STUDY OF INTERMEDIATES FROM TRANSITION METAL EXCITED-STATE
ELECTRON-TRANSFER REACTIONS

Progress Report
for Period August 1, 1989 - July 31, 1992

Morton Z. Hoffman

Department of Chemistry
Boston University
Boston, Massachusetts 02215

July 31, 1992

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-86ER13603

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

ds
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PROGRESS REPORT

During the period covered by this progress report, the conventional and fast-kinetics techniques of photochemistry, photophysics, radiation chemistry, and electrochemistry were used for the characterization of the intermediates that are involved in transition metal excited-state electron-transfer reactions. The intermediates of interest were the excited states of Ru(II) and Cr(III) photosensitizers, their reduced forms, and the species formed in the reactions of redox quenchers and electron-transfer agents. Of particular concern has been the back electron-transfer reaction between the geminate pair formed in the redox quenching of the photosensitizers, and the dependence of its rate on solution medium and temperature in competition with transformation and cage escape processes.

Following are the most important results of the research conducted during the period covered by this progress report. They are keyed to the relevant publications at the end of the report which, except for the papers in preparation, are included for reference.

Cage Escape Yields in the Quenching of Ru(II) and Cr(III) Photosensitizers

A major project during this grant period was the determination of the yields of redox products released into bulk solution upon the electron-transfer quenching of the excited states of Ru(II)- and Cr(III)-diimine complexes. Inasmuch as the efficiency of release of charge-separated products is the most critical quantity that limits the overall yield of useful species from a photochemical redox system, it is necessary to understand, in a quantitative manner, the important thermodynamic, kinetic, and solution medium factors.

Ru(II) Systems. We had already reported in 1988 that the values of the efficiency of escape of the charge-separated species into bulk solution (η_{ce}), which reflect the competition between back electron transfer within the geminate quenching

pair (k_{bl}) and diffusion of the redox products out of the solvent cage (k_{ce}), in the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} are a function of $[MV^{2+}]$ and ionic strength (μ). We had proposed that ion-pair aggregation, preferential solvation of the reactants and their excited and redox conjoiners, and the dependence of k_{ce} on μ were the cause of the functionalities. A correction to the values of the redox yields, based on a reassessment of the molar absorptivity of $^*Ru(bpy)_3^{2+}$, was recently published [7]. With this information we have been able to evaluate the effect of μ on the yield of MV^{+} in the presence of EDTA, a sacrificial electron donor [13]. We also investigated the possible role of $C_2O_4^{2-}$ as a sacrificial electron donor in the $Ru(bpy)_3^{2+}/MV^{2+}$ system [4]. Despite the attractive properties of $C_2O_4^{2-}$ as a reducing agent (its oxidation produces the highly unstable $C_2O_4^{\cdot-}$ radical, which, upon decarboxylation, yields the strongly reducing $CO_2^{\cdot-}$ radical), it reacts too slowly ($k = 10^4$ - 10^5 $M^{-1}s^{-1}$) with $Ru(bpy)_3^{3+}$ to be effective. We estimated the one-electron oxidation potential of $C_2O_4^{2-}$ to be of the order of -1.6 to -1.7 V, assuming that the self-exchange rate constant for the $C_2O_4^{2-}/C_2O_4^{\cdot-}$ couple to be in the vicinity of diffusion control [1].

We examined the same quenching reaction in the presence of triethanolamine (TEOA), a sacrificial donor that does not contribute to the ionic strength of the solution or to ion-pairing of the species. The oxidation of TEOA generates a radical that transforms, via H-abstraction from the parent molecule into a reducing radical, which, in turn, reduces MV^{2+} , apparently quantitatively without competitive degradation. TEOA can be used as an effective sacrificial donor in this system at ≥ 0.05 M; at lower concentrations, its efficiencies of scavenging $Ru(bpy)_3^{3+}$ and its oxidized radical are less than unity. TEOA is also effective in the pH 8.5-11.5 range; in less alkaline solution, its protonation diminishes its ability to act as a scavenger. In even more alkaline solution, secondary processes between MV^{2+} and the products of the TEOA degradation reactions yield additional equivalents of MV^{+} . The presence of 0.1 M TEOA at pH 10.0, in the limit of $\mu \rightarrow 0$, has no discernible effect of η_{ce} . With an increase in μ , η_{ce} decreases as expected; k_{ce} decreases as μ is increased for the

escape of like-charged species into bulk solution. However, k_{ce} has even a lower value in the presence of 0.1 M TEOA than in its absence at those higher ionic strengths, suggesting that even neutral species, which would normally be viewed as "innocent" solutes, can cause subtle variations in the structure of the solvent cage and the value of η_{ce} [10].

