Ruthenium Polypyridyls
A Case Study

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A brief perusal of activity in inorganic photochemistry during the last ten years will invariably lead to the conclusion that the tris-2,2'-bipyridylruthenium(II) dication (Ru(bpy)$_3$$^{2+}$) is among the most studied of metal complexes. How did this interest begin and what has lead to its rapid growth throughout the discipline? To answer the first question one need only prepare a dilute solution of Ru(bpy)$_3$$^{2+}$ and irradiate it with a black light in a partially darkened room. Even the most experienced spectroscopist who has witnessed the result thousands of times cannot help but be impressed by the beautiful red-orange emission which emanates from the solution. This phenomenon of visible light emission from fluid solutions spurred early photophysical studies to characterize the luminescence and identify the luminescent excited states (1-5). Following these beginnings in the darkened laboratories of luminescence spectroscopists, it was discovered that the excited state of Ru(bpy)$_3$$^{2+}$ could participate in redox processes in fluid solution (6-10). Shortly thereafter it was recognized that, because of these photoredox properties, the complex might function as a photocatalyst for the decomposition of water into hydrogen and oxygen (11). These developments brought Ru(bpy)$_3$$^{2+}$ into the limelight of inorganic photochemistry and are responsible for the recent flurry of activities which surround the complex.

As a result of the intense interest which this species has generated, Ru(bpy)$_3$$^{2+}$ has played a key role in the development of concepts and methodology of inorganic photochemistry. Its participation in a rich variety of photochemical processes has stimulated the development of experimental techniques and conceptual models which have wide applicability in diverse situations throughout inorganic photochemistry.

Ground State Properties

In a study of a class of inorganic complexes designed to illustrate the application of major principles of inorganic photochemistry, where does one start? The natural emphasis of inorganic photochemistry is on the structure and reactivity patterns of excited state species formed by absorption of light. However, successful interpretation of photochemical events is often heavily dependent upon detailed knowledge of the structure and reactivity of related ground state species. This case study therefore will begin with a brief summary of several ground state properties of Ru(bpy)$_3$$^{2+}$ which are relevant to its photochemistry.

The ground state structure of one enantiomer of the hexafluorophosphate salt of Ru(bpy)$_3$$^{2+}$, determined by x-ray crystallography, is illustrated in Figure 1 (12). The complex ion possesses $D_{3h}$ symmetry and the Ru–N bond length of 206.6 pm is somewhat shorter than the 210.4 pm value in Ru(NH$_3$)$_6$$^{2+}$ (13), indicating significant π-backbonding between Ru(II) and the π* orbitals of bpy. A five line $^{13}$C NMR spectrum is observed for the solvated species (14) and the $^1$H NMR spectrum (15) can be interpreted in terms of four coupled spins in each of six equivalent pyridine rings (see Fig. 2). The solution NMR data are therefore consistent with retention of $D_{3h}$ symmetry for the solvated species. Resolution of the enantiomers by recrystallization of the diastereomeric antimony tartarate salt (16, 17) can be achieved, and these are found to be thermally stable with respect to racemization (16, 18).

A good deal of the photochemical interest in Ru(bpy)$_3$$^{2+}$ stems from its photoredox properties, which are closely interrelated to redox properties in the ground state. Values of standard potentials for oxidation and reduction of Ru(bpy)$_3$$^{2+}$ (19, 20) which are useful in establishing excited state redox potentials, are shown in eqns. (1) and (2).

$$\text{Ru(bpy)}_3^{2+} + e^- \rightarrow \text{Ru(bpy)}_3^{3+} \quad E^o = -1.28 \text{ V} \quad (1)$$

$$\text{Ru(bpy)}_3^{3+} + e^- \rightarrow \text{Ru(bpy)}_3^{2+} \quad E^o = +1.26 \text{ V} \quad (2)$$

The monovalent, divalent, and trivalent cations are noted for their thermal inertness toward labilization of bpy, leading to their potential participation in a variety of reversible electron transfer processes.

Excited States of Ru(bpy)$_3$$^{2+}$: Absorption and Emission Spectroscopy

Absorption Spectroscopy

With some knowledge of the ground state structure and chemical properties of Ru(bpy)$_3$$^{2+}$, the stage is set to begin consideration of its photochemical properties. Since each electronic excited state formed by absorption of a photon has an electron distribution and an equilibrated structure that is different from the ground state, each state may be viewed as a chemical species with distinct reactivity patterns. Some knowledge of the energies and electronic distribution of the excited states relative to the ground state can be obtained by measurement of the absorption spectrum and assignment of the features. The absorption spectrum of Ru(bpy)$_3$$^{2+}$ is shown in Figure 3 along with assignments of the orbital promotions which have been proposed (21, 22).

