of PhLi with $(CO)_5WPPh_3$ followed by methylation with $CH_3O-SO_2F$.

**Supplementary Material Available:** The synthesis and IR and NMR spectra of $N(CH_3)_4{}^+(CO)_5WCOR^-$ species **1**, **3**, **4**, **5** and **6**; the photolysis of $N(CH_3)_4{}^+(CO)_5WCOR^-$ species, **2**, **3**, **4**, and **6**; the IR and NMR spectra of the $N(CH_3)_4{}^+(CO)_5WR^-$ products **9m**, **10m**, **11m**, and **13m**; and the preparation and spectra of **11e** and **12e** (3 pages). Ordering information is given on any current masthead page.

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# Reactions of the Excited States of Substituted Polypyridinechromium(III) Complexes with Oxygen, Iron(II) Ions, Ruthenium(II) and -(III), and Osmium(II) and -(III) Complexes

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**Abstract:** The series of complexes $CrL_3{}^{3+}$ where L is a bipyridine or phenanthroline derivative has been used to investigate the mechanism of the quenching of the luminescence of $*CrL_3{}^{3+}$ by $O_2$, $Fe_{aq}{}^{2+}$, $RuL_3{}^{2+}$, $Os(bpy)_3{}^{2+}$, $Ru(bpy)_3{}^{3+}$, and $Os(bpy)_3{}^{3+}$ in aqueous solution at 25 °C. The rate constants for the quenching of the $*CrL_3{}^{3+}$ emission by $O_2$ are insensitive to the reduction potential of the chromium(III) complex. It is concluded that the reaction with $O_2$ is by energy transfer. The $*CrL_3{}^{3+}$ emission is quenched much more efficiently by $Ru(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$ than by $Ru(bpy)_3{}^{3+}$ and $Os(bpy)_3{}^{3+}$. The rate constants for the quenching of the $*CrL_3{}^{3+}$ emission by $RuL_3{}^{2+}$, $Os(bpy)_3{}^{2+}$, and $Fe_{aq}{}^{2+}$ are sensitive to the reduction potential of the chromium(III) complex with the quenching by $Fe_{aq}{}^{2+}$ showing a linear relation between the logarithm of the quenching rate constant and the reduction potential. The ruthenium(II) and osmium(II) complexes show a more complex behavior with the quenching rate constant increasing less rapidly with driving force than is expected on the basis of the Marcus model. The rate constant for the $CrL_3{}^{2+}$–$*CrL_3{}^{3+}$ exchange is estimated as $1 \times 10^8$ $M^{-1}$ $s^{-1}$ in 1.0 M sulfuric acid at 25 °C and is compared with the corresponding ground-state exchange rate. The relation between ground- and excited-state exchange rates and Stokes shifts is discussed.

There is currently considerable interest in the reactions of the excited states of metal complexes.[1-6] This interest derives in part from the use of these complexes in model systems for the study of the conversion and storage of solar energy.[7,8] An additional reason for this interest is that the electron transfer reactions of excited states can be very exothermic and consequently such reactions can be used to test the predictions of theoretical models in the so-called inverted region.[9]

Table I. Emission Lifetimes, Emission Maxima, and Reduction Potentials of Polypyridinechromium(III) Complexes ($CrL_3^{3+}$) at 25 °C

| ligand, L | $\tau_0$, $\mu$s 1 M HCl | $\tau_0$, $\mu$s 1 M $H_2SO_4$ | $\tau_0$, $\mu$s 1 M DCl | $\lambda_{max}$, nm[a] 1 M HCl | $E°$, V[b] 1 M LiCl | $*E°$, V[b] 1 M LiCl | $E_{Ru}°$, V[b,c] 1 M $H_2SO_4$ |
|---|---|---|---|---|---|---|---|
| bpy | 66 | 76 | 64 | 728 | $-0.26^d$ | 1.44 | 1.26 |
| 4,4'-$(CH_3)_2$bpy | 180 | 210 | | 728 | $-0.45$ | 1.25 | 1.10 |
| 5-Cl(phen) | 156 | 180 | | 728 | $-0.17$ | 1.53 | 1.36 |
| 5-Br(phen) | 160 | | | 728 | $-0.15$ | 1.55 | 1.37 |
| phen | 270 | 325 | 274 | 728 | $-0.28^d$ | 1.42 | 1.26 |
| 5-$(CH_3)$phen | 310 | 380 | | 732 | $-0.30$ | 1.39 | 1.23 |
| 4,7-$(CH_3)_2$phen | 580 | 642 | | 735 | $-0.45$ | 1.23 | 1.09 |
| terpy | ~0.05 | | | 775 | $-0.17$ | 1.43 | |

[a] Uncorrected emission maximum. Because of the narrowness of the emission lines the true maxima are not expected to differ significantly from the uncorrected maxima. [b] Potentials vs. NHE. [c] Reduction potentials for the corresponding $RuL_3^{3+}$ complexes, ref 2. [d] The same potential was obtained in 1 M $H_2SO_4$.

Depending upon the system, an excited state can undergo either oxidation, reduction, or energy transfer reactions.[1-11] It is often difficult to determine which reaction is occurring. Energy transfer can give rise to electron transfer products and electron transfer reactions can produce nonoxidized (or reduced) products. Therefore, additional means are needed to determine the mechanism of an excited-state reaction. Under favorable circumstances a knowledge of the thermodynamics of the ground- and excited-state reactions of the donors and quenchers can aid in assigning mechanisms.[2,4] Studies of the charge-transfer excited states of polypyridineruthenium(II) complexes have demonstrated the utility of this approach and it was hoped that this approach could also be used to characterize the reactions of the ligand-field excited states of polypyridinechromium(III) complexes. The emission spectra of the chromium(III) complexes are very similar while their reduction potentials change significantly on changing the substituents on the ligands. Therefore, it is expected that for a series of polypyridinechromium(III) complexes and a given quencher the energy transfer quenching rate will be roughly constant[12] while the electron transfer rate will change.[13]

In the present paper we report the results of a study of the kinetics of the reactions of the excited states of a series of polypyridinechromium(III) complexes $CrL_3^{3+}$ (L a 2,2'-bipyridine or 1,10-phenanthroline derivative) with $Fe_{aq}^{2+}$, $RuL_3^{2+}$, $Ru(bpy)_3^{3+}$, $Os(bpy)_3^{2+}$, $Os(bpy)_3^{3+}$, and $O_2$ and we have estimated the rate constant for the $CrL_3^{2+}$-$*CrL_3^{3+}$ electron exchange reaction. The rate constants determined in this work are compared with those for the analogous $RuL_3^{2+}$ reactions and with the predictions of current theories.

## Experimental Section

**Materials.** The polypyridinechromium(III) complexes were prepared by adding under argon a 1 M perchloric acid solution of chromium(II) to a slurry of a twofold stoichiometric excess of the ligand in water. The resultant green mixture was stirred for 1 h. Saturated bromine water was then added (the precipitate turned yellow) and the mixture was filtered. The solid was redissolved in water, the pH was adjusted to ~6, and the solution was extracted with chloroform until the chloroform was free of ligand. Perchloric acid was added to give the perchlorate salt which was separated and washed with water, alcohol, and ether.

The trisbipyridine complex was characterized by published spectra;[14] the other chromium(III) complexes were characterized by their Cr and Cl analysis. The chromium(III) complexes were used as perchlorate salts except for the studies of the quenching by Ru(3,4,7,8-$(CH_3)_4$phen)$_3^{2+}$. For this experiment the chromium(III) complex was converted to the chloride salt by using a Bio-Rad Dowex 1-X8 anion exchange resin in its chloride form. The ruthenium complex was then added and the solution was deaerated using an argon stream. The concentration of the ruthenium complex was determined spectrophotometrically. The polypyridineruthenium(II) complexes used were those prepared previously.[2] All other chemicals were reagent grade and were used without further purification.

**Flash Photolysis and Emission Intensity Measurements.** The emission or absorbance measurements were made using the dye laser system previously described.[15] The untuned broad-band output of coumarin 440 dye (438-444 nm) was used and the pulse width (full width at half-height) was ~0.6 $\mu$s. The emission intensities were monitored at the wavelength of maximum emission of the chromium(III) complexes by use of a Hamamatsu R928 or an EMI 9818KB photomultiplier.

All lifetime measurements were made using solutions deaerated by bubbling with argon for about 15 min. For the $O_2$ quenching experiments the solutions were either air or $O_2$ saturated. The $O_2$ concentration of the solutions was calculated by assuming that air is 21% $O_2$ and that the Ostwald solubility coefficient is 0.0287 for 1.0 M HCl at 25 °C and 0.0308 for water at 25 °C.[16] These coefficients correspond to oxygen concentrations of $1.2 \times 10^{-3}$ and $2.5 \times 10^{-4}$ M in 1.0 M HCl, and $1.3 \times 10^{-3}$ and $2.6 \times 10^{-4}$ M in water, for air- and oxygen-saturated solutions, respectively.

