciting beam) was either a 450-W xenon or a 30-W tungsten lamp filtered to remove light below 350 nm. The light passed through a Bausch and Lomb grating monochromator situated ~50 cm after the sample and was detected as described for the lifetime measurements. An EMI 9818KB photomultiplier was used for measurements at longer wavelengths. A block diagram of the flash-photolysis apparatus is shown in Figure 1.

Results

The positions of the absorption maxima and the corresponding molar absorptivities as well as the positions of the emission maxima for the polypyridineruthenium(II) complexes are summarized in Table I. The absorption spectra of some of the complexes listed in Table I have been reported previously;[11,20] where comparisons can be made, the positions of the absorption maxima determined in this and the earlier studies are in good agreement. The emission lifetimes (τ_0) of the complexes in water at 25 °C are also included in this table; the emission intensity measurements show that the lifetimes are the same (±3% experimental error) in water and H_2SO_4, HCl, NaCl, Li_2SO_4, and $MgCl_2$ at the 0.5 M level.

In Table II the reduction potentials of the polypyridineruthenium(III) complexes determined from cyclic voltammetry measurements are presented. For $Ru(bpy)_3^{2+}$ and Ru-

Table III. Rate Constants for the Quenching of Polypyridineruthenium(II) (RuL_3^{2+}) Emission by Ferric Ions and Dioxygen at 25 °C in Aqueous Solutions^{a}

Ligand, L	$10^{-9}k_q$, $M^{-1}\,s^{-1}$ $Fe^{3+\,b}$	 $O_2{}^{c}$
4,4′-$(CH_3)_2$bpy	2.9	4.2
bpy	2.7	3.3
3,4,7,8-$(CH_3)_4$phen	3.4	5.8
3,5,6,8-$(CH_3)_4$phen	2.5	3.6
4,7-$(CH_3)_2$phen	3.0	4.5
5,6-$(CH_3)_2$phen	2.6	4.7
5-(CH_3)phen	2.6	5.0
5-(C_6H_5)phen	2.7	4.7
phen	2.8	4.2
5-Br(phen)	2.3	4.0
5-Cl(phen)	2.3	3.4

^{a} These were calculated from eq 10 and 11 using the lifetime values in Table I. Errors are estimated to be ±5%. ^{b} In 0.5 M sulfuric acid. ^{c} In H_2O.

$(phen)_3{}^{2+}$ cyclic voltammograms could be determined in both 1.0 M aqueous sulfuric acid and in acetonitrile containing 0.1 M tetra-*n*-propylammonium hexafluorophosphate and the $E_{1/2}$ values obtained for the aqueous solutions (with respect to hydrogen) were 0.030 V lower than for the acetonitrile solutions (with respect to saturated calomel). With a number of the other complexes, however, cyclic voltammetry in aqueous solution was precluded by the insolubility of the ruthenium(II) perchlorate salts in aqueous media and/or the rapidity of the reduction of the ruthenium(III) complex by water. Thus, for these, the cyclic voltammetry was carried out in acetonitrile and the reduction potentials for the complexes in 1.0 M sulfuric acid were calculated by subtracting 0.030 V. At sweep rates of 200 mV s^{-1} the separation of anodic and cathodic waves (~60 mV) indicated a reversible one-electron process; consequently all the $E_{1/2}$ values used were obtained at this sweep rate. With the exception of the 3,5,6,8-$(CH_3)_4$phen complex (for which a potential of 0.90 V in 0.1 M HNO_3 has been reported[11]) the reduction potentials of the ruthenium(III) complexes (Table II) are in good agreement with previously reported values,[11,14] when allowance is made for the different media used.

The reduction potential for the formation of the emitting state of the ruthenium(II) complexes (eq 7) are also included in Table II.

$$RuL_3{}^{3+} + e \rightleftharpoons {}^*RuL_3{}^{2+} \qquad {}^*E^0 \qquad (7)$$

These potentials were calculated using $^*E^0 = -0.84$ V for the 2,2′-bipyridine complex[7,17,25] and adding the corresponding $^*\Delta G^0$ to the sum of the ΔG^0 values for reactions 8 and 9.

$${}^*Ru(bpy)_3{}^{2+} + RuL_3{}^{2+} \rightleftharpoons Ru(bpy)_3{}^{2+} + {}^*RuL_3{}^{2+} \quad (8)$$

$$Ru(bpy)_3{}^{2+} + RuL_3{}^{3+} \rightleftharpoons Ru(bpy)_3{}^{3+} + RuL_3{}^{2+} \quad (9)$$

The value of ΔG^0 for reaction 8 was assumed to be equal to the difference in the positions of the emission maxima of $^*Ru(bpy)_3{}^{2+}$ and $^*RuL_3{}^{2+}$, an assumption which requires that the $Ru(bpy)_3{}^{2+}$ and $RuL_3{}^{2+}$ produced in the luminescent decay possess the same amount of vibrational excitation, and that there is cancellation of the associated entropy changes.

Table IV. Emission Intensity Ratios (I_0/I) from Solutions of $Ru[3,4,7,8\text{-}(CH_3)_4phen]_3{}^{2+}$ and Fe^{3+} in 0.5 M Sulfuric Acid as a Function of Fe^{3+} Concentration and Incident Light Intensity (I^{in}) at 25 °C^{a}

$10^4[Fe^{3+}]$, M	$10^{10}I^{in}$, einstein $cm^{-2}\,s^{-1}$ 0.217	 2.17	 137
2.0	1.89	2.11	5.56
3.0	2.47	2.87	9.01
4.0	2.82	3.07	10.1
5.0	3.29	3.70	10.9

^{a} The ruthenium(II) complex was 4.73×10^{-6} M initially.