Although each of these states might, in principle, exhibit a distinct reactivity pattern, there is abundant evidence that competitive, radiationless decay processes are much faster than these potential photochemical processes in most instances. The detailed pathways of the upper level radiationless decays are not known, but it is known that formation of the

Figure 1. The structure of Ru(bpy)$_3^{2+}$. (12)
lowest excited states occurs rapidly and with high efficiency following excitation in any of the absorption bands shown in Figure 3a. The techniques that have been used to reach this conclusion are largely dependent upon emission spectroscopy as discussed below. However, the anticipated importance of the lowest levels draws attention to the long wavelength tail of the absorption spectrum where some evidence of these levels is found. This region is characterized by a slight shoulder around 550 nm when the absorption measurement is made on Ru(bpy)$_2^{3+}$ in an ethanol-methanol glass at 77K (23) (see Fig. 3b). The extinction coefficient is approximately 600 M$^{-1}$cm$^{-1}$ in this region. If the contribution from absorption to a presumed low energy excited state is estimated as indicated in Figure 3b, the radiative lifetime for this state, $\tau_o$, can be calculated from the integrated area under the absorption curve according to the Strickler-Berg equation (24). This calculation yields a value of roughly 1 $\mu$s assuming a non-degenerate excited state. Larger values are obtained if a degenerate excited state is assumed, but the calculated value remains smaller than the experimental value of 13.9 $\mu$s at 77K from emission measurements (23) described below. Since the conditions necessary for accurate calculation of $\tau_o$ by the Strickler-Berg equation are undoubtedly not present in Ru(bpy)$_2^{3+}$, the order-of-magnitude agreement tends to confirm that the 550 nm shoulder is indeed a direct absorption into the luminescent state.

**Emission Spectroscopy**

Excitation of Ru(bpy)$_2^{3+}$ in any of its absorption bands leads to a single emission band which is illustrated in Figure 4. This indicates that some fraction of the initial excited states produced by light absorption decay to a common set of excited states responsible for emission. The fraction of the luminescent set of excited states which undergo radiative decay may be expressed as

$$\Phi_r = k_r/(k_r + k_{nr})$$(3)

where $k_r$ and $k_{nr}$ represent the rate constants for radiative and nonradiative decay of this luminescent set of states, respectively (see Fig. 5). The net luminescence quantum yield, $\Phi_l$, is a measure of the ratio of number of photons emitted to the number of photons absorbed, and $\Phi_l$ is related to $\Phi_r$ through the relationship
form of the luminescent states, or 2) all excited states attained over the range of wavelengths studied (250–550 nm) could relax with unit efficiency (Ψ_m = 1) into the luminescent levels. Since the first conclusion has generally been considered implausible, most studies have proceeded on the assumption that the second statement is the correct conclusion.

The importance of this conclusion is manifested in general statements of its applicability to any open d-shell metal complex (26) and in continued efforts to establish its validity in the case of Ru(bpy)_3^2+. Although flash photolysis studies have suggested that Ψ_m may be less than unity (27), recent studies have extended the excitation wavelength dependence of Φ_l to encompass direct irradiation into the region where the 0-0 band of the luminescent states is believed to be located (28). Since this constitutes a direct measurement of Φ_l, which is found to be equal to Φ_m, it follows that Φ_m is unity.

A photochemical technique employing photoreduction of S_2O_5^-^2 by excited Ru(bpy)_3^2+, illustrated in Figures 6a and 6b, has been used to evaluate Φ_m (29). This technique also serves to illustrate the ability of Ru(bpy)_3^2+ to function as a photoreductant, a property that will be discussed in further detail at a later point in this case study. The reaction of Ru(bpy)_3^2+ with S_2O_5^-^2 yields Ru(bpy)_3^3+, SO_4^2-, and the strongly oxidizing SO_3^2 radical. Once formed, this radical reacts with ground state Ru(bpy)_3^2+ to yield a second Ru(bpy)_3^2+ complex ion (See Fig. 6a).

Experimentally, the quantum yield for disappearance of Ru(bpy)_3^2+, Φ_{Ru(bpy)_3^2+}, was followed by monitoring the 450 nm absorption of Ru(bpy)_3^2+, and measurements were made as a function of [S_2O_5^-^2]. From a plot of 1/[Φ_{Ru(bpy)_3^2+}] versus 1/[S_2O_5^-^2] (see Fig. 6b) the limiting value of Φ_{Ru(bpy)_3^2+} at high [S_2O_5^-^2] is found to be 2.0. This value can occur only if all of the Ru(bpy)_3^2+ excited states which are formed react to yield Ru(bpy)_3^3+ and SO_4^2-, and all of the SO_3^2 radical does go on to react with Ru(bpy)_3^2+ to form additional Ru(bpy)_3^2+. This result is consistent with the conclusion that Φ_m is unity, and serves to illustrate complementary functions of chemical reactivity and spectroscopy in inorganic photochemistry.