A stock solution of $Fe_{aq}^{2+}$ was prepared by dissolving ferrous ammonium sulfate in 1.0 M $H_2SO_4$ and stored under argon. The stock solution was analyzed spectrophotometrically by complexing the iron(II) with phenanthroline. For the $Ru(bpy)_3^{3+}$ quenching studies a $Ru(bpy)_3^{2+}$ solution was standardized spectrophotometrically[2] and then oxidized with $PbO_2$. This solution (including the $PbO_2$) was then either placed in a spectrophotometric cell with a pinch of the chromium complex, degassed, and centrifuged, or the solution was filtered, placed in a cell containing the chromium(III) complex and 0.02 mL of 0.01 M cerium(IV), and then degassed. The $Os(bpy)_3^{3+}$ solutions were analyzed spectrophotometrically ($\epsilon$ 750 at 550 nm)[17] after the addition of a small amount of cerium(IV).

The steady-rate quenching measurements were made on a Perkin-Elmer Model MPF-4 spectrofluorimeter. The solutions were excited at ~400 nm and the emission intensities were monitored at the wavelength of maximum emission.

**Cyclic Voltammetry Measurements.** Cyclic voltammograms of each chromium complex were run on a PAR 173 potentiostat with a PAR 179 programmer using a saturated calomel electrode as reference, a platinum wire for the auxiliary electrode, and a hanging mercury drop electrode as the working electrode. The medium used was 1.0 M LiCl and 2 drops of a titron X (~0.05%) solution was added to the chromium solution before running the voltammogram. The voltammograms were recorded on an $x$-$y$ recorder for sweep rates < 0.2 V s$^{-1}$ and on an oscilloscope for faster sweep rates. The trisbipyridine and trisphenanthroline chromium complexes were also studied in 1.0 M HCl and 1.0 M $H_2SO_4$.

## Results

The emission lifetimes of the polypyridinechromium(III) complexes measured in deaerated 1.0 M hydrochloric and 1.0 M sulfuric acid at 25 °C are shown in Table I. This table also includes the wavelengths of the emission maxima. Except for the terpyridine complex, the standard deviation of the measured lifetimes is less than 5%. The lifetimes of the $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ doublet ($^2E$,$^2T_1$) excited states in 1.0 M NaCl at 22 °C have been determined to be 63 and 360 $\mu$s, respectively, using flash absorption spectroscopy[18,19] and 77 and 270 $\mu$s, respectively, from emission measurements.[1b,24] These

values may be compared with 66 and 270 $\mu s$, respectively, in 1 M HCl at 25 °C measured here. The lifetimes determined in this work did not change on changing the solvent from 1.0 M HCl to 1.0 M DCl or on lowering the ionic strength. On the other hand, as has been reported previously,[20] the lifetimes are longer in sulfuric acid than in hydrochloric acid.

The reduction potentials of the polypyridinechromium(III) complexes determined by cyclic voltammetry are also presented in Table I. The reduction potentials for $Cr(phen)_3^{3+}$ and $Cr(bpy)_3^{3+}$ remained unchanged on changing the medium from 1.0 M LiCl to 1.0 M $H_2SO_4$. The half-wave potentials of the bipyridine complexes have been previously measured in aqueous solution[21,22] and the results are consistent with the values reported here. The differences between the potentials of the phenanthroline complexes measured in a 50% ethanol–water solution[23] are the same as those determined in this work. Table I includes the reduction potentials of the doublet ($^2E,^2T_1$) excited states of the chromium(III) complexes:

$$*CrL_3^{3+} + e^- \rightarrow CrL_3^{2+} \tag{1}$$
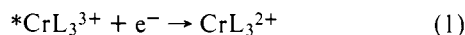
These values were calculated by combining the excitation energy with the ground-state reduction potentials of the complexes. The excitation energy was taken as the energy of the emission maximum. This procedure is justified since the emission from the $^2E$ state of $Cr(bpy)_3^{3+}$ shows a very small Stokes shift (<3 nm) and the entropy change for the transition is small.

Attempts were made to determine the $Cr(bpy)_3^{4+/3+}$ potential in 1.0 M trifluoromethanesulfonic acid by cyclic voltammetry. No oxidation peak was observed at a solid graphite electrode before the anodic limit of the medium occurred. On this basis the reduction potential is estimated to be greater than +1.6 V.

The quenching of the emission by a number of substrates was studied. For flash experiments, the reciprocal of the lifetime was plotted as a function of the quencher concentration with the least-squares slope giving the quenching rate constant $k_q$ (eq 2). For the steady-state luminescence measurements, the reciprocal of the intensity was plotted as a function of the quencher concentration (eq 3). Linear plots were obtained throughout. The quenching rate constants were calculated from the Stern–Volmer constants $K_{sv}$ using $k_q = K_{sv}/\tau_0$ where $\tau_0$ is the lifetime of the emitting state of the chromium(III) complex.

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[Q] \tag{2}$$

$$\frac{1}{I} = \frac{1}{I_0} + \frac{K_{sv}[Q]}{I_0} \tag{3}$$

The quenching of the emission of the $CrL_3^{3+}$ complexes by $O_2$ was studied in 1.0 M HCl. Table II shows these results. The rate constant for quenching of the $Cr(bpy)_3^{3+}$ complex by $O_2$ has been reported by Maestri et al.[24] as $1.7 \times 10^7$ $M^{-1}$ $s^{-1}$ in 1.0 M NaCl at 22 °C. This value may be compared with $2.6 \times 10^7$ $M^{-1}$ $s^{-1}$ in 1.0 M HCl at 25 °C determined in this work. The quenching rate does not change significantly on changing the medium from 1.0 M HCl to 1.0 M DCl ($2.7 \times 10^7$ vs. $2.6 \times 10^7$ $M^{-1}$ $s^{-1}$) or on reducing the ionic strength ($2.9 \times 10^7$ $M^{-1}$ $s^{-1}$, $D_2O$, 25 °C). For many of the chromium complexes the $O_2$ quenching was studied by both the laser flash method and by steady-state illumination. In all cases the same quenching constant obtained was within the experimental error of the measurements.

The results for the quenching of the $CrL_3^{3+}$ emission by $Fe_{aq}^{2+}$ in 1.0 M $H_2SO_4$ are shown in Table II. The $Fe_{aq}^{2+}$ quenching was studied by both flash and steady-state methods. The rate constant for the quenching of the $Cr(bpy)_3^{3+}$ emission by $Fe_{aq}^{2+}$ has been previously reported as $4.1 \times 10^7$ $M^{-1}$ $s^{-1}$

**Table II.** Rate Constants for the Quenching of Polypyridinechromium(III) ($RuL_3^{3+}$) Emission by Oxygen and by Ferrous Ions at 25 °C

| | $10^{-7}k_q$, $M^{-1}$ $s^{-1}$ | |
|---|---|---|
| ligand, L | $O_2{}^a$ | $Fe_{aq}^{2+b}$ |
| bpy | 2.6, 2.7,$^c$ 2.9$^e$ | 1.6 |
| 4,4'-$(CH_3)_2$bpy | 4.2 | 0.082 |
| 5-Cl(phen) | 3.7 | 4.8 |
| 5-Br(phen) | 4.0 | |
| phen | 4.9, 5.0,$^e$ 4.4$^f$ | 1.5 |
| 5-$(CH_3)$phen | 6.4 | 1.0 |
| 4,7-$(CH_3)_2$phen | 8.8 | 0.089 |

$^a$ In 1 M hydrochloric acid. $^b$ In 1 M sulfuric acid. $^c$ In 1 M DCl. $^e$ In $D_2O$. $^f$ In $H_2O$.

**Table III.** Rate Constants for the Quenching of $CrL_3^{3+}$ Emission by $RuL_3^{2+}$, $Os(bpy)_3^{2+}$, $Ru(bpy)_3^{3+}$, and $Os(bpy)_3^{3+}$ in 1.0 M Sulfuric Acid at 25 °C$^a$

| | $10^{-8}k_q$, $M^{-1}$ $s^{-1}$ | |
|---|---|---|
| quencher | $Cr(bpy)_3^{3+}$ | $Cr(phen)_3^{3+}$ |
| $Ru(bpy)_3^{2+}$ | 6.1 | 8.3 |
| $Ru(4,4'-(CH_3)_2bpy)_3^{2+}$ | 11 | |
| $Ru(3,4,7,8-(CH_3)_4phen)_3^{2+}$ | ~13 | |
| $Ru(4,7-(CH_3)_2phen)_3^{2+}$ | 11 | 14 |
| $Ru(5-(CH_3)phen)_3^{2+}$ | 9.9 | |
| $Ru(phen)_3^{2+}$ | 9.1 | |
| $Ru(5-Cl(phen))_3^{2+}$ | 6.1 | 8.1 |
| $Ru(5-NO_2(phen))_3^{2+}$ | 1.8 | 2.6 |
| $Os(bpy)_3^{2+}$ | 15 | 15 |
| $Ru(bpy)_3^{3+}$ | 0.06 | |
| $Os(bpy)_3^{3+}$ | <0.01 | |