Table V. Steady-State Concentrations of $RuL_3{}^{3+}$ in Solutions of $RuL_3{}^{2+}$ and Fe^{3+} at 25 °C at Constant Light Intensity in 0.5 M $H_2SO_4{}^{a}$

Ligand, L	$10^3[Fe^{3+}]$, M	$[Ru(III)]_e/[Ru(II)]_d{}^{c}$
4,4′-$(CH_3)_2$bpy	1.0	0.40
	3.0	~0^{d}
	1.0^{b}	0.17
bpy	0.50	0.07
3,4,7,8-$(CH_3)_4$phen	0.20	0.66
	0.30	0.73
	0.40	0.72
	0.50	0.70
	0.15^{b}	0.34
	0.25^{b}	0.38
	0.40^{b}	0.42
	0.55^{b}	0.40
	0.40^{b}	~0^{d}
3,5,6,8-$(CH_3)_4$phen	0.40^{b}	0.60
4,7-$(CH_3)_2$phen	0.20	0.41
5,6-$(CH_3)_2$phen	0.30	0.18
5-(CH_3)phen	0.20	0.10
5-(C_6H_5)phen	0.70	0.10
phen	0.30	0.07
5-Br(phen)	0.30	⩽0.04
5-Cl(phen)	0.40	⩽0.04

^{a} The initial concentration of $RuL_3{}^{2+}$ was 4.3 to 5.1×10^{-6} M. The incident light intensity was 1.37×10^{-8} einstein $cm^{-2}\,s^{-1}$. ^{b} In 0.5 M HCl. ^{c} The steady-state concentration of Ru(III) produced in the light under these conditions divided by the initial (dark) Ru(II) concentration. ^{d} Fe^{2+} was added.

In order to obtain meaningful Stern–Volmer constants the quenching of the emission intensity of the polypyridineruthenium(II) complexes by Fe^{3+} ion was studied at very low incident light intensity. The buildup of the steady state of electron-transfer products (see eq 4–6) renders this impossible at high light intensity. Stern–Volmer constants K_{SV} calculated from the slopes of plots of the emission intensity ratios I_0/I (obtained at very low light intensity)[26] as a function of quencher concentration (eq 10)

$$I_0/I = 1 + K_{SV}[Q] \qquad (10)$$

were used to calculate the second-order rate constants for quenching k_q presented in Table III using eq 11

$$k_q = K_{SV}/\tau_0 \qquad (11)$$

and the lifetime (τ_0) values reported in Table I. The dependence of the buildup of steady-state electron-transfer products in solutions of Fe^{3+} and $RuL_3{}^{2+}$ was studied at higher light intensity. The dependence of I_0/I on Fe^{3+} concentration and incident light intensity is shown for the 3,4,7,8-$(CH_3)_4$phen complex in Table IV. In Table V the yield of steady-state electron-transfer products (calculated from I_0/I measurements as described below) is presented as a function of the ligand identity and Fe^{3+} concentration at constant light intensity. The steady-state calculations for the 4,4′-$(CH_3)_2$bpy and 3,4,7,8-$(CH_3)_4$phen were confirmed by direct measurements of the decrease in the transmittance of ruthenium(II) solutions (containing Fe^{3+}) as a function of incident light intensity.

The absorbance changes following the flash photolysis of

Table VI. Rate Constants for the Reduction of RuL_3^{3+} by Iron(II) in 0.5 M Sulfuric Acid at 25 °C as Measured by Stopped-Flow and Flash-Photolysis Methods, k_q/k_t, and k_{el}/k_t Calculated from Steady-State Measurements

Ligand, L	k_t,[a] $M^{-1}\ s^{-1}$	k_q/k_t[d]	k_{el}/k_t[e]
4,4'-$(CH_3)_2$bpy	2.1×10^5	1.4×10^4	1.5×10^4
bpy	4.9×10^6 [a] 5.2×10^6 [b]	5.2×10^2	4.0×10^2
3,4,7,8-$(CH_3)_4$phen	6.1×10^4	5.6×10^4	5.7×10^4
3,5,6,8-$(CH_3)_4$phen	2.7×10^5	9.3×10^3	8.3×10^3
4,7-$(CH_3)_2$phen	3.4×10^5	8.8×10^3	1.0×10^4
5,6-$(CH_3)_2$phen	1.8×10^6	1.4×10^3	1.0×10^3
5-CH_3phen	3.0×10^6	8.6×10^2	4.9×10^2
5-C_6H_5phen	4.6×10^6	5.9×10^2	2.9×10^2
phen	5.6×10^6	5.0×10^2	3.0×10^2
5-Cl(phen)	1.8×10^7 [a,c] 2.2×10^7 [b]	1.2×10^2	0.5×10^2

[a] Stopped-flow measurement unless otherwise indicated. [b] Flash photolysis measurement. [c] In 1.0 M H_2SO_4. [d] Calculated from the k_q values in Table III and the k_t values in this table. [e] Calculated from steady-state measurements (eq 12).