On the basis of the types of studies cited above, considerable confidence can be placed in the unit efficiency for population of the luminescent states following excitation through the visible and near-ultraviolet region. This leaves the question of the rate at which the luminescent states are populated following upper-level excitation yet to be explored. Two basic approaches have been taken to this question. In the first approach, the absence of upper state emission processes or by radiationless relaxation from upper states directly to the ground state represented by k_r and k_{nr}, respectively, in Figure 5.

There are several techniques which have been employed to estimate Φ_{inc}. In the first of these, Φ_l was measured as a function of excitation wavelength (23). The techniques for performing luminescence quantum yield measurements on transition metal complexes have been reviewed (25), and the dependence of Φ_l on excitation wavelength can be measured with a high degree of precision. In these initial measurements, excitation was at energies above the 0-0 band of the luminescent levels, and the results of these measurements on Ru(bpy)_3^2+ in ethanol-methanol glass at 77K and in methanol at room temperature indicate that Φ_l is, to a good approximation, independent of the excitation wavelength. Since Φ_l is an intrinsic property of the luminescent levels which cannot depend upon the excitation condition, it is concluded that Φ_{inc} is independent of the excited state formed under excitation at different wavelengths. From these early studies one could reach either of two possible conclusions: 1) the constancy of Φ_{inc} could result from the dissipation of some constant fraction of the excited states at a point in the kinetic pathway prior to

\[ \Phi_l = \Phi_{inc} \Phi_r \]  

where Φ_{inc} represents the fraction of the excited state species which relax into the luminescent state. The quantity Φ_{inc} is particularly significant for photochemical purposes since any photoactivity from upper excited levels, illustrated by k_r in Figure 5, will cause Φ_{inc} to deviate from unity. Deviation could also be caused by upper state emission processes or by radiationless relaxation from upper states directly to the ground state represented by k_r and k_{nr}, respectively, in Figure 5.


Figure 4. Luminescence spectrum of Ru(bpy)_3^2+ in aqueous solution at ambient temperature (55).

Figure 5. Energy transfer processes in metal complexes.

Figure 6. Photo-oxidation of Ru(bpy)_3^2+ by S_2O_5^-^2 (29): a) Quantum yield for disappearance of starting material as a function of [S_2O_5^-^2]; b) Proposed reaction scheme.

\[ \tau_0' = \frac{\tau_0}{\Phi_l} \]  

(5)

to yield estimates for the lifetimes, \tau_0', of the upper levels. Since the decay of these levels leads to formation of the luminescent
state, $\tau^*$ provides an estimate of the rate of population of this state. Conservative estimates by this approach suggest $\tau^* \ll 0.1$ ns (5, 23).

The second approach to this question utilizes risetimes for luminescence following pulsed excitation. In practice, the limit on measurements of risetimes is related to the length of the excitation pulse. Recent estimates (30) based partially upon picosecond laser measurements (31) of a similar compound $[\text{Ru(bpy)}_2(\text{CH}_3\text{OH})]^{2+}$ indicate that the risetime is $\ll 0.1$ ns. Hence, the actual value remains unmeasured, but the limit of $\ll 0.1$ ns appears to be quite reliable.

The lifetime of the luminescence of $\text{Ru(bpy)}^{2+}$ has been measured over a wide range of temperatures and environmental conditions. In many instances, luminescence quantum yields, $\Phi_l$, have been measured in conjunction with lifetimes. Since $\Phi_{\text{exc}}$ is unity, the luminescence yield may be equated with the efficiency of the radiative process from the lowest energy levels, $\Phi_l$, leading to the relationship

$$\tau_{\text{obs}}(T) = \frac{\tau(T)}{\Phi_l(T)} \quad (6)$$

Hence, combined measurements of $\tau$ and $\Phi_l$ yield experimental values of $\tau_{\text{exc}}$.

For the purposes of discussion it is convenient to divide measurements of $\Phi_l$ and $\tau$ into two broad temperature regions. In the low temperature region, $\lesssim 100$K, the $\text{Ru(bpy)}^{2+}$ complex is generally photoinert, and extensive studies of the luminescence lifetime have yielded detailed information concerning the nature of the lowest excited levels. At higher temperatures, $\gtrsim 100$K, the complex displays luminescence as well as a variety of photochemical processes where rates can often be estimated with the help of luminescence lifetime measurements. While this region is less amenable to spectroscopic studies, it is more significant from the photochemical viewpoint.