$^a$ Additional quenching rate constants ($M^{-1}$ $s^{-1}$), not included in the table, follow: $Ru(bpy)_3^{2+}$ + $*Cr(4,4'-(CH_3)_2bpy)_3^{3+}$, $2.0 \times 10^8$; $Ru(5-Cl(phen))_3^{2+}$ + $*Cr(5-(CH_3)phen)_3^{3+}$, $8.4 \times 10^8$; $Ru(5-(CH_3)phen)_3^{2+}$ + $*Cr(4,7-(CH_3)_2phen)_3^{3+}$, $11 \times 10^8$.

at pH 3.0, ionic strength 1 M, 25 °C.[25] The rate constants for quenching by a number of ruthenium and osmium polypyridine complexes are reported in Table III. For a number of the couples the excited-state electron transfer reactions are thermodynamically unfavorable. However, no correction was made for the reverse electron transfer reaction in view of the more rapid rate of reaction of the products of the quenching reaction to produce ground-state reactants. The 3+ ruthenium and osmium ions quenched much less efficiently than the 2+ ions. Although the quenching by the osmium(III) complexes was almost unobservable at the concentrations used ($\sim 1 \times 10^{-3}$ M), quenching by the ruthenium(III) complexes was significant. The rate constant for the quenching of $Cr(bpy)_3^{3+}$ emission by $Ru(bpy)_3^{2+}$ has been previously reported as $4.0 \times 10^8$ $M^{-1}$ $s^{-1}$ at pH 3.0, ionic strength 0.2 M, 25 °C.[25] The rate observed here is faster owing presumably to the higher ionic strength (1.0 M) used in this work.

## Discussion

The chromium polypyridine complexes show two emission bands. These have been assigned to the $^2E \rightarrow {}^4A$ and $^2T_1 \rightarrow {}^4A$ transitions.[26] For $Cr(bpy)_3^{3+}$ the lifetime of the two emissions (at 695 and 727 nm) have been shown to be the same[24] and the emitting states are therefore believed to be in thermal equilibrium. For simplicity the two doublet levels will be referred to simply as the $^2E$ state. The excited state(s) produced by light absorption decays rapidly to the emitting states. The geometry of the ground and emitting states can be inferred to be very similar by the lack of any Stokes shift between the absorption and emission wavelengths.[26] Further,
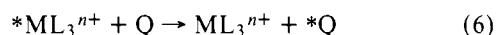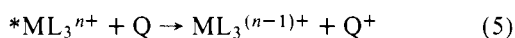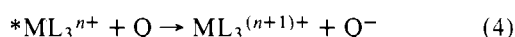
both states have the same $t_{2g}^3$ electronic configuration with the same number of bonding and antibonding electrons.

For the group of polypyridinechromium(III) complexes studied here the results show that, although modification of the ligand has little effect on the emission maxima, the lifetime and reduction potentials change significantly on changing the substituents on the ligands. The lifetimes are also dependent on the nature of the medium; the lifetimes of all the complexes are about 15% longer in $H_2SO_4$ than in HCl. It has been suggested[18] that the medium effect is due to pairing of the complex with an anion of the medium and that by increasing this ion pairing the vibrational freedom of the ligand is decreased. The data here show that the addition of methyl groups to either the bipyridine or the phenanthroline ligand increases the excited-state lifetime and that the phenanthroline complexes have longer lifetimes than their bipyridine analogues. The terpyridine complex has the shortest lifetime by over three orders of magnitude.

The fact that the chromium(III) lifetimes are independent of whether the solvent is $H_2O$ or $D_2O$ is curious since the lifetimes of the polypyridineruthenium(II) complexes, which show little change in lifetime with increasing ionic strength, increase on replacing $H_2O$ by $D_2O$.[2] The ruthenium(II) complexes also show very different trends in lifetime with phenanthroline substitution. This suggests that the mechanism by which the excited states undergo nonradiative decay is substantially different in the chromium and ruthenium complexes. This may be related to the different natures of the excited states: ligand field in the case of the chromium(III) complexes and charge transfer for the ruthenium(II) systems.
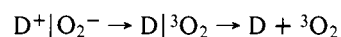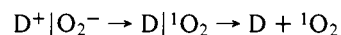
It is evident from Table I that the reduction potentials of the chromium(III) complexes parallel those of the ruthenium(III) (and iron(III)) complexes with the chromium potentials approximately 1.5 V more negative. The potentials for reduction of the excited states are also about 1.7 V more positive than the corresponding ground-state reduction potentials. This uniform shift of the excited-state reduction potential is due to the similarity in the wavelengths for maximum emission of the chromium complexes.

**Quenching Experiments.** The quenching of the excited states of transition metal complexes has been shown to proceed by three mechanisms:

$$*ML_3{}^{n+} + Q \rightarrow ML_3{}^{(n+1)+} + Q^- \qquad (4)$$

$$*ML_3{}^{n+} + Q \rightarrow ML_3{}^{(n-1)+} + Q^+ \qquad (5)$$

$$*ML_3{}^{n+} + Q \rightarrow ML_3{}^{n+} + *Q \qquad (6)$$

The polypyridineruthenium complexes employ all three mechanisms depending on the nature of $Q^{2-6,10,11}$ and it can be expected that, with the proper choice of quencher, the chromium complexes will also exhibit all three.

**Quenching by Oxygen.** The mechanism of the quenching of the charge-transfer excited state of $Ru(bpy)_3{}^{2+}$ by oxygen has been the subject of much discussion.[27-29] The observation that singlet oxygen is produced in the $O_2$ quenching of $Ru(bpy)_3{}^{2+}$[27] does not by itself establish an energy transfer mechanism. Lin and Sutin[28] have suggested a redox mechanism

$$*D + O_2 \rightleftharpoons *D|O_2 \rightarrow D^+|O_2^-$$

$$D^+|O_2^- \rightarrow D|{}^1O_2 \rightarrow D + {}^1O_2$$

$$D^+|O_2^- \rightarrow D|{}^3O_2 \rightarrow D + {}^3O_2$$

(where species separated by a | denote cage encounter pairs) that can account for the production of singlet oxygen. Direct evidence for electron transfer products in the $O_2$ quenching reaction is provided by the studies of Winterle, Kliger, and Hammond.[29] The quenching by an electron transfer mecha-
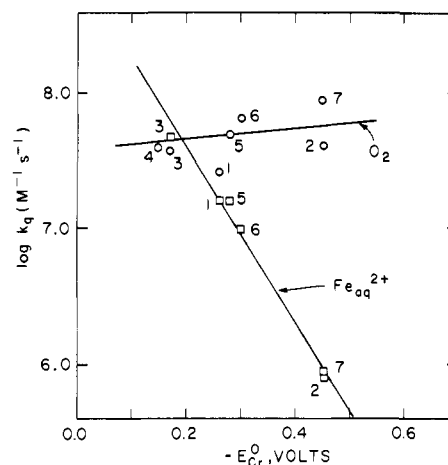


**Figure, 1.** Plot of the logarithm of the rate constant for the quenching of the emission of $CrL_3{}^{3+}$ complexes by $O_2$ in 1.0 M HCl (circles) and by $Fe_{aq}{}^{2+}$ in 1.0 M $H_2SO_4$ (squares) vs. the reduction potential for the $CrL_3{}^{3+,2+}$ couple at 25 °C: 1, L = bpy; 2, L = 4,4'-$(CH_3)_2$bpy; 3, L = 5-Cl(phen); 4, L = 5-Br(phen); 5, L = phen; 6, L = 5-$(CH_3)$phen; 7, L = 4,7-$(CH_3)_2$phen.

nism would suggest that the quenching rate constant should be sensitive to the reduction potential of $D^+$. In the case of the ruthenium(II) complexes, this was not found, nor was it expected, since all the oxygen quenching rate constants were close to the diffusion-controlled limit.[2] The rate constants for oxygen quenching of the chromium(III) complexes, on the other hand, are considerably slower than the diffusion-controlled limit. However, the reduction potentials of the chromium(IV) complexes are not known. If, as our measurements suggest, the reduction potential for the $Cr(bpy)_3{}^{4+/3+}$ couple is $>1.6$ V vs. NHE then the potential for the reaction

$$Cr(bpy)_3{}^{4+} + e^- \rightarrow *Cr(bpy)_3{}^{3+} \qquad (7)$$
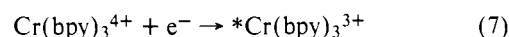
is more positive than $-0.1$ V. Using an $O_2$ potential of $-0.33$[30a] and a p$K$ of 4.7[30b] for $HO_2$, we calculate the reaction

$$*Cr(bpy)_3{}^{3+} + O_2 + H^+ \rightarrow Cr(bpy)_3{}^{4+} + O_2H$$
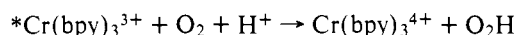
to be endergonic in 1.0 M HCl. It is unlikely that in these systems a mechanism with an unfavorable driving force will provide the predominant quenching mode. Furthermore, while the change in potential for the $CrL_3{}^{4+/3+}$ couple upon ligand substitution is not known, it will probably be significant. Thus one would expect to see a marked variation in quenching rate with ligand substitution if the oxygen quenching made use of an electron transfer mechanism. The data in Table I show that the rate constant for oxygen quenching of the chromium(III) emission increases by a factor of 3 on going from the bipyridine to the dimethylphenanthroline complex. If the reduction potentials for the $*CrL_3{}^{4+/3+}$ couples (eq 7) parallel the $CrL_3{}^{3+/2+}$ potentials then a plot of log $k_q$ vs. $E_{3,2}{}^0$ should reveal any systematic variation of the oxygen quenching rate with driving force. Figure 1 shows that there is very little dependence of the quenching rates on the reduction potentials of the (ground-state) chromium(III) complexes. This may be contrasted with the marked potential dependence of the $Fe_{aq}{}^{2+}$ quenching rates evident in Figure 1.