Table VII. Rate Constants for the Quenching of Polypyridineruthenium(II) (RuL_3^{2+}) Emission by Europium(III)[a] and Chromium(III) Ions[b] at 25 °C in Aqueous Solutions[c]

Ligand, L	$10^{-5}k_q$, Eu(III) $M^{-1}\ s^{-1}$	$10^{-7}k_q$, Cr(III) $M^{-1}\ s^{-1}$
4,4'-$(CH_3)_2$bpy	~5	1.0
bpy	≤0.8	1.2
4,7-$(CH_3)_2$phen	21	1.3
5,6-$(CH_3)_2$phen	7.5	1.4
5-(CH_3)phen	4.2	1.3
phen	~1	1.4
5-Br(phen)	≤0.5	1.3
5-Cl(phen)	≤0.5	1.2

[a] $MgCl_2$ was added to adjust the sum of the europium(III) and Mg^{2+} concentrations to 0.9 M; the acid concentration was 0.025 M HCl. The predominant europium(III) species in these solutions is $EuCl^{2+}$ so that the ionic strength is ~2.7 M. [b] $MgCl_2$ was added to maintain the ionic strength at 1 M; the acid concentration was 0.04 M H_2SO_4. [c] A low incident light intensity of 4.3×10^{-10} einstein $cm^{-2}\ s^{-1}$ was used.

RuL_3^{2+} (L = bpy, 5-Cl(phen)) solutions containing Fe^{3+} occurred in two stages. The first stage, which took place in 0.1-1 μs depending on the complex and the Fe^{3+} concentration, was a decrease in absorbance at 420-460 nm (or an increase at 650-700 nm). The second stage occurred in 1-100 μs (depending on the concentration of added Fe^{2+}) and corresponded to the return of the absorbance to its initial value. These absorbance changes are expected on the basis of reactions 4-6. The amplitude of the fast absorbance change showed that RuL_3^{3+} and Fe^{2+} are formed in the quenching reaction in very high yield (with L = 5-Cl(phen) the yield is 80% as great as when L = bpy for which the absolute yield approaches 100%). Rate constants for the subsequent reaction of RuL_3^{3+} and Fe^{2+} were determined from the slow absorbance change and are presented in Table VI. This table also contains rate constants for the slower RuL_3^{3+}-Fe^{2+} reactions determined by conventional stopped-flow measurements.

Plots of I_0/I for the quenching of the Ru[4,7-$(CH_3)_2$-phen]$_3^{2+}$ emission by europium(III) and chromium(III) ions are shown in Figure 2. It is likely that the europium(III) is present mainly as $EuCl^{2+}$ under the conditions used. The data in Table VII show that only the 4,7-$(CH_3)_2$phen, 5,6-$(CH_3)_2$phen, and 5-(CH_3)phen complexes show appreciable quenching by europium(III). The other ruthenium(III) complexes listed in the table showed little or no quenching and are included for comparison purposes only. The low solubility of Ru[3,4,7,8-$(CH_3)_4$phen]$_3^{2+}$ precluded accurate measurements on this system. Nevertheless the I_0/I ratios for the quenching of the emission of the tetramethyl complex by europium(III) revealed the presence of steady-state concentrations of Eu^{2+}. This result was confirmed by flash-photolysis measurements on the 4,7-$(CH_3)_2$phen complex which showed that the Eu^{2+} was formed in about 100% yield. Table VII also contains rate constants for the quenching of RuL_3^{2+} emission by chromium(III). The chromium(III) solutions used in the quenching measurements were prepared daily by dissolving chromium potassium sulfate in 0.25 M sulfuric acid; the spectra of these solutions resembled those of solutions prepared by dissolving chromium(III) perchlorate in perchloric acid, confirming that the freshly prepared sulfate solutions contained predominantly the hexaaquochromic ion or the outer-sphere chromium(III) sulfate complex and very little of the inner-sphere chromium(III) sulfate complex.

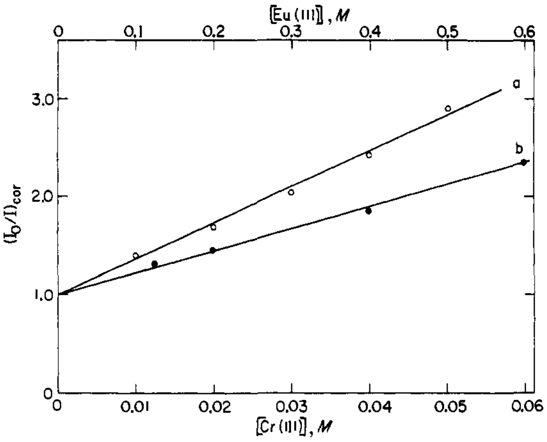


Figure 2. Stern-Volmer plots for the quenching of the Ru[4,7-$(CH_3)_2$phen]$_3^{2+}$ emission at 25 °C: a, europium(III) in ~0.025 M HCl and $MgCl_2$ with total europium(III) and magnesium concentrations equal to 0.9 M; b, chromium(III) in 0.04 M H_2SO_4 with $MgCl_2$ added to keep the ionic strength at 1 M. The emission data have been corrected for the absorption of the incident light by the hexaaquochromium(III) ion.

Discussion

The Absorption and Emission Properties of the Ruthenium(II) Complexes. The intense visible absorption of the polypyridineruthenium(II) complexes has been assigned to spin-allowed charge-transfer from the metal d orbitals to the π* orbitals of the ligand.[27] The emission from the dπ* states in these complexes has also been well characterized.[12,27,28] Crosby and co-workers[12,28,29] have shown that this emission arises from three closely spaced electronic states with symmetries A_1, E, and A_2 in order of increasing energy. These states are in rapid equilibrium and the lifetime and emission properties of the excited state are primarily determined by those of the A_2 state (except at very low temperatures).