We extended these studies of the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system to include the variation of solution medium and temperature. In aqueous solution, η_{ce} increases with increasing temperature for a given ionic strength; at low μ , η_{ce} ranges between 0.14 and 0.26 at 7-65° C. Inasmuch as the viscosity and dielectric constant of the bulk solvent are, ostensibly, the only parameters that vary with temperature, it is possible to calculate k_{ce} from the diffusion equations, thereby extracting the dependence of k_{bt} on temperature; these analyses were done for $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixtures of 0, 25, 50, and 75% (v/v) CH_3CN . From plots of $\ln k_{bt}$ vs $1/T$, values of the activation energy of geminate pair back electron transfer were obtained; $E_a = 0.11, 0.065, 0.056$, and 0.055 eV for the solution media given above. By the application of the Marcus theory for intramolecular electron transfer, the values of E_a were used to evaluate λ , the reorganization energy, which varies from 1.0 eV in H_2O to 1.3 eV in 75% (v/v) CH_3CN . Analyses are currently underway to determine if this behavior is simply due to the changes in the dielectric constant of the medium, or whether variations in the center-to-center distance between donor and acceptor are implicated. If the latter is the case, there will be important ramifications concerning the use of the distance parameter in the theory of intramolecular electron-transfer reactions [16].

The determination of η_{ce} by pulsed-laser flash photolysis requires that the absorption spectrum of the excited state, as well as those of the redox products, be known quantitatively; the quality of the value of η_{ce} and the subsequent analyses that are based on that quantity are only as good as the knowledge of ϵ for the excited state at the wavelength of observation. Because $\text{Ru}(\text{bpy})_3^{2+}$ has an absorption maximum at about 450 nm in fluid solution, the monitoring of the spectral changes

that occur upon flash photolysis is conveniently done at that wavelength; literature values of ϵ_{450} for $^*\text{Ru}(\text{bpy})_3^{2+}$ range from 2,100 to 7,700 $\text{M}^{-1}\text{cm}^{-1}$. We used three pulsed-laser techniques to evaluate the absorption spectrum of the excited state: complete conversion of the ground state, energy transfer to anthracene, and benzophenone actinometry. The first two techniques, which involve excitation with the 532-nm laser line, gave reliable and reproducible values of $\epsilon_{452} = 4.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, independent of the composition of the $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solvent. Inasmuch as $\epsilon_{452} = 1.46 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ for the ground state, the value of $\Delta\epsilon_{450}$, the difference in the ϵ -values of the excited- and the ground state at 450 nm, can be taken as $-9.8 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$. The benzophenone actinometry method, which requires use of the 355-nm laser line, gave ϵ -values for $^*\text{Ru}(\text{bpy})_3^{2+}$ that are too high by as much as 50%, and that depended on the region of the solution interrogated by the analyzing beam; the error results from the competitive absorption of the photons of the flash by the more highly absorbing excited state. We believe that $\text{Ru}(\text{bpy})_3^{2+}$ can now serve as a reliable actinometer for the 532-nm frequency-doubled Nd:YAG pulsed-laser line [11].

The theories of intramolecular electron transfer, when applied to the back electron transfer process between the geminate redox pair within the solvent cage, predict a "bell-shaped" dependence of k_{bt} on ΔG° of the reaction as the system traverses the "normal" and "inverted Marcus" regions. There have been a number of demonstrations of this phenomenon in electron-transfer quenching processes in which η_{ce} varies with the redox energetics of the geminate redox pair. We wished to explore its generality by determining η_{ce} for the oxidative quenching by MV^{2+} of the lowest luminescent states of nine $\text{Ru}(\text{II})$ bpy/phen complexes in varying $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solution media; the complexes have oxidation potentials that vary by 0.6 V, leading to a ΔG° range of -1.4 to -2.0 eV for the back electron transfer reaction. By assuming that k_{ce} is approximately constant for most of the complexes studied, we found that the dependence of k_{bt} in the highly exergonic region on ΔG° to be very weak, decreasing somewhat as the exergonicity of the reaction increase: within the inverted region, unlike the

strong dependence and "bell-shaped" behavior shown for reductive quenching. For complexes that deviated from the general behavior with unusually low values of η_{ce} , the variation was attributed to the large size of the ligands which increases the intra-pair distance and decreases the value of k_{ce} . We suggested that specific interactions between the geminate pair species and the molecules that make up the cage may be very important, especially in mixed solvents. We also cautioned that comparisons of values of η_{ce} in different solution media must be done very carefully inasmuch as the variation of solvent will have often unpredictable effects on the solvation of the ionic species and their ion-pairing and aggregation; it was premature to speculate on the somewhat limited data available for the dependence of η_{ce} on solvent composition [8].