The types of results which have been obtained from measurements in the low temperature region are illustrated in Figure 7 (32-36). The luminescence decay follows first order kinetics over the entire temperature range, suggesting that the luminescence originates from a set of levels in thermal equilibrium whose relative populations are altered significantly by temperature variations between 2 and 100K. The four level model illustrated in Figure 7 has been used (32-34) as the basis for empirical fitting of the experimental temperature dependence of $\tau$ and $\Phi_l$.

**Models for the Charge Transfer Excited State**

While the experimental evidence for the contribution of several levels to the luminescence over the low temperature range is quite strong, the theoretical description of these levels continues to be a matter of debate. One model, termed the electron-ion parent coupling (EIP) model (33, 36) assumes $D_3$ symmetry is retained in the $\pi^*$ excited state, and that spin-orbit coupling of electrons in the $d^5$ core is larger than electron-electron interaction between the core and the promoted $\pi^*$ electron. The $\pi^*$ orbital is assumed to have $A_2$ symmetry, and coupling of the double group representation of the $\pi^*$ electron with the double group representation of the $d^5$ core yields states of $A_1$, $E$, and $A_2$ symmetry. The assumptions built into this model suggest that it is inappropriate to attach spin labels to these states (37).

Although this model correlates well with the results of the empirical $\tau(T)$ and $\Phi_l(T)$ fitting procedure, the procedure is not unique, suggesting other models could equally well rationalize the data. A variety of recent results suggest that other models must be sought to explain all of the details of the electronic excited states of $\text{Ru(bpy)}^{2+}$. These results stem from several techniques which include resonance Raman (38, 39), single-crystal polarized absorption (40-42), photoelectric (43, 44), flash photolysis (45-47), single-crystal polarized emission (48), luminescence (49), and circular dichroism (50) measurements. The results of these measurements have spurred further theoretical developments (51) and the formulation of a major new model (52) denoted as the electronic structural (ES) model to interpret the full absorption spectrum of $\text{Ru(bpy)}^{2+}$.

Detailed analysis of all of these methods goes beyond the scope of this case study; however, presentation of several of the conclusions and some discussion of the flash photolysis results are in order. It has been concluded (48) that $\text{Ru(bpy)}^{2+}$ does not retain its $D_3$ symmetry in the ground and/or excited state in polymethylmethacrylate (PMMA) or EPA glasses. Furthermore, resonance Raman results (38, 39) suggest that the $\pi^*$ electron in the $\pi^*$ excited state resides on a single bpy moiety on the vibrational time scale, consistent with reduction of symmetry to less than $D_3$ in this excited state. Comparison of the excited state absorption spectrum (45-47) with that of $\text{Na}^{+}\text{bpy}^{-}$ (53), shown in Figure 8, is consistent with a fully reduced bpy$^-$ ring being present in the $\pi^*$ excited state, again suggesting localization of the $\pi^*$ electron in a single ligand (54). On the other hand, measurements of luminescence lifetimes, energies, and quantum yields of heterochelates of Ru(II) with both bpy and 1,10-phenanthroline (phen) are consistent with delocalization of the promoted electron throughout the ligand framework (49).

In addition to the questions about the degree of delocalization of the promoted electron and the symmetries of the
sublevels of the $d\pi^*$ excited state, the question of the spin parentage of this state remains one of current interest in inorganic photochemistry. While the EIP model denies the appropriateness of spin labels and stresses the use of symmetry labels (57), the ES model maintains that the luminescent $d\pi^*$ state may be properly labeled as a triplet with less than ten percent singlet character due to spin-orbit coupling (52).

**Photosubstitution Processes**

Measurements of lifetimes and quantum yields over a wide range of temperatures above 100K in both aqueous (55, 56) and nonaqueous (58, 59) solvents have served to extend the low temperature spectroscopic models for the luminescent $d\pi^*$ state into the realm where net photochemical products are sometimes formed. The results of measurements of $\tau$ and $\Phi_1$ in fluid aqueous solutions (55) are illustrated in Figure 9. In the temperature range of these measurements, the set of levels deduced at low temperatures (see Fig. 7) have reached the high temperature limit with regard to the Boltzmann population distribution, and an additional level must be added. Equations (7) and (8), based upon the kinetic model in Figure 9, are used in the fitting procedure.