The quenching of the emission of a number of other chromium(III) complexes by $O_2$ has been studied by Pfeil in a water–methanol–ethylene glycol (1:2:1) solution.[31] The rate constants obtained in this medium together with the results of the present study are plotted in Figure 2 as a function of the energy of the $^2E$ state. Despite differences in the medium, the rate of reaction of the excited states with $O_2$ decreases with increasing energy of the $^2E$ state. This type of behavior has
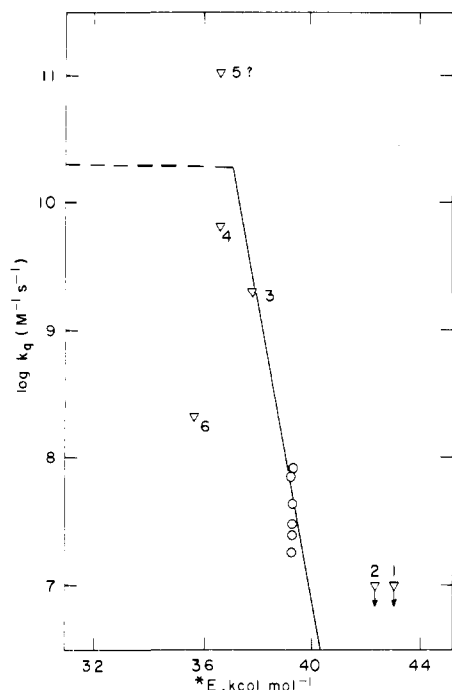
**Figure 2.** Plot of the logarithm of the rate constant for the quenching of the emission of chromium(III) complexes by $O_2$ vs. the energy of the $^2E$ state: circles, $CrL_3^{3+}$, this work, 1.0 M HCl, 25 °C; triangles, methanol-water-ethylene glycol (2:1:1), extrapolated to 25 °C, ref 31; dashed line, diffusion-limited rate constant (W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962)); 1, $Cr(tn)_3^{3+}$; 2, $Cr(en)_3^{3+}$; 3, *trans*-$Cr(NH_3)_2(NCS)_4^-$; 4, $Cr(NCS)_6^{3-}$; 5, $Cr(acac)_3$; 6, $Cr(CN)_6^{3-}$. The rate constant for the $Cr(acac)_3$ is in doubt owing to the long extrapolation of the data to room temperature.

been ascribed to the insulating properties of the ethylenediamine-type ligands. However, with the inclusion of the polypyridine complexes, this behavior must be attributed to other factors.

Oxygen quenching of triplet states of aromatic molecules shows a similar trend of decreasing quenching rate with increasing donor energy. Gijzeman, Kaufman, and Porter[32] found that the quenching rate constants decreased as the triplet energy increased above 43 kcal mol$^{-1}$. This effect was observed despite the fact that the $^1\Delta_g$ and $^1\Sigma_g$ states of $O_2$ are at 22 and 37 kcal mol$^{-1}$, respectively.[33] They argued that the rate of energy transfer is proportional to the Franck-Condon factors for the donor molecule. (The Franck-Condon factors for the $O_2$ molecule do not enter because they are very small except for the 0-0 transition.) This factor is a function of $\Delta E$, the difference between the energy of the excited donor molecule $*E$ and the energy that the $O_2$ molecule can accept upon promotion to its excited state. For the present system $\Delta E$ is given by

$$\Delta E = *E - E_{O_2}$$

where $E_{O_2}$ is the energy of the oxygen singlet state. $\Delta E$ is thus the amount of energy remaining on the donor as vibrational excitation. Since Siebrand[34a] has shown that the Franck-Condon factor is a monotonically decreasing function of $\Delta E$, the efficiency of the quenching should decrease when the excited-state energy exceeds the singlet energy significantly.

The rate constants for the $O_2$ quenching of organic triplets and of the chromium(III) complexes both start to decrease at similar energies ($\sim$39 kcal mol$^{-1}$, Figure 2). This suggests that the $^1\Sigma_g$ rather than the $^1\Delta_g$ level of oxygen is populated in the energy transfer reaction. The rate of decrease of the quenching rate constant with increasing energy gap (Figure 2) is, however, greater than is expected from decreases in the Franck-Condon

factor alone. This suggests that other factors may be contributing to the rate decrease. It has been proposed[1] that the charge on the chromium complex can have an important effect on the rate constant for energy transfer. Wasgestian and Hammond[35] found that the rate constant for energy transfer quenching of anthracene by a number of chromium complexes is a maximum for the neutral $Cr(acac)_3$ and decreases for either positively or negatively charged complexes (e.g., $Cr(en)_3^{3+}$ and $Cr(CN)_6^{3-}$). A rough correlation of the quenching rate constant with the charge of the complex is also apparent for oxygen quenching of the chromium(III) complexes.[31] However, we do not believe that charge should be an important rate-determining factor in energy transfer reactions between two species one of which is uncharged. In support of this view the rate constant for energy transfer from naphthalene to the chromium complexes does not correlate with the charge of the complex.[35] Furthermore, in the oxygen quenching of ruthenium(II) complexes the quenching rate constant does not show any significant correlation with the charge of the complex.[2]

The energetics of the reaction and the Franck-Condon factors are probably the most important rate-determining parameters for the energy transfer reactions discussed here. If $\Delta E$ is negative (that is, if the reaction is transferring energy uphill) the rate should be slow. In the energy transfer from aromatics discussed above[35] naphthalene has a $\Delta E > 0$ for energy transfer to all of the chromium complexes ($k_q \sim 10^8$–$10^9$ M$^{-1}$ s$^{-1}$), naphthacene has $\Delta E < 0$ for all of the complexes (no quenching), and the $\Delta E$ for quenching of anthracene is both positive and negative (with rate constants varying from $10^7$ to $10^9$ M$^{-1}$ s$^{-1}$).

Another factor that may be of importance in energy transfer reactions is the number of "active" hydrogen atoms on the ligands. Robbins and Thomson[34b] have shown that for a number of chromium(III) complexes the rate of intramolecular energy transfer (the $^2E \to {}^4A$ radiationless transition) is related to the number of active hydrogen atoms. The theory they discuss predicts this relationship if the difference between the 0-0 levels of the $^2E$ and $^4A$ states of the chromium(III) complexes is assumed to remain constant (which is not the case for the complexes they considered). Thus for an intermolecular energy transfer process with $\Delta E > 0$ an increase in the number of active hydrogen atoms might also be expected to increase the energy transfer rate (by increasing the magnitude of the Franck-Condon terms). Caution must be exercised in using this argument, however, because changing the ligands will usually also change the $^2E$ energy level.

From the above discussion it is apparent that three factors need to be considered: the energy gap, the number of active hydrogens (both of which affect the Franck-Condon factors), and the charge on the complex. When $\Delta E$ becomes negative the rate of energy transfer decreases dramatically. If $\Delta E$ is positive the rate is unaffected unless the excess energy cannot be distributed over both molecules. The first is seen in the chromium(III) quenching of anthracene and the second in the quenching of the chromium(III) complexes by oxygen. When $\Delta E$ is positive and the excess energy can be distributed over both molecules then the other two factors may become manifest. From the data at hand it is difficult to reach any firm conclusions. Nevertheless it is possible that the rate constants for oxygen quenching of the chromium(III) complexes lacking active hydrogen atoms ($Cr(CN)_6^{3-}$, $Cr(SCN)_6^{3-}$, and $Cr(bpy)_3^{3+}$) are lowered relative to the rate constants for the complexes containing active hydrogen atoms and this could contribute to the abruptness of the rate constant decrease in Figure 2.
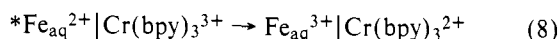
The oxygen quenching of the polypyridineruthenium(II) complexes can also be considered in terms of energetics. The ruthenium complexes have an excited state energy of approximately 50 kcal mol$^{-1}$,[2] which is above the "slow down"

region for oxygen quenching of both the chromium complexes and aromatic triplets.[32] While it may be argued that this is due to differences in how fast the Franck–Condon factors decrease for the ruthenium complexes compared to the other two systems, we believe that a better explanation may lie in the redox mechanism for the ruthenium(II) complexes proposed earlier.