It now became important to see if, indeed, the "bell-shaped" curve dependence of k_{bt} on ΔG° was reproducible for the reductive quenching of a single Ru(II) complex by a large number of electron donors in a range of solution media. The complex chosen was $\text{Ru}(\text{decby})_3^{2+}$ (decby = 4,4'-bis-(ethylcarboxy)-2,2'-bipyridine), which has a ground-state reduction potential of -0.9 V vs SCE. Reductive quenching was effected by 14 aromatic amines and methoxybenzenes in 50% (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$, giving a range of ΔG° for the back electron-transfer reaction from -1.1 to -2.2 eV. Because of the variation in the sizes of the donors, the calculated value of k_{ce} was corrected for that quantity, obtained from computer-assisted molecular modelling. Although the data remained somewhat scattered, the "bell-shaped" trend was clear with an apparent reorganization energy of less than 1.5 eV. In order to examine the dependence of η_{ce} on the solvent composition, two quenchers (diphenylamine and 3,3'-dimethylbenzidine), which give the highest and lowest values of η_{ce} , were used from 95% (v/v) $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ to neat CH_3CN . In general, η_{ce} increases sharply from a rather low value in the mainly aqueous system as the mole fraction of CH_3CN increases, approaching a plateau at around 0.8 mole fraction CH_3CN , and then rising dramatically again as the system reaches neat CH_3CN . The general trend is consistent with an

increase in the value of k_{ce} as the bulk viscosity and dielectric constant of the solvent decrease with an increase in the mole fraction of CH_3CN . However, the variations in η_{ce} go beyond those anticipated by the changes in the bulk solvent parameters. The results can be explained qualitatively in terms of the preferential solvation of the geminate redox pair by CH_3CN in the water-rich solvent, causing a change in the value of k_{bt} ; as the composition of the bulk solution changes, the composition of the solvent cage changes in a nonlinear manner. The important conclusion is that, in mixed solvents, the composition of the solvent cage may not reflect that of the bulk solvent, and the specific nature of the solvation will be dictated by the character of the species involved in the unique reaction [14].

Because $\text{C}_2\text{O}_4^{2-}$, EDTA, and TEOA are sacrificial electron donors, charge separated products can build up in solution upon continuous photolysis; for systems that contain a Ru(II) photosensitizer, MV^{2+} , and one of these as a reductive quencher, MV^{*+} is formed. If the mechanism of the reaction is known, the quantum yield of MV^{*+} formation, $\Phi(\text{MV}^{*+})$, can be algebraically related to η_{ce} via the efficiencies of quenching and the other competing steps. We demonstrated the efficacy of this approach with $\text{Ru}(\text{bpz})_3^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine) and $\text{Ru}(\text{bpm})_3^{2+}$ ($\text{bpm} = 2,2'$ -bipyrimidine) as a function of $[\text{MV}^{2+}]$, $[\text{quencher}]$, and pH [1, 2].

We applied the same approach to the reductive quenching of the excited states of complexes of the form $\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z^{2+}$ (where m and $z = 0,1,2,3$ and $0 < m + z < 3$), which have varying ground- and excited-state redox potentials, in order to evaluate η_{ce} as a function of the driving force of geminate pair back electron transfer. Quenching by EDTA and TEOA resulted in different apparent dependencies of k_{bt} on the thermodynamics; the bell-shaped curve for EDTA occurred over a rather narrow energy range of less than 0.30 eV, while TEOA exhibited only a portion of such a curve over the energy range, similar to that which had been reported for other neutral amines. We noted that this EDTA study was the first in which such a highly charged reductive quencher had been used in a purely aqueous medium at a

high ionic strength. We suggested that the specific interactions among the geminate species, ions, and solvent molecules would contribute significantly to the structure and overall potential energy of the solvent cage. Furthermore, unlike the case of TEOA, one-electron oxidized EDTA is believed to undergo irreversible transformation within the solvent cage; η_{ce} would reflect the kinetic competition of the transformation and back electron-transfer steps, with k_{ce} not being of any major consequence [5].

