and the products are singlets, the proposed reaction path involving nucleophilic $H_2O$ attack on TBP would necessitate the crossing of triplet and singlet surfaces.

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$$cis\text{-}Rh(NH_3)_4Cl_2^{+}(aq) \rightarrow basal\text{-}Rh(NH_3)_4Cl^{2+}(aq) + Cl^{-}(aq) \quad \text{(i)}$$

represents the energy differences between $G_{cis}$ and $G_B$) plus the excitation energy ($E_3$) from $G_B$ to $T_B$. Vanquickenborne's calculation[9] suggests $E_3$ to be <5000 cm$^{-1}$; therefore, for the condition $E_1 > E_2 = E_3 + E_D$ to hold, $E_D$ should be ≲13 000 (~37 kcal). $E_D$ is an unknown quantity. The activation energy $E_a$ for the aquation of halides from Rh(III) complexes falls in the 9000 cm$^{-1}$ range;[28] but these reactions are probably interchange associative in character.[29] However, analogous Co(III) substitution reactions are largely dissociative in character, with $E_a$ values of ~8000 cm$^{-1}$ noted for aquations of Co(III)–chloroamine complexes. Thus, we do not consider an $E_a$ value less than or equal to 13 000 cm$^{-1}$ to be unreasonable.

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(35) In this context it should be noted that the recent emission studies[5] have allowed the calculation of reaction rates from LF excited states of Rh(III) complexes. For example $Cl^-$ aquation from excited $Rh(NH_3)_5Cl^{2+}$ in ambient aqueous solution ($k = 1.4 \times 10^7$ s$^{-1}$) is ~14 orders of magnitude faster than from the ground state ($k = 5.8 \times 10^{-8}$ s$^{-1}$). $NH_3$ aquation from the same excited state is somewhat slower ($k = 1.5 \times 10^6$ s$^{-1}$) but represents rate accelerations of comparable or greater magnitude over the thermal analogue.

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# "Intersystem Crossing" Yields in Ruthenium(II) and Osmium(II) Photosensitizers

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Originally the efficiencies, $\phi'$'s, of populating the sensitizing charge-transfer excited states of Ru(II) and Os(II) photosensitizers were claimed to be unity. Recent experimental results have raised questions concerning this claim. This paper reexamines the question of the $\phi'$'s of these photosensitizers. With both photochemical and spectroscopic data, the early claim of unity $\phi'$'s is supported.

## Introduction

Since the introduction of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, as a luminescent photosensitizer,[1] it and related metal complexes have provided a wealth of new and potentially useful photochemical systems and reactions.[2–11] One of the key advantages of these metal complexes is the very high efficiency of populating the emitting–sensitizing state following excitation in upper levels. Originally, on the basis of the invariance of the luminescent yield with wavelength, Demas and Crosby[12] claimed that the efficiency of populating the excited state, $\phi'$, was unity.

This claim of a unity $\phi'$ for $[Ru(bpy)_3]^{2+}$ and other complexes having charge-transfer (CT) sensitizing states has recently come into question.[11] On the basis of flash photolysis work, a $\phi'$ of ~0.5 was suggested for $[Ru(bpy)_3]^{2+}$. Similarly, excited-state electron-transfer reactions to $Fe^{3+}$ [6] and energy-transfer studies to Cr(III) complexes seemed to indicate that $\phi'$ for $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) might be 0.5–0.6 times as large as that of $[Ru(bpy)_3]^{2+}$.[13] Although the flash-photolytic work has probably been shown to be in error because of an incorrect assumption concerning the $*[Ru(bpy)_3]^{2+}$ excited-state absorption,[5,9,13] there still seem to be conflicting claims and uncertainties concerning the correctness of $\phi'$ for Ru(II) and Os(II) sensitizers.

In view of the pivotal role of $[Ru(bpy)_3]^{2+}$ and related Ru(II) and Os(II) complexes in inorganic photochemistry, we felt it essential to address the question of the $\phi'$'s of these complexes. We believe that there is strong evidence to show that $\phi'$ is much greater than these claims would suggest. Indeed, we find no compelling reason to believe that $\phi'$ is less than unity. Our evidence is based on existing and new spectroscopic and photochemical data.