The above discussion can be summarized as follows: (1) The predominant mechanism of the $O_2$ quenching of the $CrL_3^{3+}$ emission is by energy transfer based on (a) the unfavorable energetics of an electron transfer reaction, (b) the insensitivity of the rate constants to ligand substitution (i.e., redox potential), and (c) the falloff in rates for the series of chromium(III) complexes with increasing donor energy. (2) Different factors are important in determining the rate of the $O_2$ quenching of the emission of the $RuL_3^{2+}$ complexes.

**Quenching by Iron(II).** The ferrous quenching of the $Cr(bpy)_3^{3+}$ excited state has been shown to give rise to $Cr(bpy)_3^{2+}$ and $Fe_{aq}^{3+}$ (pH 3, ionic strength 1.0 M).[25] Thus net electron transfer takes place in this system. By analogy, the quenching of the other chromium complexes by $Fe_{aq}^{2+}$ is also likely to give rise to electron transfer products. These products could be produced in either of two ways. They may result from direct electron transfer quenching, or they may be formed following an energy transfer step. In the latter case the excited iron(II) generated by the energy transfer would have to reduce the ground state of the $CrL_3^{3+}$ complex. Since there is an excited state of iron(II) (probably the $^3T_{1g}$ state) lying at 14 400 $cm^{-1}$ above the ground state,[36] energy transfer from the doublet states of the chromium(III) complexes to produce this iron(II) state is energetically feasible. The reduction potential of the iron(II) excited state is ~−1.1 V. The $CrL_3^{3+}$ complexes have reduction potentials in the range of −0.2 to −0.5 V and thus electron transfer from the excited iron(II) to the ground-state $CrL_3^{3+}$ would be thermodynamically favorable. However, a Stokes shift for the iron(II) excited state will reduce the favorableness of the electron transfer. In forming the iron(II) excited state an electron is promoted to an antibonding level. This type of transition usually has a Stokes shift which would make the reduction potential of the iron(II) excited state significantly more positive than −1.1 V. Nevertheless, it is doubtful whether this effect will be large enough to render the reduction unfavorable for some of the chromium(III) complexes.

For an energy transfer path that gives rise to electron transfer products to play a predominant role reaction 8 must be faster than reaction 9.

$$*Fe_{aq}^{2+}|Cr(bpy)_3^{3+} \rightarrow Fe_{aq}^{3+}|Cr(bpy)_3^{2+} \qquad (8)$$

$$Fe_{aq}^{2+}|*Cr(bpy)_3^{3+} \rightarrow Fe_{aq}^{3+}|Cr(bpy)_3^{2+} \qquad (9)$$

Although the driving forces for reactions 8 and 9 are comparable, the energy transfer interpretation is improbable for the following reasons: (1) In reaction 8 the $*Fe_{aq}^{2+}$ loses an antibonding $e_g$ electron while in reaction 9 the $Fe_{aq}^{2+}$ loses a nonbonding $t_{2g}$ electron. This would give the latter reaction a smaller reorganization energy. (2) In reaction 9 an electron is transferred from a $t_{2g}$ orbital on the $Fe^{2+}$ to a $t_{2g}$ orbital on the $Cr^{3+}$, while in reaction 8 the orbital symmetry is less favorable. For these reasons the $Fe_{aq}^{2+}$ quenching of $Cr(bpy)_3^{3+}$ is ascribed to a direct electron-transfer mechanism.

The logarithm of the quenching rate constant is plotted against the logarithm of the equilibrium constant for the electron-transfer reaction

$$Fe_{aq}^{2+} + *CrL_3^{3+} \rightarrow Fe_{aq}^{3+} + CrL_3^{2+}$$
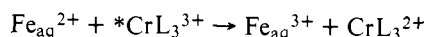
in Figure 3. The single line is indicative of an electron-transfer quenching mechanism for all the chromium(III) complexes studied. The line has an intercept of 1.7 and a slope of 0.43. The
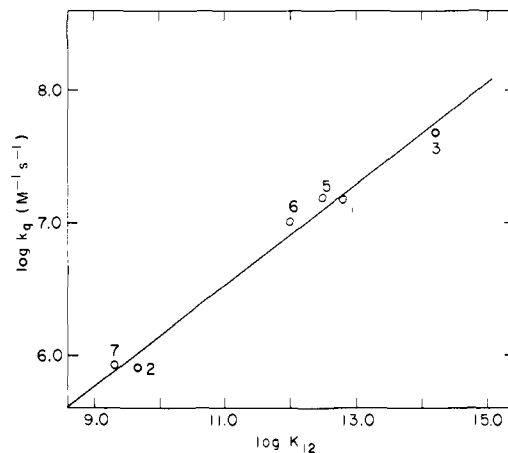


Figure 3. Plot of the logarithm of the rate constant for the quenching of the emission of $CrL_3^{3+}$ complexes by $Fe_{aq}^{2+}$ vs. the logarithm of the equilibrium constant for the electron transfer reaction in 1.0 M $H_2SO_4$ at 25 °C: 1, L = bpy; 2, L = 4,4'-$(CH_3)_2$bpy; 3, L = 5-Cl(phen); 5, L = phen; 6, L = 5-$(CH_3)$phen; 7, L = 4,7-$(CH_3)_2$phen.

Marcus theory for electron transfer reactions[13] predicts a relationship of the type

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}} \qquad (10)$$

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

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 $10^{11}$ $M^{-1}$ $s^{-1}$. Using rate constants of 4.0 $M^{-1}$ $s^{-1}$ for the $Fe_{aq}^{2+}$–$Fe_{aq}^{3+}$ exchange[37] and $1 \times 10^8$ $M^{-1}$ $s^{-1}$ for the $CrL_3^{2+}$–$*CrL_3^{3+}$ exchange

$$*CrL_3^{2+} + CrL_3^{3+} \rightleftharpoons CrL_3^{3+} + *CrL_3^{2+} \qquad (11)$$

the observed slope is in good agreement with the value ~0.40[38] predicted by the equation

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

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

The intercept, however, is less than the theoretical value of 4.3. The $CrL_3^{2+}$–$*CrL_3^{3+}$ exchange rate calculated from the experimental line is ~60 or a factor of $10^6$ slower than the expected value (see below).

A great number of reactions of polypyridine complexes with iron(II) aquo ions have recently been summarized.[39] This summary shows that while reactions with $Fe_{aq}^{2+}$ generally give a free-energy plot that has the proper slope, the intercept is too low by several orders of magnitude. Of particular relevance to the present discussion, the reactions of $Fe_{aq}^{2+}$ with polypyridineruthenium(III) complexes give an intercept that yields an exchange rate for the ruthenium complexes that is ~$10^6$ too low.[2] One explanation that has been advanced for this discrepancy is that the cross-reaction may be nonadiabatic while the exchange reactions of the iron and ruthenium or chromium couples are adiabatic.[2] If this is the case then the Marcus equation needs to be modified to[40]

$$k_{12} = p_{12} \left( \frac{k_{11}k_{22}K_{12}f_{12}}{p_{11}p_{22}} \right)^{1/2} \qquad (12)$$