In an extension of this work, we have used the variation of the redox potentials of the complexes to apply the theory of intermolecular electron transfer to the values of k_q and the theory of intramolecular electron transfer to the values of η_{ce} and k_{bt} , and to exam the prospects for the use of these photosensitizers in schemes that involve the catalytic reduction of H_2O to H_2 and CO_2 to CH_4 . [15] In work that is currently in progress, we are using TEOA as the sacrificial reductive quencher in nonaqueous solvents, and in aqueous solvent mixtures. With the use of an homologous series of complexes and a single donor, we are gaining insights into the role of solvent composition and the effect of temperature on cage release yields.

Cr(III) Systems. The long-lived luminescent excited states of Cr(III)-polypyridyl complexes are also very good oxidizing agents, with $^*E_{red}^0$ -values of 1.1-1.4 V, depending on the substituents on the bpy and phen ligands. Although the photochemistry and photophysics of these complexes are very well known [3], they have not been employed in electron-transfer quenching systems to any great extent; there have been some measurements of η_{ce} , and an application of a few of the results to the theory of intramolecular electron transfer. Of great interest was a published report of a unitary cage escape yield of Cr(II) in the quenching of $^*Cr(bpy)_3^{3+}$ by $C_2O_4^{2-}$, whereas our previous experience had shown that quenching by I^- gave a yield of zero. Because of the significant differences between analogous Cr(III) and Ru(II) complexes (d^3 vs d^6 systems, MC vs MLCT excited states, sub-ms vs sub- μ s lifetimes, ionic charge), we have chosen to examine in parallel the reactions of these excited states with reductive quenchers. At issue is the role of ion-pairing and the orbital nature

of the excited states in the determination of η_{ce} .

We first determined k_q as a function of μ for the quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ by $\text{C}_2\text{O}_4^{2-}$, EDTA, TEOA, and ascorbate ion in aqueous solution, and compared the results with those obtained for analogous Ru(II) complexes. As expected, there is no ionic strength dependence for neutral TEOA; for the anionic quenchers, k_q decreases as μ is increased. The Bronsted-Bjerrum equation was applied to the results; the ionic charges on the reacting species were taken as fixed quantities, and values of the apparent distance of closest approach was calculated, and were compared with corresponding values obtained from computer-assisted molecular modelling. For the quenching by EDTA, the distance parameters were virtually the same. However, for $\text{C}_2\text{O}_4^{2-}$ with $^*\text{Cr}(\text{bpy})_3^{3+}$ and $^*\text{Ru}(\text{bpz})_3^{2+}$, the apparent distance was significantly smaller than the modelled one; it should be noted that the molecular geometries of all the complexes are identical. It is possible that $\text{C}_2\text{O}_4^{2-}$, being rather small, is able to reside within the interligand pockets of the complexes, even, perhaps, in the ground state. In that case, simple models of electrostatically-induced ion-pairing may not be sufficient to describe the situation. For ascorbate ion, which also quenches $^*\text{Ru}(\text{bpy})_3^{2+}$ and $^*\text{Ru}(\text{bpm})_3^{2+}$, the apparent distance is larger or smaller than the modelled distance (11 Å), depending on the driving force of the quenching reaction. Thus, for $^*\text{Ru}(\text{bpz})_3^{2+}$ and $^*\text{Ru}(\text{bpy})_3^{2+}$, which have E_{red}^0 -values of 1.7 and 0.9 V, respectively, the apparent distances of closest approach are 19 and 9 Å, respectively. Within the validity of the use of the Bronsted-Bjerrum treatment, these results may serve as a demonstration of the distance dependence of electron-transfer reactions that has been predicted theoretically by others.

Our studies have also included an evaluation of η_{ce} for the quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ by sacrificial and reversible quenchers. We agree with the published value that η_{ce} for $\text{C}_2\text{O}_4^{2-}$ is unity, independent of ground- and excited-state concentrations and ionic strength, indicating that the decarboxylation of the $\text{C}_2\text{O}_4^{\cdot-}$ radical occurs significantly more rapidly than does the back electron-transfer reaction. For