## Experimental Section

**Complexes.** Tris(2,2′-bipyridine)ruthenium(II) chloride was from G. Frederick Smith Chemical Co. and was recrystallized twice from water. The $[Ru(phen)_3]Cl_2$ was made by reduction of $RuCl_3$ with oxalate in the presence of phen. $[Ru(phen)_3]I_2$, isolated by precipitation with NaI, was recrystallized from water. $[Ru(phen)_3]Cl_2$ was formed by reaction of the iodide salt with $Ag_2O$ followed by neutralization with HCl. $Ru(bpy)_2(CN)_2$ and $Ru(phen)_2(CN)_2$ were obtained by reaction of $Ru(L)_2(C_2O_4)_2$ with aqueous NaCN; purification was by dissolving the complex in methanol and passing it through silica gel and alumina columns.

**Wavelength Dependence of the Quantum Yield.** Relative luminescence yields vs. excitation wavelength were obtained by using an optically dense quantum-counter comparator.[14] A schematic representation of this system is shown in Figure 1. Two 1 cm thick cylindrical quantum-counter cells were mounted side by side on a kinematic mount in the excitation path. Samples were rear-viewed by an IR-sensitive photomultiplier tube. One quantum-counter cell contained an optically dense solution of the metal complex, and the other cell contained a 5 g/L Rhodamine B (RhB) reference quantum counter in methanol. At each excitation wavelength, a series of phototube current readings were taken for the unknown ($X$'s). The quantum-counter mount was then moved to position the RhB counter in the excitation beam, and a second series of current readings ($S$'s)

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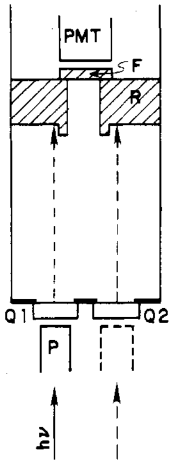

**Figure 1.** Schematic diagram of relative quantum yield comparator for optically dense measurements. The monochromator excitation beam, *hν*, enters the comparator through a light baffle P. Q1 and Q2 are the two cells containing a Rhodamine B quantum counter and the sample under study. R is further light baffling. PMT is an RCA C7164R red-sensitive photomultiplier. F is a Corning CS 2-62 red-pass filter to attenuate any transmitted exciting light. The comparator assembly is kinematically mounted so that Q1 and Q2 can be moved into the excitation beam.

were taken for the standard. The process was repeated at all of the wavelengths of interest, and a sample-to-reference intensity, $R(1,\lambda)$, was calculated at each wavelength:

$$R(1,\lambda) = [(1/N_X)\sum_{i=1}^{N_X} X_i/(1/N_S)\sum_{i=1}^{N_S} S_i]_\lambda \qquad (1)$$

where $N_X$ and $N_S$ are the number of readings taken at each wavelength for the unknown and reference samples, respectively. For avoidance of any bias between the two cell positions, the reference and unknown cells were interchanged, and the entire process was repeated to obtain an $R(2,\lambda)$ curve as in eq 1. The final relative sensitivity of the unknown to the RhB, $R(\lambda)$, was obtained by first normalizing the $R(1,\lambda)$, and $R(2,\lambda)$ curves independently to an average value of unity to yield $\bar{R}(1,\lambda)$ and $\bar{R}(2,\lambda)$. Then $R(\lambda)$ was calculated from

$$R(\lambda) = 0.5[\bar{R}(1,\lambda) + \bar{R}(2,\lambda)] \qquad (2)$$

The relative quantum yield of each metal complex, $\phi_X(\lambda)$, was then calculated from

$$\phi_X(\lambda) = K[R(\lambda)][\phi_S(\lambda)] \qquad (3)$$

Here $\phi_S(\lambda)$ is the relative quantum yield of the reference counter vs. wavelength and $K$ is the normalization factor which made $\phi_X(\lambda)$ average unity over the range of interest.

Details of the complete instrumentation and measurement procedure as well as tabulation of $\phi_S(\lambda)$ for the RhB counter used in this work are given elsewhere.[14] The accuracy of this method is probably the best available especially since the $\phi_S(\lambda)$ for the standard sample actually used in this work was calibrated by an absolute method.