where $p$ is the probability of electron transfer in the activated complex. Equation 12 reduces to the normal Marcus equation when all the reactions involved in the comparison are adiabatic (i.e., when $p_{12} = p_{11} = p_{22} = 1$). If $p_{11} = p_{22} = 1$ but $p_{12} \ll 1$ then a plot of $\log k_{12}$ vs. $\log K_{12}f_{12}$ will yield an intercept that
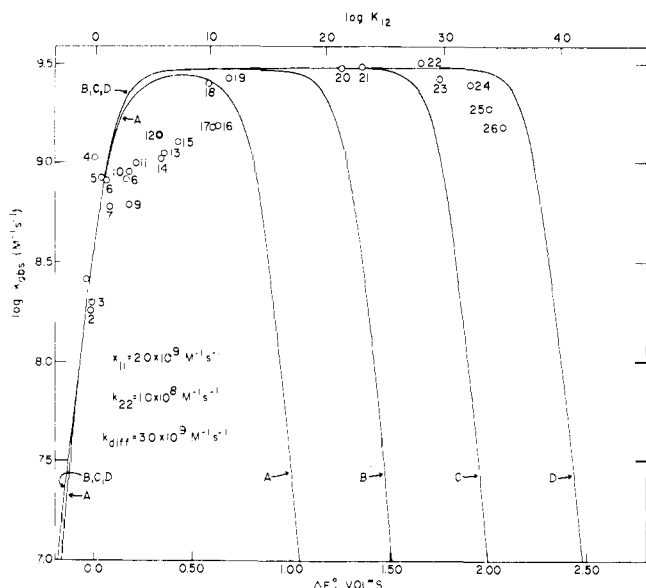
**Figure 4.** Plot of the logarithm of the rate constant for the quenching of the emission of $CrL_3^{3+}$ by $ML'_3^{2+}$ (points 1–17) and of $RuL_3^{2+}$ emission by $ML'_3^{3+}$ (points 18–26) vs. the potential difference (logarithm of the equilibrium constant) for the electron transfer reaction. Solid lines are calculated from the Marcus cross-reaction equation corrected for diffusion with the following values for $Z$ (M$^{-1}$ s$^{-1}$): A, $3 \times 10^{10}$; B, $3 \times 10^{11}$; C, $3 \times 10^{12}$; D, $3 \times 10^{13}$. 1, L = phen, L' = 5-(NO$_2$)phen, M = Ru; 2, L = bpy, L' = 5-(NO$_2$)phen, M = Ru; 3, L = 4,4'-(CH$_3$)$_2$bpy, L' = bpy, M = Ru; 4, L = 4,7-(CH$_3$)$_2$phen, L' = 5-(CH$_3$)phen, M = Ru; 5, L = 5-(CH$_3$)-phen, L' = 5-Clphen, M = Ru; 6, L = phen, L' = 5-Clphen, M = Ru; 7, L = bpy, L' = 5-Clphen, M = Ru; 8, L = phen, L' = phen, M = Ru; 9, L = bpy, L' = bpy, M = Ru; 10, L = bpy, L' = phen, M = Ru; 11, L = bpy, L' = 5-(CH$_3$)phen, M = Ru; 12, L = phen, L' = 4,7-(CH$_3$)$_2$phen, M = Ru; 13, L = bpy, L' = 4,7-(CH$_3$)$_2$phen, M = Ru; 14, L = bpy, L' = 4,4'-(CH$_3$)$_2$bpy, M = Ru; 15, L = bpy, L' = 3,4,7,8-(CH$_3$)$_4$phen, M = Ru; 16, L = bpy, L' = bpy, M = Os; 17, L = phen, L' = bpy, M = Os; 18, L = bpy, L' = bpy, M = Cr; 19, L = 4,4'-(CH$_3$)$_2$bpy, L' = bpy, M = Cr; 20, L = bpy, L' = phen, M = Co; 21, L = 4,4'-(CH$_3$)$_2$bpy, L' = phen, M = Co; 22, L = bpy, L' = bpy, M = Os; 23, L = 4,4'-(CH$_3$)$_2$bpy, L' = bpy, M = Os; 24, L = bpy, L' = 4,4'-(CH$_3$)$_2$bpy, M = Ru; 25, L = 4,4'-(CH$_3$)$_2$bpy, L = 4,4'-(CH$_3$)$_2$bpy, M = Ru; 26, L = bpy, L = bpy, M = Ru. Points 18, 19, and 22–26 are from C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977); points 20 and 21 are from C. Creutz, unpublished results.

corresponds to $k_{22}p_{12}^2$ rather than to $k_{22}$. Since $p_{12} \ll 1$, the uncorrected intercept will give an exchange rate that is too low by $p_{12}^2$, which is the behavior seen in this work. This interpretation requires that the $Fe_{aq}^{2+}$-$Fe_{aq}^{3+}$ and $CrL_3^{2+}$-*$CrL_3^{3+}$ exchange reactions be adiabatic (which is probably true for at least the chromium complex) while the $Fe_{aq}^{2+}$-*$CrL_3^{3+}$ cross-reaction is not. Whatever the explanation, we may conclude that the free-energy dependence of the $Fe_{aq}^{2+}$-*$CrL_3^{3+}$ reactions is "normal" for electron transfer reactions of this type and we accordingly estimate the rate constant for the $CrL_3^{2+}$-*$CrL_3^{3+}$ exchange to be of the order of $10^8$–$10^9$ M$^{-1}$ s$^{-1}$.

**Quenching by Ruthenium(II) and Osmium(II).** The quenching of the excited tris(bipyridine)chromium(III) complex by tris(bipyridine)ruthenium(II) has been shown to result in electron-transfer products.[25] Since the Ru(II) excited state is at a higher energy than the Cr(III) excited state (2.1 eV[39] vs. 1.7 eV), an energy transfer process is unlikely and we propose that the $RuL_3^{2+}$ quenching of $Cr(bpy)_3^{3+}$ and of the $CrL_3^{3+}$ complexes studied proceeds by electron transfer. A plot of log $k_q$ vs. log $K_{12}$ ($\Delta E°$) for the $RuL_3^{2+}$ quenching of these complexes (Figure 4) shows that the quenching rate does indeed depend on the driving force for electron transfer; the plot, however, does not yield the expected slope of 0.50.
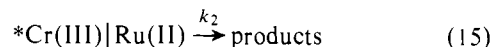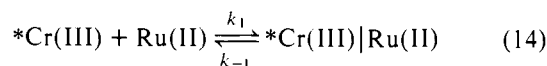
By varying the ligands on both the chromium(III) and the

ruthenium(II) complexes it is possible to study reactions with very small equilibrium constants. The self-exchange rate of the excited $CrL_3^{3+}$ complexes (eq 11) can be estimated from these measurements by using

$$\log k_{12} = 0.50 \log (k_{11}k_{22}) \qquad (13)$$

When the data close to log $K_{12} = 0$ are considered, a line with a slope of 0.41 and an intercept of 8.7 is obtained. The intercept yields a rate constant of $\sim 1 \times 10^8$ M$^{-1}$ s$^{-1}$ for the *$CrL_3^{3+}$-$CrL_3^{2+}$ exchange using $2 \times 10^9$ M$^{-1}$ s$^{-1}$ for the rate constant for the $RuL_3^{2+}$-$RuL_3^{3+}$ exchange.[2,41] The $CrL_3^{2+}$-*$CrL_3^{3+}$ rate constant agrees well with the value estimated above from the $Fe_{aq}^{2+}$ reactions. The slope of the curve in Figure 4 decreases dramatically when the equilibrium constant increases above $\sim 50$ ($\Delta E° > 0.1$ V). While it is expected that the rate constants will become less dependent on the driving force as they approach the diffusion-controlled limit, the observed rates tend to decrease more rapidly with driving force than is predicted by eq 10.

In order to explore further this behavior the Marcus equation was modified to take account of the very fast observed rates using eq 14–17.[2]

$$*Cr(III) + Ru(II) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} *Cr(III)|Ru(II) \qquad (14)$$

$$*Cr(III)|Ru(II) \overset{k_2}{\rightarrow} \text{products} \qquad (15)$$

$$k_{12} = k_1k_2/k_{-1} \qquad (16)$$

$$k_{obsd} = \frac{k_1k_2}{k_{-1} + k_2} \qquad (17)$$

In terms of this scheme $k_{12}$ is the observed rate when $k_2 \ll k_{-1}$ (i.e., $k_{12}$ is the activation-controlled electron transfer rate). It is also the rate that is calculated in Marcus' electron transfer theory.[13] If eq 10, 16, and 17 are combined then the dependence of $k_{obsd}$ on driving force can be calculated. Assuming $k_1 = 3 \times 10^9$ M$^{-1}$ s$^{-1}$ [42] ($k_1$ is the diffusion-limited rate constant for the reaction), $k_{11} = 2 \times 10^9$ M$^{-1}$ s$^{-1}$ [2,41] (the rate constant for the $RuL_2^{2+}$-$RuL_3^{3+}$ exchange), and $k_{22} = 1 \times 10^8$ M$^{-1}$ s$^{-1}$ (the rate constant for the $CrL_3^{2+}$-*$CrL_3^{3+}$ exchange) the calculated $k_{obsd}$ values are plotted in Figure 4 as a function of driving force for a number of different values of $Z$. As expected, the data for the quenching of the chromium(III) excited states by ruthenium(II) and osmium(II) fall near the theoretical line at low driving force but as the equilibrium constant increases above $\sim 50$ ($\Delta E° > 0.1$ V) the rate constants do not increase as much as predicted by Marcus theory. The latter type of behavior has been seen previously in reactions between $Cu_{aq}^{2+}$ ions and *$RuL_3^{2+}$ excited states.[15] However, in the latter case the reactions are also characterized by large driving forces. Similar behavior has also been seen in the quenching of the excited state of $Cr(bpy)_3^{3+}$ by aliphatic amines,[43] but the reactions of the aliphatic amines are irreversible and there is doubt about the values of their half-cell potentials.

The effect of driving force on electron transfer reactions is a subject of continuing interest.[43,44] The prediction that at high enough driving force the rates should begin to decrease has not been borne out experimentally except for a small effect noted for reactions of $RuL_3^{2+}$ excited states with a number of reductants.[9] The potential at which a rate decrease is predicted by the Marcus equations is highly dependent on the choice of $Z$. At $Z = 10^{11}$ M$^{-1}$ s$^{-1}$ (the value of $Z$ suggested by Marcus[13]) the rate constants for these systems are predicted to start decreasing at log $K_{12} > 13$ ($\Delta E° > 0.8$ V). If $Z$ is increased to $3 \times 10^{12}$ M$^{-1}$ s$^{-1}$ no decrease is expected until log $K_{12} \sim 27$ ($\Delta E° \sim 1.6$ V). The rate constant profile is thus strongly dependent upon the choice of $Z$ in the high driving force regime.