Inspection of Table I shows that, although the positions of the absorption and emission maxima are not markedly affected by substitution, the lifetimes of the emitting states (Table I) and the reduction potentials of the complexes (Table II) are sensitive to changes in the substituent. In line with previous observations,[28] the emission lifetimes are greatly increased by the introduction of phenyl groups in the 4,7 positions of the phenanthroline ring system. However, the lifetimes do not otherwise appear to be especially sensitive to substitution in the 4,7 positions, since the lifetimes of the 4,7 and 5,6 dimethyl derivatives are comparable. Also of interest is the result that introduction of a methyl group in the 4,4′ positions of bipyridine *decreases* the emission lifetime of the complex, whereas the lifetime of the phenanthroline complex is increased by methyl substitution. By contrast, the emission lifetime of the bipyridine and the phenanthroline complexes are both increased by phenyl substitution.

Ground and Excited State Potentials. It is evident from Table II that the reduction potentials of the ruthenium(III) complexes parallel those of the iron(III) complexes, with the reduction potentials of the former systems generally lying about 0.2–0.3 V higher than those of the latter. Similarly, the potentials estimated for the reduction of ruthenium(III) to the emitting states tend to lie about 2.1 V more negative than the potentials for reduction to the corresponding ground states. This approximately constant potential difference is a consequence of the similar emission (and absorption) maxima of the ruthenium(II) complexes. So far as the effect of substituents is concerned, the +3 oxidation state is stabilized by electron-donating groups such as methyl whereas the +2 state is stabilized by electron-withdrawing groups such as chloro, bromo, and nitro. As expected, there is a correlation between the potentials and the $\mathrm{p}K_\mathrm{a}$'s of the free ligands.[30]

Steady-State Concentrations. In terms of the electron-transfer scheme summarized in eq 4–6 the steady-state concentrations of *Ru(II) and of Ru(III) (or Fe^{2+}) are given by eq 12a[31] and 12b, respectively,

$$[{*}\mathrm{Ru(II)}] = \frac{(2.3 \times 10^3)I^{\mathrm{in}}A_\mathrm{D}}{k_0 + k_\mathrm{q}[\mathrm{Fe}^{3+}]} \qquad (12a)$$

$$k_\mathrm{el}[{*}\mathrm{Ru(II)}][\mathrm{Fe}^{3+}] = k_\mathrm{t}[\mathrm{Ru(III)}]^2 \qquad (12b)$$

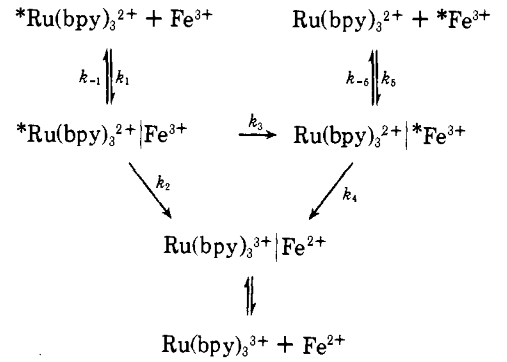
where $A_\mathrm{D} = \epsilon_\mathrm{D}([\mathrm{Ru(II)}]_0 - [\mathrm{Ru(III)}])$, A_D and ϵ_D are the absorbance of the ruthenium(II) complex (corrected for the ruthenium(III) concentration) and its molar absorptivity, respectively, and I^{in} is the incident light intensity (einstein $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$). Since the emission intensity is proportional to [*Ru(II)], the ratio of measured emission intensity (at constant incident light intensity) from a sample containing Fe^{3+} to that from a reference sample without ferric is given by eq 12c.

$$\frac{I_\mathrm{ref}}{I} = \frac{[{*}\mathrm{Ru(II)}]_\mathrm{ref}}{[{*}\mathrm{Ru(II)}]} = \frac{[\mathrm{Ru(II)}]_\mathrm{ref}(k_0 + k_\mathrm{q}[\mathrm{Fe}^{3+}])}{([\mathrm{Ru(II)}]_0 - [\mathrm{Ru(III)}])k_0} \qquad (12c)$$

The steady-state concentration of Ru(III) produced under illumination and the ratios $k_\mathrm{el}/k_\mathrm{t}$ can be calculated from the above equations.[17] The $k_\mathrm{el}/k_\mathrm{t}$ ratios may be compared with $k_\mathrm{q}/k_\mathrm{t}$ ratios calculated from the k_t values for the reaction of Ru(III) with Fe^{2+} determined from the stopped-flow and flash-photolysis experiments and the k_q values obtained in the quenching measurements. The results of these calculations are reported in Tables V and VI. It will be seen (Table V) that the steady-state concentrations vary from as high as 70% of the initial $\mathrm{Ru[3,4,7,8\text{-}(CH_3)_4phen]_3}^{2+}$ concentration to less than a few percent of the initial $\mathrm{Ru[5\text{-}Cl(phen)]_3}^{2+}$ concentration. As expected, the steady-state concentrations are eliminated by the addition of Fe^{2+} ion. Inspection of Table VI shows that the $k_\mathrm{el}/k_\mathrm{t}$ and $k_\mathrm{q}/k_\mathrm{t}$ ratios are very similar for a given complex and, as expected, are largest for the less oxidizing ruthenium(III) complexes. The agreement between the two ratios is poorer for the more powerful oxidants—probably because of scavenging of ruthenium(III) by trace impurities in the latter systems. The latter explanation is supported by the results of the flash photolysis experiments which indicate similar yields for the formation of Ru(III) in the Fe^{3+} quenching of the excited state of $\mathrm{Ru(bpy)_3}^{2+}$ and $\mathrm{Ru(5\text{-}Cl(phen))_3}^{2+}$. The steady-state and flash-photolysis measurements are thus consistent and can be readily interpreted in terms of eq 4–6 with $k_\mathrm{el} \approx k_\mathrm{q}$ for all of the systems studied.