$$\tau(T) = [k_{1r} + k_{1q} + k_{2q} \exp(-\Delta E/kT)]^{-1} \tag{7}$$

$$\Phi_1 = k_{1r} \tau(T) \tag{8}$$

According to this model the net loss of excitation energy arises from radiative ($k_{1r}$) and nonradiative ($k_{1q}$) processes from the luminescent charge transfer levels as well as a thermally activated nonradiative decay ($k_{2q}$) from a higher energy set of triplet $d-d$ levels which could be of $A_2$ or $E$ symmetry. Identification of these higher levels as $d-d$ states is based upon the observed photosubstitution behavior at elevated temperatures, consistent with established reactivity patterns for $d^6$ metal complexes. Empirical fits of the lifetime and quantum yield data for Ru(bpy)$_2$($d_5^+$) and Ru(bpy)$_2$($d_6^+$) in H$_2$O and in D$_2$O indicate that $k_{1r}$ and $k_{2q}$ are insensitive to deuteration whereas $k_{1q}$ is not. This suggests that $k_{1q}$ is associated with a weakly-coupled radiationless process whereas the $k_{2q}$ decay is a strong-coupled process (60, 61). The fitting procedure also indicates that the values of $k_{1r}$ and $k_{1q}$ in fluid water solutions deviate substantially from the high temperature limits predicted by the EIP model. These deviations, as well as large solvent deuteration effects on $\tau$ in aqueous solutions (62), have led to the conclusion that some charge-transfer-to-solvent (CTTS) character is mixed into the CTTL states in fluid aqueous solutions (55, 56).

The occurrence of a strong-coupled deactivation pathway at elevated temperatures has significant photochemical ramifications. Such a pathway is generally associated with a photochemical process as opposed to a photophysical process, and as the dissipation of excitation energy via this pathway becomes significant, photochemical degradation of Ru(bpy)$_2^{2+}$ is anticipated. Since $k_{1q}$ shows a deuterium effect whereas $k_{2q}$ does not, the deuterium effect on $\tau$ begins to disappear as the term $k_{2q} \exp(-\Delta E/kT)$ in eqn. (10) becomes dominant. This term dominates at temperatures above 323K, where reduction of the deuterium effect on $\tau$ is symptomatic of substantial photochemistry via the strong-coupled pathway (62).

Although the model presented in Figure 9 provides an adequate interpretation of the luminescence data in fluid aqueous solutions, studies over an extended temperature range in aqueous LiCl (58), as well as in a series of organic solvents (57, 58), indicate that modification of eqn. (7) to incorporate a second exponential term is necessary. This modification is shown in eqn. (9).

$$\tau(T) = [k_1 + A_1 \exp(-\Delta E/kT) + A_2 \exp(-\Delta E/kT)]^{-1} \tag{9}$$

According to eqn. (9), $k_1 = k_{1r} + k_{1q}$ accounts for the contribution from the lowest set of CTTL levels. The temperature-dependent term, $A_1 \exp(-\Delta E/kT)$, arises from a second set of CTTL levels approximately 148 cm$^{-1}$ above the lowest sets. As before, the term $A_2 \exp(-\Delta E/kT)$ indicates the presence of a set of $d-d$ levels responsible for photosubstitution at elevated temperatures.

Detailed studies (63) of photosubstitution of [Ru(bpy)$_3$]$_2$([SCN])$_2$ in dimethylformamide (DMF) reveal that two products, [Ru(bpy)$_2$(DMF)(NCS)]$^+$ and [Ru(bpy)$_2$(NCS)$_2$]$^+$, are formed. Quantum yields for disappearance of Ru(bpy)$_2^{2+}$ and for formation of [Ru(bpy)$_2$(DMF)(NCS)]$^+$ are found to be dependent on [SCN$^-$], whereas the quantum yield for [Ru(bpy)$_2$(DMF)(NCS)$_2$]$^+$ is roughly independent of [SCN$^-$] as illustrated in Figure 10. Although no model which accounts for all of the experimental data has been found, the mechanism is believed to include formation of both ion pairs and ion triplets by excited state *Ru(bpy)$_2^{2+}$, which react to form [Ru(bpy)$_2$(DMF)(NCS)]$^+$ and [Ru(bpy)$_2$(NCS)$_2$]$^+$, respectively. This mechanism is illustrated in eqns. (10) and (11) below.
Although the mechanism of Figure 11a will undoubtedly be the subject of further study and discussion, it leads to a particularly startling conclusion which is quite consistent with all existing data: Ru(bpy)$_3^{2+}$ is relatively phototoxic with regard to formation of the five-coordinate intermediate from the d-d excited state. Thus, whether the net quantum yield for disappearance of Ru(bpy)$_3^{2+}$ is small, as in H$_2$O/C$	ext{I}^-$ at 298K, or large, as in CH$_2$Cl$_2$/C$	ext{I}^-$ at 298K, a substantial fraction of the excitation energy is dissipated through Ru—N bond cleavage.