EDTA, which also irreversibly transforms within the solvent cage, η_{ce} is 0.5. On the other hand, for other quenchers that we have examined (TEOA, I^- , phenol, free pyrimidine bases), $\eta_{ce} < 0.01$, suggesting that k_{bt} in these cases is very large. This apparent paradox is surprising, suggesting that collisional deactivation of the excited state upon quenching in Cr(III) is strongly competitive with electron transfer. As in the case of the Ru complexes, the quality of these η_{ce} value depends on one's quantitative knowledge of the absorption spectrum of $^*Cr(bpy)_3^{3+}$. There are reports in the literature about the use of Fe^{2+} in acidic solution to quench the excited state, in which ϵ -values are calculated from the yield of $Cr(bpy)_3^{2+}$, the absorption spectrum of which is well known; the assumption is made that η_{ce} is unity. Given our experience with η_{ce} -values for $^*Cr(bpy)_3^{3+}$ as described above, we thought it prudent to reexamine this reversible system as a function of $[Fe^{2+}]$ and the concentrations of the acids used to set the pH: HCl, H_2SO_4 , $HClO_4$. We found that η_{ce} was <1 , and varied from 0.2 to 0.9, dependent, in a complex manner, on the concentrations of all the species and the nature of the anion present. The results are being interpreted in terms of ion-pair equilibria and aggregation. It is very clear that even in seemingly simple systems, the ionic and solvent interactions are very complex, as evidenced by the variations in the values of η_{ce} with the solution medium.

Characterization of Ru(II) Photosensitizers

The redox properties of the complexes of the form $Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z^{2+}$ (RuL^{2+}) display a smooth progression. It became important to examine further the progression of other properties, and to extend the series of diazene complexes to other isomers.

One-electron Reduced Complexes. The one-electron reductions were investigated in aqueous solution using radiation chemical and electrochemical techniques, leading to the characterization of the one-electron reduced products ($RuL^{\bullet+}$) and their conjugate acids ($RuLH^{2+}$). Because the ease of reduction of the ligands follows the trend

bpz > bpm > bpy, the electron added to RuL^{2+} is localized on the ligand that is most easily reduced. The E° values for the $\text{RuL}^{2+}/\text{RuL}^{*+}$ couples range from -0.50 V to -1.22 V for $\text{Ru}(\text{bpz})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$, respectively. All the RuL^{*+} absorption spectra show intense bands ($\epsilon_{\text{max}} \sim 10^4 \text{ M}^{-1}\text{cm}^{-1}$) in the 340 and 480 nm regions that arise from ligand-localized transitions within the uniquely reduced ligand, with the visible band also overlapped by a MLCT band; the absorption bands of RuLH^{*2+} are shifted somewhat to the blue. From the variation of the absorbance as a function of pH, the pK_a values of RuLH^{*2+} are obtained; they range from 6.3 to 9.2 for $\text{Ru}(\text{bpm})_2\text{-(bpmH}^{*+})^{2+}$ to $\text{Ru}(\text{bpy})_2(\text{bpzH}^{*+})^{2+}$, respectively, and correlate linearly with $E^\circ(\text{RuL}^{2+}/\text{RuL}^{*+})$, with separate lines for bpz and bpm acceptor ligands. From the values of pK_a and $E^\circ(\text{RuL}^{2+}/\text{RuL}^{*+})$, $E^\circ(\text{RuL}^{2+}, \text{H}^+/\text{RuLH}^{*2+})$ were obtained. The kinetic data for the reduction of the complexes by $\text{CO}_2^{\cdot-}$ and MV^{2+} , and the reduction of MV^{2+} by RuL^{*+} and RuLH^{*2+} were interpreted with use of the Marcus theory. For the reaction $\text{CO}_2^{\cdot-} + \text{RuL}^{2+} \rightarrow \text{CO}_2 + \text{RuL}^{*+}$, the value of the electronic transmission coefficient (k) is 1, and the intrinsic barrier ($\Delta G^\ddagger(0)$) equals 57.3 kJ mol^{-1} . For the $\text{CO}_2/\text{CO}_2^{\cdot-}$ self-exchange reaction, $\Delta G^\ddagger(0) = 97.0 \text{ kJ mol}^{-1}$ and $k = 1.4 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. For the reactions involving the $\text{MV}^{2+}/\text{MV}^{*+}$ and $\text{RuL}^{2+}/\text{RuL}^{*+}$ or $\text{RuL}^{2+}, \text{H}^+/\text{RuLH}^{*2+}$ couples, values of $\Delta G^\ddagger(0) = 20.5$ and 32.2 kJ mol^{-1} were obtained in alkaline and acidic solution, respectively, by assuming adiabatic behavior, i.e. $k = 1$. The difference between these two values has been attributed to an additional intrinsic barrier associated with the protonation/deprotonation process. The results permitted an evaluation to be made of the utility of these complexes as electron-transfer photosensitizers [6, 9].