The Detailed Mechanism of the Ferric Ion Quenching. As discussed in the introduction, the observation that $\mathrm{Ru(bpy)_3}^{3+}$ and Fe^{2+} are produced in the quenching reaction does not *per se* establish an electron-transfer quenching mechanism. Spin-allowed energy transfer from $*\mathrm{Ru(bpy)_3}^{2+}$ to Fe^{3+} is also possible since the ${}^4T_{1g}(t_{2g})^4\,(e_g)$ state of Fe^{3+} is believed to lie about 1.5 V above the ${}^6A_{1g}$ ground state. This excited state would be a very powerful oxidant ($E^0 \sim +2.2$ V) and could very rapidly oxidize $\mathrm{Ru(bpy)_3}^{2+}$ to form $\mathrm{Ru(bpy)_3}^{3+}$ and Fe^{2+} (Scheme I). The products of the energy-transfer quenching would thus be indistinguishable from those produced by direct electron-transfer quenching.[1]

Scheme I



We now turn to relative rate considerations in an effort to establish whether energy-transfer or electron-transfer quenching is likely to predominate in these systems. The reported k_q values in Table III are seen to be very large and are certainly close to the diffusion-limited values. It is not, however, likely that they have all attained the diffusion-controlled limit as the rate constants do not parallel the size of the ruthenium complex. Furthermore the values do weakly correlate with the reduction potentials of the complexes and there is no reason to expect that the diffusion-controlled rate constants for the various complexes should correlate with their reduction potentials. Thus we tentatively assume that the observed k_q values approach but have not fully attained diffusion-limited values.[32] Focusing now on Scheme I, for energy transfer to lead to electron-transfer products, oxidation of $\mathrm{Ru(bpy)_3}^{2+}$ by excited Fe^{3+} ion must be much more rapid than the dissociation of $\mathrm{Ru(bpy)_3}^{2+}|{*}\mathrm{Fe}^{3+}$ into $\mathrm{Ru(bpy)_3}^{2+}$ and $*\mathrm{Fe}^{3+}$ ions ($k_4 > k_{-5}$). This requires that electron transfer between $\mathrm{Ru(bpy)_3}^{2+}$ and $*\mathrm{Fe}^{3+}$ be diffusion controlled.[33] If it is now assumed that the observed quenching rate constant (which is close to the diffusion-controlled limit) is due to energy-transfer quenching, then the rate constant for electron-transfer quenching must be smaller and consequently below the diffusion-controlled limit ($k_2 < k_{-1}, k_{-5}$). This argument then leads to the conclusion that, for the energy-transfer path to be responsible for the observed electron-transfer products, oxidation of ground state $\mathrm{Ru(bpy)_3}^{2+}$ by excited Fe^{3+} ion has to be more rapid than the oxidation of the excited $\mathrm{Ru(bpy)_3}^{2+}$ by ground state Fe^{3+} ion ($k_4 > k_2$). This reactivity order is, however, highly unlikely for several reasons: oxidation of the ruthenium(II) excited state by Fe^{3+} has a larger driving force (by ~0.5 V) and the reorganization energy for this reaction involving ground state Fe^{3+} should be smaller since the electron added to Fe^{3+} enters a t_{2g} orbital; in contrast, for excited Fe^{3+} the electron must enter an e_g orbital and larger distortions are required about the iron. Finally, when ground state Fe^{3+} is the oxidant the symmetries of the electron being transferred and the vacancy on the oxidant (both π) are matched while they are not when excited Fe^{3+} is the oxidant. The high yield of electron-transfer products ($k_\mathrm{el} \approx k_\mathrm{q}$) observed in this work thus appears to be inconsistent with energy transfer being the major quenching mode.

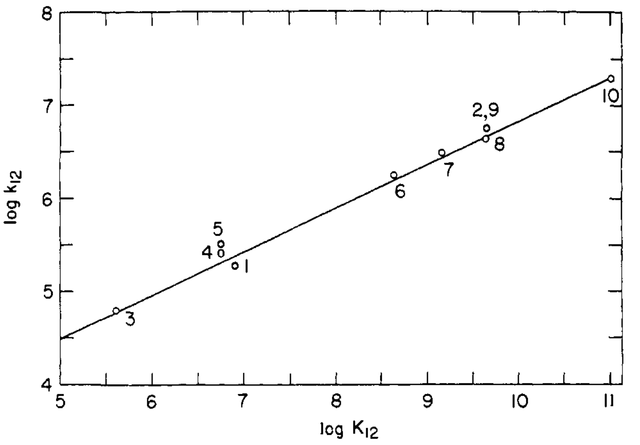


Figure 3. Plot of the logarithm of the rate constant for the reduction of RuL_3^{3+} complexes by iron(II) vs. the logarithm of the equilibrium constants for the reactions in 0.5 M H_2SO_4 at 25 °C: 1, L = 4,4′-$(CH_3)_2$bpy; 2, L = bpy; 3, L = 3,4,7,8-$(CH_3)_4$phen; 4, L = 3,5,6,8-$(CH_3)_4$phen; 5, L = 4,7-$(CH_3)_2$phen; 6, L = 5,6-$(CH_3)_2$phen; 7, L = 5-CH_3(phen); 8, L = 5-C_6H_5(phen); 9, L = phen; 10, L = 5-Cl(phen).