**Photoredox Reactions**

The greatest activity in inorganic photochemistry in recent years has undoubtedly arisen from studies of the participation of *Ru(bpy)$_3^{2+}$ in bimolecular electron transfer processes. These processes are believed to be characteristic of the luminescent charge transfer state which is formed with unit efficiency following excitation, and can therefore proceed with large quantum yields. The vectorial charge separation upon excitation of this state has been estimated to be approximately 3 Å (59), which suggests that it might reasonably undergo oxidation via loss of the promoted electron or reduction via the electron deficient metal core. It is informative to describe this state with regard to both its thermodynamic potentials and its kinetic properties in electron transfer processes.

Two basic approaches have been utilized in determinations of the standard electrode potentials for oxidation and reduction of Ru(bpy)$_3^{2+}$. In the first of these, the thermodynamic free energy of the excited state, $\Delta G^*$, is approximated by the excitation energy of the thermally equilibrated charge transfer state (67–69). A correction for entropy changes due to an assumed threefold degeneracy in the excited state is sometimes introduced, but is quite small relative to the excitation energy (67, 70). This yields a $\Delta G^*$ value of 2.10 V which can be combined with ground state oxidation and reduction potentials (18, 20) to yield redox potentials for Ru(bpy)$_3^{2+}$ illustrated in Figure 12 (67, 71). A second approach based upon quenching of the luminescence by a series of quenchers with known, graded potentials has also been utilized (70). This technique, which is dependent upon kinetic considerations discussed below as well as thermodynamic properties, yields results similar to those illustrated in Figure 12. These two techniques have been applied to a variety of tris complexes of Ru(II) with substituted bpy ligands illustrated in the table below (69). These complexes may be utilized in conjunction with Ru(bpy)$_3^{2+}$ to yield a series of photoredox agents with a wide range of oxidation and reduction potentials.

The kinetics associated with participation of Ru(bpy)$_3^{2+}$ in outer sphere electron transfer processes (72–75) are dependent upon the thermodynamic potentials discussed above as well as the self-exchange processes illustrated below (69).

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$

$$\text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Ru(bpy)}_3^{2+}$$
Consideration of the orbitals involved in the electron transfer, indicated by the configuration associated with each species, suggests that the self-exchange rate for \( ^*{\text{Ru(bpy)}}^3/\text{Ru(bpy)}^2 \) should be similar to that for the ground state \( \text{Ru(bpy)}^2/\text{Ru(bpy)}^+ \) exchange. Analogous reasoning suggests that the \( ^*{\text{Ru(bpy)}}^3/\text{Ru(bpy)}^2 \) self-exchange rate should be comparable to that for \( \text{Ru(bpy)}^2/\text{Ru(bpy)}^+ \). Measurements of the ground state self-exchange rates yield values of \( \geq 10^9 \) M\(^{-1}\) s\(^{-1}\) for \( \text{Ru(bpy)}^2/\text{Ru(bpy)}^+ \) and \( \text{Ru(bpy)}^+/\text{Ru(bpy)}^2 \) and \( \leq 10^7 \) M\(^{-1}\) s\(^{-1}\) for both of the excited state self-exchange processes in eqns. (12) and (13) above (69).

In view of the large oxidation and reduction potentials available in the charge-transfer excited state as well as its large self-exchange rate constants, it is not surprising to find that \( ^*{\text{Ru(bpy)}}^3 \) participates in a wide range of bimolecular redox reactions. Two primary approaches have been utilized to study these processes: 1) Stern-Volmer quenching of the luminescence from the charge-transfer state by redox active quenchers, and 2) direct observation of the absorption spectra of redox products formed in flash photolysis experiments.

The Stern-Volmer technique is widely used in the determination of quenching constants, but it is difficult to deduce from a single study which of the following processes is responsible for quenching:

\[
^*\text{Ru(bpy)}^3 + Q \rightarrow ^*\text{Ru(bpy)}^2 + Q^- \quad (14) \\
\text{oxidative quenching}
\]

\[
^*\text{Ru(bpy)}^2 + Q \rightarrow ^*\text{Ru(bpy)}^+ + Q^- \quad (15) \\
\text{reductive quenching}
\]

\[
^*\text{Ru(bpy)}^+ + Q \rightarrow ^*\text{Ru(bpy)}^3 + ^*Q \quad (16) \\
\text{energy transfer quenching}
\]