## Results and Discussion

Spectroscopically each of the ruthenium(II) complexes is characterized by low-lying charge-transfer (CT) excited states. The most intense of these with $\epsilon \sim 8000$–15 000 in the 430–450-nm region have been referred to as CT "singlets". The absorption tails out to longer wavelengths. At room temperature near the state energies of the thermally equilibrated emitting levels, $E_0$'s, the $\epsilon$'s are typically several hundred. At room temperature in fluid solutions, the emissions are reasonably intense, broad structureless bands which peak at ~600–650 nm and overlap only slightly with the absorption tail. The emissions have all been assigned to (d–$\pi^*$) CT transitions. Originally the emitting state was believed to be a triplet CT state, and the emissions thus were phosphorescences.[12,15,16] Crosby and co-workers[17] have more recently shown that spin–orbit coupling is so great that singlet–triplet spin labels are probably erroneous; it is thus appropriate to speak of the emissions only as CT luminescences rather than as fluorescences or phosphorescences. For similar reasons, the use of the term intersystem crossing with these complexes is without meaning. We have therefore adopted the $\phi'$ to stand for the efficiency of relaxation from the upper excited states to the emitting state.

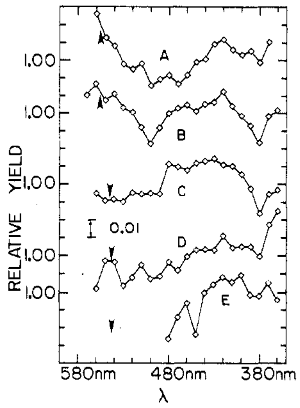

**Figure 2.** Relative quantum yield vs. excitation wavelength for optically dense solutions of the metal complexes: A, $[Ru(bpy)_3]^{2+}$ (10 g/L in methanol); B, $[Ru(bpy)_3]^{2+}$ (15 g/L in water); C, $Ru(bpy)_2(CN)_2$ (5.4 g/L in methanol); D, $[Ru(phen)_3]^{2+}$ (16.2 g/L in methanol); E, $Ru(phen)_2(CN)_2$ (saturated solution in methanol). The excited-state zero-point energy for each complex is indicated by an arrowhead. Relative yields between samples cannot be compared.

Relative luminescence quantum yields vs. excitation are shown in Figure 2. Systems include $[Ru(bpy)_3]^{2+}$ in both water and methanol (Figure 2A,B), as well as $Ru(bpy)_2(CN)_2$ (Figure 2C), $[Ru(phen)_3]^{2+}$ (Figure 2D), and $Ru(phen)_2(CN)_2$ (Figure 2E) in methanol. The state energies, $E_0$'s, for the emitting levels of the complexes are $18.0 \times 10^3$ cm$^{-1}$ for $[Ru(bpy)_3]^{2+}$, $18.4 \times 10^3$ cm$^{-1}$ for $[Ru(phen)_3]^{2+}$, and $18.4 \times 10^3$ cm$^{-1}$ for both cyano complexes.[18,19] $E_0$'s were estimated by using the Fleischauer criteria[20] as applied to the 77 K emission spectra of each complex in chemically similar glasses. The wavelength equivalents of the $E_0$'s are indicated by arrows for each curve.

The $Ru(phen)_2(CN)_2$ system was not soluble enough to permit measurements at low excitation energies and will not be discussed further. In all of the remaining systems the luminescence yields remained constant to within 2% on going from the intense CT states at ~430–450 nm to excitation into the region inverse to the emission where the emitting state would absorb.

We turn now to the value of $\phi'$. Certainly on the basis of the $R(\lambda)$'s, $\phi'$ is wavelength independent over a wide range of excitation energies. $\phi'$ can be calculated from

$$\phi' = f_E/[(Q - 1) + f_E] \qquad (4a)$$

$$Q = R_L/R_U \qquad (4b)$$

where $R_L$ and $R_U$ are the relative luminescence yields when exciting in the low-energy-excitation region inverse to the emission and in the upper excited states, respectively, and $f_E$ is the fraction of the excitation beam in the low-energy excitation which directly excites the emitting state. The problem of estimating $\phi'$ from our spectroscopic data then reduces to one of estimating $f_E$.

Examination of the absorption spectra clearly shows that the main CT band at ~430–450 nm is too far away and too sharp to yield appreciable intensity in the lower energy excitation region.[12,19] Further, the long-wavelength absorption tail overlaps with the emission band. It thus seems reasonable that, with excitation at the zero-point energy, excitation should be predominantly in the emitting state. An $f_E$ of 0.9 seems a conservative estimate which in turn yields a $\phi'$ of at least 0.98 in all cases (based on $Q = 1.02$).