The dependence of the quenching rate constants on the oxidation potentials of the emitting states is also consistent with an electron-transfer quenching mechanism. As shown in Table III, the quenching rate constant for Ru[3,4,7,8-$(CH_3)_4$-phen]$_3^{2+}$, which has the highest excited state oxidation potential, is the largest, while the quenching rate constants for the 5-bromo- and 5-chlorophenanthroline complexes, which have the lowest excited state oxidation potentials, are the smallest observed. The change in the quenching rate constants is not large; this is expected since the rate constants are close to the diffusion-controlled limits where k_{obsd}, the measured second-order rate constant, is given by

$$k_{obsd} = \frac{k_{act}k_{diff}}{k_{act} + k_{diff}} \tag{13}$$

in which k_{diff} is the diffusion-limited rate constant and k_{act} is the true activation-controlled rate constant. Unfortunately since the rate range spanned is small, this reactivity pattern alone cannot provide strong support for the electron-transfer quenching mechanism.

It is noteworthy that the quenching rate constants for oxygen reported in Table III also show a weak dependence on the RuL_3^{2+} excited state oxidation potential. It is conceivable that these reactions may also involve an electron-transfer quenching pathway in which Ru(III)|O_2^- is produced initially (see also footnote 26, ref 17). The singlet oxygen product observed by Demas et al.[34] would then result from rapid reaction of Ru(III) and O_2^-.

The Rate Constants for the Back-Reactions. Since the quenching rate constants for the $*RuL_3^{2+}|Fe^{3+}$ reactions are so similar, the steady-state concentrations of the electron-transfer products are primarily determined by the rate constants for the reactions of the RuL_3^{3+} complexes with Fe^{2+}. As expected, these rate constants increase with the reduction potentials of the ruthenium(III) complexes. The logarithms of the rate constants are plotted against the logarithms of the equilibrium constants for the electron-transfer reactions in Figure 3. A good straight line is obtained with intercept = 2.0 and slope = 0.51. Using rate constants of 4.2 and 2×10^9 M^{-1} s^{-1} for the Fe^{2+}-Fe^{3+} and RuL_3^{2+}-RuL_3^{3+} exchanges, respectively,[35-38] the observed slope is in good agreement with the value ~0.41[39] predicted by the Marcus equations[16]

$$\log k_{12} = 0.50 \log k_{11}k_{22} + 0.50(1 + \alpha) \log K_{12} \tag{14}$$

$$\alpha = (\log K_{12})/4 \log (k_{11}k_{22}/Z^2)$$

where k_{11} and k_{22} refer to the exchange reactions, k_{12} and K_{12} to the cross-reactions, and Z is a collision number usually taken to be 10^{11} M^{-1} s^{-1}; the intercept is, however, much smaller than the theoretical value of 5.

One explanation that has been proposed for the relatively slow rates of the cross-reactions focuses on differences in the nonelectrostatic contributions to the work required to bring the various pairs of reactants together.[40,41] The interaction between the aquo Fe^{2+} and Fe^{3+} ions is an interaction between two hydrophilic ions, while the interaction between the polypyridine ML_3^{2+} and ML_3^{3+} ions is that between two hydrophobic species; by contrast, the interaction between Fe^{2+} and ML_3^{3+} is of the hydrophilic–hydrophobic type. This difference in the types of interactions could result in a relatively slow cross-reaction rate if the hydrophilic–hydrophobic interaction were particularly unfavorable. However, the present study shows that the quenching of RuL_3^{2+} emission by Fe^{3+} ions is close to diffusion controlled and this result appears incompatible with an unfavorable hydrophilic–hydrophobic interaction in cross-reactions of this type. Furthermore, the stability constants for the $*RuL_3^{2+}/Q$ precursor complexes evaluated from static quenching measurements with quenchers such as $Mo(CN)_8^{4-}$, $IrCl_6^{3-}$, and $PtCl_4^{2-}$ in aqueous and organic solvents are in good agreement with the values predicted on the basis of simple electrostatic considerations.[42] We may conclude that such work term arguments do not adequately explain the slowness of the ground state cross-reactions. It may be that nonadiabatic factors are more important in these systems (and in others) than has been previously appreciated.