In the low driving force regime the observed rate is only weakly dependent on $Z$, that is, changing the value of $Z$ will not greatly affect the results at low $\Delta E°$. It is evident from Figure 4 that the observed rates for the reactions of the $RuL_3^{2+}$ excited states are consistent with eq 10 if $Z \approx 1 \times 10^{13}$ M$^{-1}$ s$^{-1}$ However, this value of $Z$ is almost certainly too large since its use will result in calculated exchange rate constants for a number of systems that are much larger than the observed values.[44] The disagreement of the *$RuL_3^{2+}$ rates in the very exothermic region with the predictions of eq 10 is more likely due to nuclear tunneling effects, as has been discussed previously.[9,40] The rate constants predicted by a nuclear tunneling model will decrease less rapidly with $\Delta E°$ than those calculated from eq 10. (In a nuclear tunneling description the decrease in rate constant results from an increase in nuclear tunneling distance with increasing exothermicity of the reaction.) Alternatively, in terms of a radiationless transition formalism the rates in the very exothermic region are expected to decrease exponentially with the first power of the energy gap[45] (cf. the $O_2$ quenching discussion above).

**Quenching by Osmium(III) and Ruthenium(III) Complexes.**
The quenching of *$CrL_3^{3+}$ by oxidants may involve either energy transfer or the formation of a chromium(IV) product. Recently[46] $Fe(CN)_6^{3-}$ quenching of $Cr(bpy)_3^{3+}$ has been ascribed to oxidative quenching. In the present studies we looked for further evidence of oxidative quenching by using stronger oxidants. $Os(bpy)_3^{3+}$ was found to be an extremely ineffective quencher and only on upper limit could be placed on the quenching rate. Significant quenching was, however, found with $RuL_3^{3+}$. If the quenching is by an electron transfer mechanism

$$*CrL_3^{3+} + ML_3^{3+} \rightarrow CrL_3^{4+} + ML_3^{2+}$$
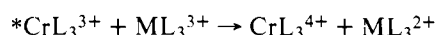
then $Ru(bpy)_3^{3+}$ is expected to quench better than its osmium analogue because of the more favorable driving force for the ruthenium reaction (1.25 vs. 0.82 V). However, the ruthenium(III) complex also has an absorption band at 674 nm which is close to the wavelength of the chromium emission. Moreover, the osmium(III) and the ruthenium(III) complexes also have spin-forbidden transitions at longer wavelengths. Therefore, the possibility that the quenching by $Os(bpy)_3^{3+}$ and $Ru(bpy)_3^{3+}$ involves energy rather than electron transfer cannot be excluded at this time.

**Excited-State Electron Exchange Reactions.** The rate constant for the $Cr(bpy)_3^{2+}$-*$Cr(bpy)_3^{3+}$ exchange (eq 11) estimated in the present work is $1 \times 10^8$ M$^{-1}$ s$^{-1}$.[47] This value may be compared with the rate constant of $\sim 2 \times 10^9$ M$^{-1}$ s$^{-1}$ for the corresponding ground-state $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ reaction:[48]

$$Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+} \rightleftharpoons Cr(bpy)_3^{3+} + Cr(bpy)_3^{2+}$$

$$\text{(18)}$$
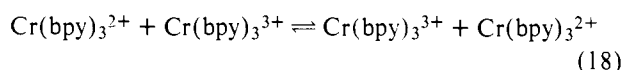
Because of the very similar sizes and charge types of the pair of reactants in the ground- and excited-state reactions the work terms and solvent reorganization barriers for the two reactions will be the same. Consequently if the two reactions are adiabatic they can differ only in their inner-sphere barriers. For the excited-state and ground-state exchanges these barriers are given by eq 19 and 20, respectively[49]

$$*\Delta G_{in}{}^{\ddagger} = \frac{3f_2 f_3*}{f_2 + f_3*}(a_2 - a_3*)^2 \qquad \text{(19)}$$

$$\Delta G_{in}{}^{\ddagger} = \frac{3f_2 f_3}{f_2 + f_3}(a_2 - a_3)^2 \qquad \text{(20)}$$

where $f_i$ is a breathing force constant, $a_i$ is the metal–ligand bond length, and $i$ is the charge of the reactant. The value of $(a_2 - a_3)$ for the $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ exchange is probably close to zero, based on structural data for the related Fe-

$(phen)_3^{2+}$-$Fe(phen)_3^{3+}$ system.[50] It is likely that $(a_2 - a_3*)$ is also close to zero since *$Cr(bpy)_3^{3+}$ differs from $Cr(bpy)_3^{3+}$ only in the arrangement of the (nonbonding) metal $t_{2g}$ electrons. The assumption about the bond length differences is consistent with the absence of a Stokes shift for the *$Cr(bpy)_3^{3+}$ emission. The Stokes shift is in general given by

$$E_s = \sum_j \tfrac{1}{2}(f_{ij}* + f_{ij})(a_{ij}* - a_{ij})^2$$
$$+ \sum_{l,k} \tfrac{1}{2}(f_{lk}* + f_{lk})(a_{lk}* - a_{lh})^2 + E_s \text{ (solvent)} \quad \text{(21)}$$

where the first summation is over the metal–ligand vibrations and the second is over the intraligand vibrations. The third term is the contribution to the Stokes shift from the difference in the polarization of the solvent surrounding the ground and excited states. The second and third terms may be neglected when the ground- and excited-state orbitals are metal centered. Thus a good approximation for the Stokes shift for the $CrL_3^{3+}$ complexes considered here is

$$E_s = 3(f_3* + f_3)(a_3* - a_3)^2 \qquad \text{(22)}$$

Equations 19, 20, and 22 can be combined to give the difference between the inner-sphere reorganization energy for the ground- and excited-state exchange reactions as

$$\Delta(G_{in}{}^{\ddagger}) = (*\Delta G_{in}{}^{\ddagger} - \Delta G_{in}{}^{\ddagger})$$
$$= \frac{3f_2}{f_2 + f_3}\left[ (*f_3 - f_3)a_2^2 + \frac{E_s}{6}\left(\frac{a_3* + a_3 - 2a_2}{a_3* - a_3}\right) \right]$$

where it has been assumed that *$f_3 = f_3$ except for the first term. The first term arises from differences between the force constants of the ground and excited states while the second term is a measure of whether the distortion giving rise to the Stokes shift is favorable or not with respect to the electron exchange. The first term is expected to be small when both states have the same number of $e_g$ and $t_{2g}$ electrons.[51] Five possibilities exist for the second term: (1) $E_s = 0$ (i.e., $(a_3* - a_3) = 0$). Under these conditions $\Delta(\Delta G_{in}{}^{\ddagger}) = 0$ and the inner-sphere barriers for the ground- and excited-state exchange reactions are the same. (2) If *$a_3 > a_3$ and $a_2 > \tfrac{1}{2}(a_3* + a_3)$ then *$\Delta G_{in}{}^{\ddagger} < \Delta G_{in}{}^{\ddagger}$. (3) If *$a_3 > a_3$ but $a_2 < \tfrac{1}{2}(a_3* + a_3)$ then *$\Delta G_{in}{}^{\ddagger} > \Delta G_{in}{}^{\ddagger}$. (4) If *$a_3 < a_3$ and $a_2 > \tfrac{1}{2}(a_3* + a_3)$ then *$\Delta G_{in}{}^{\ddagger} > \Delta G_{in}{}^{\ddagger}$. (5) If *$a_3 < a_3$ but $a_2 < \tfrac{1}{2}(a_3* + a_3)$ then *$\Delta G_{in}{}^{\ddagger} < \Delta G_{in}{}^{\ddagger}$. The case observed depends upon whether the excited state has expanded or compressed metal–ligand bonds compared to the ground state. If only the number of $t_{2g}$ electrons is changed very little effect on bond length is expected;[50] however, if a $t_{2g}$ to $e_g$ (or $e_g$ to $t_{2g}$) promotion occurs then a significant change in both bond lengths and force constants is likely.[50,51] Thus relatively large differences in ground- and excited-state exchange reaction rates should be observable for ligand field excited states of low-spin $d^6$ complexes.[52,53] For the $CrL_3^{2+}$-$CrL_3^{3+}$ system case 1 probably obtains and the $Cr(bpy)_3^{2+}$-$Cr(bpy)_3^{3+}$ and the $Cr(bpy)_3^{2+}$-*$Cr(bpy)_3^{3+}$ exchange reactions are expected to proceed at similar rates. We conclude that the difference of an order of magnitude between the observed and calculated exchange rates reflects experimental uncertainties and the various approximations introduced.