Clarification of which of these processes is responsible for Stern-Volmer behavior can be obtained by studying the dependence of the quenching constants for a given quencher on the excited state oxidation potential of a series of closely related Ru(II)-polypyridyl complexes such as those listed in the table. Representative plots of \( \log k_q \) versus \( E_{\text{red}} \) for quenching such a series by aqueous \( \text{Eu}^{3+} \) and \( \text{Cr}^{3+} \) (79) or versus \( E_{\text{ox}} \) for quenching by aqueous \( \text{Eu}^{2+} \) (80) are shown in Figure 13. The free energy dependence of quenching by \( \text{Eu}^{3+} \) is indicative of the oxidative process (eqn. (14)), whereas the \( \text{Eu}^{2+} \) quenching data suggests a reductive process (eqn. (15)). The absence of any dependence of \( k_q \) for \( \text{Cr}^{3+} \) on excited state potentials is indicative of quenching via energy transfer (eqn. (16)), consistent with the known low energy ligand field excited states of \( \text{Cr}^{3+} \).

The direct observation of redox products in flash photolysis experiments represents the strongest evidence to support the occurrence of oxidative and reductive quenching mechanisms in \( ^*\text{Ru(bpy)}^3 \). These measurements are dependent upon determination of changes in the optical density (\( \Delta OD \)) of a solution containing the complex and quencher resulting from application of a pulse of light which excites \( ^*\text{Ru(bpy)}^3 \). From a knowledge of the absorption spectrum of the preflash solution and the difference spectrum (\( \Delta OD \)), the spectra of light-induced transients can be deduced. Since these transients often decay rapidly either by back reactions to re-form starting materials or by secondary reactions to form other products, it is generally desirable to measure transient absorptions on the time scale of the excited state decay. Modern techniques utilize pulsed laser excitation sources and fast measuring devices such as oscilloscopes, transient digitizers, or optical multichannel analyzers for this purpose.

Analysis of transient absorptions can take the form of identification of the oxidized or reduced metal complex and/or the respective quencher reduction-oxidation product. For this reason the absorption spectrum of \( ^*\text{Ru(bpy)}^3 \) (81-84), shown in Figure 14a, is an invaluable aid in analysis. The intense absorption band which occurs at approximately 510 nm in aqueous solutions has an extinction coefficient of approximately \( 14,000 \) M\(^{-1}\) cm\(^{-1}\) (82), and is a particularly useful diagnostic for formation of \( ^*\text{Ru(bpy)}^3 \). Although the spectrum of \( ^*\text{Ru(bpy)}^3 \) is well known (see Fig. 14a), the extinction coefficients of the broad band at approximately 680 nm and the sharper band at 420 nm are only 680 and 3,300 M\(^{-1}\) cm\(^{-1}\), respectively.

<table>
<thead>
<tr>
<th>Excited State Reduction Potentials for Polypyridine Ruthenium(II) Complexes *</th>
<th>( E_{\text{ox}} ) (V)</th>
<th>( E_{\text{red}} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) ( \text{4,4'}-(\text{CH}<em>{2})</em>{2}\text{bpy} )</td>
<td>-0.94</td>
<td>+0.69</td>
</tr>
<tr>
<td>2) \text{bpy}</td>
<td>-0.64</td>
<td>+0.64</td>
</tr>
<tr>
<td>3) ( 4,4'-\text{(CH}<em>{2})</em>{3}\text{phen} )</td>
<td>-1.01</td>
<td>+0.67</td>
</tr>
<tr>
<td>4) ( 5,6'-\text{(CH}<em>{2})</em>{3}\text{phen} )</td>
<td>-0.93</td>
<td>+0.86</td>
</tr>
<tr>
<td>5) ( 5-\text{CH}_{2}\text{phen} )</td>
<td>-0.90</td>
<td>+0.89</td>
</tr>
<tr>
<td>6) \text{phen}</td>
<td>-0.87</td>
<td>+0.79</td>
</tr>
<tr>
<td>7) ( 5-\text{Clphen} )</td>
<td>-0.77</td>
<td>+1.00</td>
</tr>
</tbody>
</table>

* See Reference (69)

Figure 13. Dependence of quenching constants for \( \text{Eu}^{2+}, \text{Cr}^{3+}, \) and \( \text{Eu}^{2+} \) on excited state redox potentials of a series of Ru(II) polypyridine complexes (69). The numbers refer to numbered complexes in the table.