If the reactions are not adiabatic then it is necessary to use eq 15[38,43,44]

$$k_{12} = p_{12}\left[\frac{k_{11}k_{22}K_{12}f_{12}}{p_{11}p_{22}}\right]^{1/2} \tag{15}$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/p_{11}p_{22}Z^2)}$$

where p is the probability of electron transfer in the activated complex. Equation 15 reduces to eq 14 when $p_{12} = p_1 = p_2 = 1$ (that is, when the reactions are adiabatic) or when $p_{12} = (p_1p_2)^{1/2}$ (and $f_{12} \approx 1$), a condition that has been previously discussed.[45] Note that if $p_1 = p_2 = 1$ but $p_{12} \ll 1$, eq 14 will still give the correct free energy dependence, but the k_{12} values calculated from eq 14 will be higher than the observed values. This is the type of behavior seen in the present work and also, for example, in the oxidation of a series of $Fe(phen)_3^{2+}$ complexes by aquocobalt(III).[41] The interpretation that the RuL_3^{3+}-Fe^{2+} reactions are nonadiabatic does not require that the $*RuL_3^{2+}$-Fe^{3+} reactions also be nonadiabatic since different redox orbitals are involved in the two series of reactions; in the ground state reactions a Fe^{2+} t_{2g} electron is donated to a Ru(III) metal-centered t_{2g} orbital, while in the excited state reactions a π^* ligand-centered orbital on the Ru(II) complex is the donor for the Fe^{3+} t_{2g} acceptor orbital. Electron transfer from the Fe^{2+} t_{2g} orbital to the π^* ligand-centered orbital on the Ru(III) complex (the reverse of the Fe^{3+}-*Ru(II) quenching process) is not a kinetically favorable pathway since it is endergonic by at least 1.4 V for all the RuL_3^{3+} complexes.

Europium(III) and Chromium(III) Quenching. Unlike the $*RuL_3^{2+}$-Fe^{3+} reactions where the nature of the ligands has only a small effect on k_q, the rates of the $*RuL_3^{2+}$-Eu(III) reactions vary by more than two orders of magnitude as the ligands are changed. It is apparent from Table VII that the complexes with lower reduction potentials exhibit higher quenching rate constants, a trend that is indicative of electron-transfer quenching. The assignment of an electron-transfer quenching mechanism derives further support from the continuous and flash-photolysis results. Continuous photolysis of the 3,4,7,8-$(CH_3)_4$phen complex in the presence of europium(III) revealed the formation of steady-state concentrations of Eu^{2+} while flash photolysis of solutions of the 4,7-$(CH_3)_2$phen complex showed that the Eu^{2+} was formed in almost all the quenching acts.

As is also expected for electron-transfer quenching, a plot of log k_q vs. log K_q is linear with slope 0.49 and intercept 1.55. Evidently the reactions of europium(III) with $*RuL_3^{2+}$ show the expected dependence on the driving force for the reaction. This is an important result since it is the first example of a Marcus-type correlation involving the excited states of the ruthenium complexes. Furthermore from the value of the above intercept and eq 14 (assuming α to be small), the self-exchange rate for the $*RuL_3^{2+}$-RuL_3^{3+} couple is calculated to be 2×10^6 M^{-1} s^{-1} using 4.8×10^{-4} M^{-1} s^{-1} [46] for the Eu(II)-Eu(III) self-exchange rate appropriate to this chloride concentration. The above estimate probably imposes a lower limit for the exchange rate of the excited state redox couple; as discussed earlier for the reaction of Fe^{2+} with RuL_3^{3+}, the intercepts of these linear free energy plots are often lower than predicted from the product of the individual exchange rate constants. In addition, the europium(II)-europium(III) exchange rate constant cited above features a path first order with respect to chloride and thus may apply to an inner-sphere pathway involving chloride bridging. The exchange pathway via the aquo ions, which could well be the relevant one for the present discussion, was found to be immeasurably small ($<10^{-5}$ M^{-1} s^{-1}).[46] Thus the $*RuL_3^{2+}$-RuL_3^{3+} electron exchange rate is more likely to be on the order of 10^7 M^{-1} s^{-1} or greater. In fact, there are other grounds for expecting the $*RuL_3^{2+}$-RuL_3^{3+} to be rapid. This exchange involves transfer of an electron between polypyridine π^* orbitals and the intrinsic barrier for this kind of process should not be large.[47,48]

In sharp contrast to the quenching by europium(III), the rates of the chromium(III) quenching reactions are insensitive to the nature of the ruthenium(II) complex; the values of k_q are $(1.2 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for all the complexes studied. The lack of a dependence on the reduction potential of the complex for these lower than diffusion-controlled rate constants suggests that the chromium(III) quenched reactions proceed by an energy-transfer mechanism. The ground state of the hexaaquochromic ion has a $^4A_{2g}(t_{2g})^3$ configuration and energy transfer to form the $^4T_{2g}(t_{2g})^2(e_g)$ or $^2E_g(t_{2g})^3$ excited states which have absorption maxima of 17.4 and 15.0 kK is possible.[49] The former transfer would be spin forbidden and the latter spin allowed. Similar rates for energy-transfer quenching of the ruthenium(II) emission are predicted from the similar spectral characteristics of the complexes.[13] Although energy transfer provides a very plausible mechanism for the chromium(III) quenching, it is worth pointing out that an electron-transfer pathway is not altogether ruled out by the insensitivity of k_q to the potential of the complex in a rate range well below that expected for diffusion-controlled behavior. Instead there is an increasing number of outer-sphere oxidation-reduction reactions where "rate saturation" below the diffusion-controlled limit is observed.[38,50] Nevertheless, strong evidence that the chromium(III) quenching does occur via energy transfer comes from comparison of the k_q values for europium(III) and chromium(III). The chromium(III)/(II) and europium(III)/(II) couples have very similar E^0 values (for the aquo ions −0.41 and −0.43 V, respectively)[51] and their similar reactivity toward outer-sphere oxidants (Eu(II) ~ 20 times faster than Cr(II)) at 25 °C[52] indicates that their self-exchange rates (both $<10^{-5}$ M^{-1} s^{-1} for the aquo ions by direct determination)[46,53] are also quite similar. Based on these considerations chromium(III) would be expected to have a somewhat smaller rate constant than europium(III) for electron-transfer quenching with a given RuL_3^{2+} complex. By contrast the observed europium(III) rate constants range from 0.5 to 21×10^5 M^{-1} s^{-1} while the chromium(III) rate constants are 100 to 140×10^5 M^{-1} s^{-1}. Therefore the unexpectedly rapid rate constants found for the chromium(III) quenching also suggest that a mechanism other than electron transfer is operative in these systems. Energy transfer has also been proposed as the mechanism for quenching of $Ru(bpy)_3^{2+}$ emission by chromium(III) ammines and chromium(III) hexacyanide.[54]