We next compare the ground- and excited-state exchange reactions of the $Ru(bpy)_3^{2+}$ system. In $Ru(bpy)_3^{2+}$ the metal-centered electron is excited into a ligand-centered *$\pi$ orbital. The ground- and excited-state reactions that both involve the transfer of a metal-centered electron are

$$Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+} \rightleftharpoons Ru(bpy)_3^{3+} + Ru(bpy)_3^{2+}$$
$$\text{(23)}$$
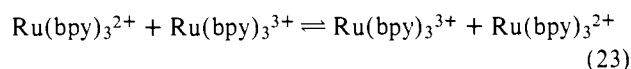
**Table IV.** Rate Constants for the Ground- and Excited-State Electron Exchange Reactions of Chromium and Ruthenium Polypyridine Complexes at 25 °C

| exchange reaction | $10^{-8}k_{ex}$, $M^{-1}$ $s^{-1}$ | medium | ref |
|---|---|---|---|
| $Cr(bpy)_3^{2+}$–$Cr(bpy)_3^{3+}$ | $\sim 20$ | 0.1 M | 48 |
| $Cr(bpy)_3^{2+}$–$*Cr(bpy)_3^{3+}$ | 1 | 1 M | this work |
| $Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$ | $20^a$ | 1 M | 41 |
| $Ru(bpy)_3^+$–$*Ru(bpy)_3^{2+}$ | $\geq 1^b$ | | 39 |
| $Ru(bpy)_3^+$–$Ru(bpy)_3^{2+}$ | $\geq 1^b$ | DMF | $2^c$ |
| $*Ru(bpy)_3^{2+}$–$Ru(bpy)_3^{3+}$ | $\sim 1^b$ | | 39 |

$^a$ The value reported $(1.2 \times 10^9 \ M^{-1} \ s^{-1})$ has been corrected for diffusion control using $1/k_{act} = 1/k_{obsd} - 1/k_{diff}$ with $k_{diff} = 3 \times 10^9$ $M^{-1} \ s^{-1}$. $^b$ Estimated in ref 39 and 2. $^c$ See footnote 47 of ref 2.

and

$$Ru(bpy)_3^+ + *Ru(bpy)_3^{2+} \rightleftharpoons *Ru(bpy)_3^{2+} + Ru(bpy)_3^+ \tag{24}$$
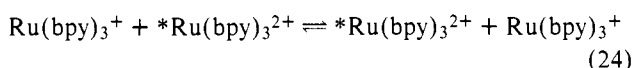
The reactions will have similar solvent reorganization barriers (see the chromium case). Although the work term is different for the two reactions, this term is small for reactions of large complexes at high ionic strength.[44] The inner-sphere barrier for the two reactions depends on the difference between the metal–ligand bond distances of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ and of $Ru(bpy)_3^+$ and $*Ru(bpy)_3^{2+}$, respectively. These differences are expected to be small for the same reasons as for the chromium reactions;[50] thus the inner-sphere barrier for both ruthenium exchange reactions should be negligible. The rates of the ground- and excited-state ruthenium exchange reactions are therefore expected to be similar. This is the case in practice: the rate constants for reactions 23 and 24 are $2 \times 10^9$ and $\geq 1 \times 10^8 \ M^{-1} \ s^{-1}$, respectively,[39] entirely analogous to the chromium bipyridine exchange.

The above considerations suggest that the Stokes shift for the $*Ru(bpy)_3^{2+}$ emission should also be zero, which is not found ($E_s \sim 1100 \ cm^{-1}$ for $Ru(bpy)_3^{2+}$).[43] However, the optical transition for the ruthenium(II) complex involves not only the redistribution of electron density in the metal $t_{2g}$ orbitals (as is the case for the chromium(III) complex) but also the addition of an electron to the ligand $\pi^*$ system. For the $*Ru(bpy)_3^{2+}$ system the Stokes shift is given approximately by

$$E_s \approx \sum_{l,k}^{\text{ligands}} \tfrac{1}{2}(f_{lk}^* + f_{lk})(a_{lk}^* - a_{lk})^2 \tag{25}$$

where the summation is over only the ligand vibrations. As required by this interpretation the Stokes shift for the $*Ru(bpy)_3^{2+}$ emission is similar in magnitude to the Stokes shifts found for aromatic systems.[54]

To conclude, the exchange rates of the excited states of the chromium and ruthenium polypyridine complexes, like those of the corresponding ground-state complexes, are very rapid (Table IV). The exchange rate and reduction potential of $*Cr(bpy)_3^{3+}$ are comparable with that of $Ru(5\text{-}NO_2\text{-}(phen))_3^{3+}$. Although the reaction of $*Cr(bpy)_3^{3+}$ with oxygen and its properties as an oxidizing agent are fairly well characterized, its properties as a reducing agent have yet to be elucidated.

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# The Chemistry of 2-Naphthyl Bis[bis(dimethylphosphino)ethane] Hydride Complexes of Fe, Ru, and Os. 2. Cleavage of sp and sp³ C–H, C–O, and C–X Bonds. Coupling of Carbon Dioxide and Acetonitrile

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**Abstract:** Reactions of HMNp(dmpe)₂ (Np = 2-naphthyl, dmpe = Me₂PCH₂CH₂PMe₂, M = Fe, Ru, or Os) with HCN, terminal acetylenes, and molecules having activated sp³ C–H bonds to give new HMR(dmpe)₂ complexes are described. A major factor determining the stability of the products appears to be the stability of the carbanion R⁻. Rate studies indicate two distinct mechanisms: (1) rapid direct electrophilic attack on the naphthyl hydride, observed with HCN, and (2) slow, rate-determining reductive elimination of naphthylene (rate constant $k_1$), followed by rapid oxidative addition of RH to the 16-electron intermediate [M(dmpe)₂]. Kinetic studies on the reaction of CH₃CN with HFeNp(dmpe)₂ in THF give $k_1 = 0.022 \pm 0.003$ min⁻¹ at 25 °C and $0.10 \pm 0.1$ min⁻¹ at 40 °C. Initial formation of cis-HFeCH₂CN(dmpe)₂, followed by slow isomerization to the more stable trans isomer is consistent with a three-center transition state for the oxidative addition. Coupling of acetonitrile and CO₂ as a route to methyl cyanoacetate has been demonstrated. Reactions of the naphthyl hydrides with some esters and ethers to cleave C–O bonds, and with alkyl and aryl halides to cleave C–X bonds, are also described.

## Introduction

Because of the potential importance of selective reactions of hydrocarbons under mild conditions, there has been a rapidly growing interest in the activation of C–H bonds by transition metal complexes.[1] Many examples of *intra*molecular[2] metallation reactions are known. *Inter*molecular[2] reactions to cleave C–H bonds are much more rare, particularly those cases where the HMC adduct has sufficient stability to be isolated or characterized spectroscopically; oxidative additions of the sp C–H bond of HCN[3] or of terminal acetylenes[3d,4] are the best known. Recent examples of intermolecular cleavage of sp³ C–H bonds include the reactions of photolytically generate (π-C₅H₅)₂W with *p*-xylene or mesitylene to give (π-C₅H₅)₂W(CH₂Ar)₂ complexes,[5] and of (cyclohexyne)-Pt(Ph₂PCH₂CH₂PPh₂) with CH₃NO₂, CH₃COCH₃, CH₃COPh, or NCCH₂Ph to give (cyclohexenyl)PtR(diphos).[6] Acetonitrile adds to certain IrL₄⁺ complexes [L₄ = (PMe₃)₄ or (Me₂PCH₂CH₂PMe₂)₂] to give complexes of the type HIr(CH₂CN)L₄⁺.[7]

Compound **1**, formed in the pyrolysis of HRuNp(dmpe)₂[8] [dmpe = Me₂PCH₂CH₂PMe₂, Np = 2-naphthyl], was prob-



**1**
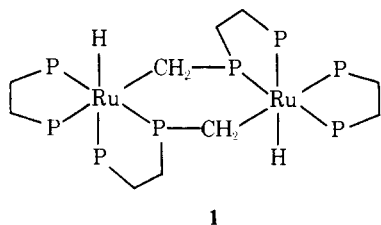
ably the first example of an intermolecular sp³ C–H cleavage, though that fact was not recognized until an X-ray structure[9] was carried out at a later date.

In the preceding paper[10] we have described the spectroscopic characterization of the HMNp(dmpe)₂ complexes [M = Fe

(**2a**), Ru (**2b**), or Os (**2c**)] in solution and their reactions with H₂ and various Lewis base ligands. The spectroscopic properties of the products—particularly the exceptionally low $\nu_{CO}$ frequency (1812 cm⁻¹) in (CO)Fe(dmpe)₂ and the high-field shift ($\delta$ 0.6 ppm) of the ethylenic protons in (C₂H₄)-Fe(dmpe)₂—indicate a very high electron density on the Fe(dmpe)₂ fragment. In this paper the implications of this high electron density for cleavage of C–H bonds having sp or sp³ hybridization at carbon are explored. Cleavage of C–O and C–halogen bonds is also described. Rate studies show two distinct types of oxidative addition mechanisms: direct electrophilic attack on HMNp(dmpe)₂, and oxidative addition to intermediate [M(dmpe)₂] formed by a rate-determining reductive elimination of naphthylene. The coupling of acetonitrile and CO₂ to give cyanoacetic acid is also described. A succeeding paper[11] in this series will deal with reactions of sp² C–H bonds. Some of the results described in the present paper have been reported briefly.[12]

## Results and Discussion

**Cleavage of sp C–H Bonds.** As described earlier,[10] diphenylacetylene reacts with **2a** to form a π-bonded acetylene complex. In contrast, acetylene itself reacts with cleavage of the sp C–H bond to form the hydridoacetylide complex **3**. The



**3**