Alternatively, we can estimate $f_E$ from the intrinsic emission lifetimes, $\tau_0$, and the Strickler–Berg formula.[21] With the assumption that the absorption bandwidth is comparable to the emission bandwidth, the extinction coefficient of the emitting state would be ~20.[22] On the basis of an observed $\epsilon$ in the low-energy-excitation region of ~200–400 nm, we obtain $f_E \approx 0.05$–$0.07$, which still yields $\phi' \approx 0.7$–$0.8$. However, on the basis of the much better resolved low-temperature absorption spectra of the CT emitters $[Ru(bpy)_3]^{2+}$ and $[Os(terpy)_2]^{2+}$ and the d–d phosphorescer *trans*-$[Rh(bpy)_2Br_2]^{2+}$, Demas and Crosby[12] have shown that both the Einstein and Strickler–Berg formulas relating $\tau_0$'s and absorption data substantially underestimate $\epsilon$'s. Thus, $\phi'$'s based on the Strickler–Berg relation are probably much too low.

Photochemical data also show $\phi'$'s to be quite high. Singlet oxygen generation efficiencies[10] for $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, and $Ru(bpy)_2(CN)_2$ were 0.85, 0.75, and 0.79, respectively. Three other Ru(II) and three Os(II) complexes all gave yields in the 0.74–0.82 range. For $Ru(phen)_2(CN)_2$ the yield was 0.68. These yields set lower limits for $\phi'$ since radiationless deactivation of the donor-$^1O_2$ exciplex or inefficient chemical generation of $^1O_2$ by the reactions $D^+|O_2^- \rightarrow D|^1O_2 \rightarrow D + {}^1O_2$ would make the $^1O_2$ formation efficiencies less than $\phi'$.[10] Also, impurities are unlikely to be sensitizers which could further raise $\phi'$ relative to observed $^1O_2$ formation efficiencies.

Electron transfer from $[Ru(bpy)_3]^{2+}$ again shows $\phi'$'s to be very high. The observed excited-state electron-transfer efficiency is 0.85 for $[Co(C_2O_4)]^{3-}$,[24] 0.94 ± 0.03 for $Fe^{3+}$,[25] and ~1.0 for $Tl^{3+}$.[26] Again these results set lower limits on $\phi'$ for $[Ru(bpy)_3]^{2+}$ of $\geq 0.90$ and are totally inconsistent with the suggestion of 0.5 from the flash-photolysis data.[11] With related poly(pyridine) ruthenium(II) complexes electron-transfer efficiencies to Cu(II) approached unity in several cases, and the data were consistent with $\phi'$ being unity in all cases.[8]

Thus, for the Ru(II) photosensitizers we can find no evidence that $\phi'$ is appreciably less than unity, and the original claim that $\phi'$ was unity[12] still seems a sound basis for interpretation of photosensitization data. While based on less definitive evidence, the assumption of $\phi' = 1$ for Os(II) is also reasonable, especially since the spin–orbit coupling in Os is greater than in Ru and any prohibition in excited-state relaxation to the sensitizing–emitting level should be further reduced.

On this basis, we feel that all interpretation of transition-metal photosensitizers should assume $\phi' = 1$. Thus, the subunity yields in excited-state electron-transfer reactions must arise from secondary processes (e.g., back electron transfer in the encounter pair $D^+|Q^-$) or competitive energy transfer to low-lying excited states of the acceptor (e.g., ligand field states in $Fe^{3+}$). In the case of energy-transfer experiments, competitive electron-transfer quenching (possibly without successful disengagement to form separated redox portions) and formation of a short-lived exciplex which undergoes some radiationless deactivation before dissociation to the energy-exchanged partners are both possible explanations of the apparent low energy-transfer efficiency. Finally, impure sensitizers could be another source of some of the apparent low energy- or electron-transfer yields.

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**Registry No.** $[Ru(bpy)_3]^{2+}$, 15158-62-0; $Ru(bpy)_2(CN)_2$, 58356-63-1; $[Ru(phen)_3]^{2+}$, 22873-66-1; $Ru(phen)_2(CN)_2$, 14783-57-4.

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