Figure 14. Absorption spectra of \( ^*\text{Ru(bpy)}^3 \) in 1N H\(_2\)SO\(_4\) (85) and \( ^*\text{Ru(bpy)}^3 \) in aqueous solution (82).
Figure 15. Difference spectrum for Ru(bpy)$_2^+$-Ru(bpy)$_3^{2+}$ generated by pulsed laser excitation of an aqueous solution of Ru(bpy)$_3^{2+}$ containing 0.06 M Eu(II), 0.0014 M Ru(bpy)$_2^+$, 0.5 M Cl$^-$ and 0.05 M H$^+$ at 25°C (86).

respectively (85). As a result, small concentrations of Ru(bpy)$_3^{2+}$ are generally not detectable in the presence of Ru(bpy)$_2^+$ and quenching species.

An example of direct observation of Ru(bpy)$_2^+$ formed by reduction of $^*$Ru(bpy)$_2^+$ is provided by flash photolysis studies of solutions containing Ru(bpy)$_2^+$ and Eu(III) (86). The difference spectrum generated by application of a 30 ns pulse from a frequency-doubled neodymium laser (530 nm) is illustrated in Figure 15. This spectrum shows net bleaching in the region around 430 nm due to depletion of Ru(bpy)$_2^+$ and a buildup of absorption at 490-510 nm. Since both Eu$^{3+}$ and Eu$^{2+}$ are transparent in this region, the absorption must be attributed to formation of Ru(bpy)$_2^+$. Further evidence for this comes from the time dependence of the emission intensity and the optical density following the laser pulse, illustrated in Figure 16. Growth of the absorption of Ru(bpy)$_2^+$ at 500 nm (curve a) occurs at a rate equal to the rate of decay of the luminescence (curve b) consistent with reductive quenching of $^*$Ru(bpy)$_2^+$ as indicated in eqn. (17).

$$^*\text{Ru(bpy)}_2^+ + \text{Eu}^{3+} \rightarrow \text{Ru(bpy)}_2^+ + \text{Eu}^{2+}$$ (17)

Once formed, Ru(bpy)$_2^+$ decays on a longer time scale (curve c) by a process believed to be the back reaction with Eu$^{3+}$ shown in eqn. (18).

$$\text{Ru(bpy)}_2^+ + \text{Eu}^{3+} \rightarrow \text{Ru(bpy)}_3^{2+} + \text{Eu}^{2+}$$ (18)

Equally strong evidence for the oxidation of $^*$Ru(bpy)$_2^+$ to Ru(bpy)$_3^{2+}$ has been obtained from studies of quenching by the methyl viologen dication, MV$^{2+}$ (70, 87-90). Oxidative quenching leads to formation of the strongly absorbing blue monocationic species, MV$^+$, which is monitored rather than the weakly absorbing oxidation product, Ru(bpy)$_3^{2+}$. The time dependence of the absorption of MV$^+$, monitored at 600 nm, and the emission of $^*$Ru(bpy)$_3^{2+}$, monitored at 615 nm is illustrated by curves a and b, respectively, in Figure 17 (88). The luminescence decay rate parallels the rate of growth of the 600 nm absorption, consistent with oxidative quenching as shown in eqn. (19).

$$^*\text{Ru(bpy)}_3^{2+} + \text{MV}^+ \rightarrow \text{Ru(bpy)}_3^{2+} + \text{MV}^+$$ (19)

As was the case with reductive quenching, decay of MV$^+$ on a longer time scale (curve c) is attributed to the back electron transfer shown in eqn. (20).

$$\text{Ru(bpy)}_3^{2+} + \text{MV}^+ \rightarrow \text{Ru(bpy)}_3^{2+} + \text{MV}^{2+}$$ (20)

These studies provide conclusive evidence for the participation of the charge-transfer excited state of Ru(bpy)$_2^+$ in oxidation and reduction processes.

Figure 16. Flash photolysis of aqueous Eu(II). Ru(bpy)$_2^+$ solution: a) Absorbance at 500 nm; b) Emission at 600 nm; c) Absorbance at 500 nm on a longer time scale (86).

Figure 17. Flash photolysis of aqueous methyl viologen. Ru(bpy)$_3^{2+}$ solution: a) emission at 615 nm; b) absorbance at 600 nm; c) absorbance at 600 nm on a longer time scale (88).

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In conclusion, it is fitting to note that Dr. Sutin, the current recipient of the ACS award for Distinguished Service in the Advancement of Inorganic Chemistry, and his colleague Dr. Creutz were among the first to recognize the possibilities for utilization of Ru(bpy)$_3^{2-}$ as a photosensitizer for splitting of water with visible light (11). This recognition has spawned a wide variety of innovative studies based upon photoinduced electron transfer reactions to accomplish this end (50). Some of these applications will be discussed in the paper “Photocatalytic Conversion and Storage of Solar Energy” by Professor Kutal in this symposium.

Acknowledgment

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Literature Cited