Excited State-Ground State Reactivity Comparisons. Reactions in which the RuL_3^{2+} excited states are either oxidized or reduced are much more rapid than the analogous reactions for the ground state complexes. This is not unexpected since ΔG^*, the free energy content of the excited state (eq 16),

$$RuL_3^{2+} \rightleftharpoons *RuL_3^{2+} \qquad \Delta G^* \tag{16}$$

is ~2 V greater than that of the ground state.[4,17,25] As discussed earlier, the self-exchange rates for the ground and excited state Ru(II)-Ru(III) couples are not likely to differ greatly.[47] Therefore from simple Marcus theory (eq 14, α small) the reactions in which the excited state is oxidized should be ~10^{18} faster than the ground state reactions, since the rate constants are related by eq 17.

$$k^*/k = e^{\Delta G^*/2RT} \tag{17}$$

It is interesting to compare the reactivity enhancement actually observed in several systems to that predicted from these simple considerations. Laurence and Balzani have reported that reduction of Tl(III) to Tl(II) is about nine orders of magnitude more rapid for $*Ru(bpy)_3^{2+}$ than for its ground state, while with Fe(III) as the oxidant their data and the present work show this rate ratio to be ~10^{12}.[5] Thus for these oxidants the observed rate ratios fall below the predicted 10^{18}. By contrast, for oxidation of $Ru[4,7\text{-}(CH_3)_2phen]_3^{2+}$ ground and excited states by europium(III), the excited state reaction is 3×10^{23} faster than the ground state reaction. (The value of k_6, the rate constant for the ground state reaction,

$$RuL_3^{2+} + Eu(III) \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} RuL_3^{3+} + Eu(II) \tag{18}$$

was calculated to be 6.8×10^{-18} M^{-1} s^{-1} using $k_{-6} = 4 \times 10^8$ M^{-1} s^{-1}, obtained in flash-photolysis experiments, and $K_{18} = 1.7 \times 10^{26}$ as calculated from the E^0 values for the europium[51] and ruthenium couples (Table II). The value of k_7, the rate constant for the excited state reaction

$$*RuL_3^{2+} + Eu(III) \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} RuL_3^{3+} + Eu(II) \tag{19}$$

is 2.1×10^6 M^{-1} s^{-1} (Table VII).) The above considerations neglect differences between the α factors for the reactions. Inclusion of these, using the full eq 14 and the intercept from the Marcus plot for the europium(III) quenching to calculate α for both the excited and ground state reactions, yields $k_7/k_6 = 10^{23}$. The remarkably good agreement between the observed and calculated rate ratios for europium(III) (which is probably, to some extent, fortuitous) lends support to the view that, for this particular excited state-ground state pair of reductants, the relative rate ratios are largely determined by thermodynamic factors. Such a simple correlation is not, however, expected in general: reactions of the ground state and excited state may differ in their degree of nonadiabaticity (eq 15). Furthermore, the intrinsic barriers to electron transfer may differ markedly for the ground and excited state reactions, as was discussed earlier for Fe^{3+} ion and its $^4T_{1g}$ ligand field excited state. Thus the correlation found for these RuL_3^{2+}-Eu(III) reactions probably arises because the intrinsic barriers to electron transfer are similar for both ground and excited state reactions and because of cancellation of other rate-determining factors.

In conclusion, the RuL_3^{2+} series of complexes has proven to be useful in determining the relative importance of electron-transfer and energy-transfer quenching mechanisms. The rate constants measured for europium(III) quenching parallel the oxidation potentials of the excited complexes, as is predicted for electron-transfer quenching. The Fe^{3+} quenching rate constants show this to only a very small extent, presumably because they are so close to the diffusion-controlled limit. By contrast, the rate constants for chromium(III) quenching are nearly constant and a factor of more than 100 below the diffusion-controlled limit, suggesting an energy-transfer mechanism since the spectral characteristics of the RuL_3^{2+} complexes are so similar. This approach to determining quenching mechanisms thus shows great promise, especially when used in conjunction with flash-photolysis results and relative rate arguments suggested by theory. Finally these studies may also have practical applications; the formation of relatively high steady-state levels of electron-transfer products in the RuL_3^{2+}–Fe^{3+} reactions renders them useful as photogalvanic systems (ref 17), while the formation of Eu^{2+} ion in the Eu(III) quenching reaction suggests that this system might be used to generate hydrogen in the presence of a suitable catalyst.[55]

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References and Notes

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