$\text{Ru}(\text{bpz})_3^+$ is stable in air-free alkaline aqueous solutions; in acidic solution, its conjugate acid (pK_a 7.1) is not. The exhaustive one-electron reduction of $\text{Ru}(\text{bpz})_3^{2+}$ can be achieved photochemically through the use of a sacrificial reductive quencher. We found that $\text{Ru}(\text{bpz})_3^+$ is generated at pH 12 with clean isosbestic points; the addition of O_2 resulted in almost quantitative conversion back to the spectrum of the parent complex. At pH 5, a completely different spectrum is formed in the absence

of air, again with clean isosbestic points; however, the addition of O_2 has no effect on the spectrum. The most interesting result is that the addition of base to the photolyte at pH 5 in the presence of air converts the spectrum almost quantitatively to that of $Ru(bpz)_3^{2+}$; acidification to pH 5 enables the cycle to be continued. It is clear that the conjugate acid of the reduced form undergoes some transformation, probably disproportionation, to an air-insensitive $Ru(II)$ complex with a enamine modified ligand. Deprotonation and two-electron oxidation with O_2 would generate the parent. Current experiments are directed toward the time resolution of these events.

New Photosensitizers. Complexes containing bpd (= 3,3'-bipyridazine) and bpr (= 4,4'-bipyrimidine), and mixed-ligand complexes of those ligands with bpy, bpz, and bpm have been synthesized as their PF_6^- salts, and characterized for their possible use as photosensitizers to effect charge separation through electron-transfer of their excited states. The absorption and emission spectra of the complexes have been characterized in a variety of solvents, and the lifetimes of their luminescent excited states have been determined by pulsed time-resolved spectrofluorimetry. The oxidation and reduction potentials of the ground states of the complexes have been determined by cyclic voltammetry, from which the potentials of the excited states have been calculated.

Energy Transfer to O_2 . Recently, we have begun a collaborative project with Professor Michael Rodgers of Bowling Green State University on the efficiencies of energy transfer from $^*Ru(II)$ and $^*Cr(III)$ complexes to O_2 , with the concomitant formation of $^1O_2$. Oxygen-saturated solutions of the complexes in D_2O were excited at 355 nm; the absorbances of the solutions were adjusted to be at or near the same value. The lifetimes of the excited states were determined also in Ar-purged solutions, and values of k_q were obtained. The luminescence from $^1O_2$ was monitored by the detection system in which all the emission from the optical cell is passed through a 1.1- μm cutoff filter. The yield of $^1O_2$ was estimated from its emission intensity extrapolated back to zero time. Although emission from the complexes was superimposed on that from $^1O_2$, it appears, from a preliminary examination of the data,

that the $^1\text{O}_2$ yields for the various complexes examined are markedly different. Currently, attempts are being made to resolve, via computer and chemical means, the emissions from the complexes and $^1\text{O}_2$. We hope to be able to measure absolute yields, and correlate them with various systems parameters, such as emission energy, nonradiative decay rates, and redox potentials. We do not overlook the possible use of metal complexes for the production of $^1\text{O}_2$; they may have some advantages over current sensitizers in the photooxidation of organic and biological molecules.

Chemistry Initiated by Ru(II) and Cr(III) Photosensitizers

The free and coordinated radical species, and complexes in unusual oxidation states that result from electron-transfer quenching are capable of further redox and atom transfer reactions. We undertook a number of projects that would use the fundamental knowledge that was gained from the basic research described above.

Initiation of Polymerization. Initially, an examination was made on the use of $\text{Cr}(\text{bpy})_3^{3+}$ as a photosensitizer to initiate the polymerization of acrylamide in aqueous solution upon 365-nm irradiation. We found that $^*\text{Cr}(\text{bpy})_3^{3+}$ is quenched by acrylamide at pH 2.4 with $k_q \sim 10^3\text{-}10^4 \text{ M}^{-1}\text{s}^{-1}$, and photosensitized polymerization occurs in air-free solution with a rate that is dependent on $[\text{monomer}]^2$ and $[\text{Cr(III)}]$; the average molecular weight of the polyacrylamide is $\sim 10^6$ daltons. A mechanism can be visualized in which reductive quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ generates an oxidized acrylamide radical, which then begins the chain by attacking the monomer. However, in pulse-laser flash photolysis studies, the yield of $\text{Cr}(\text{bpy})_3^{2+}$ is too small to be measurable, and no transient processes, other than the decay of the excited states, are observed. It would appear that despite the low efficiency of formation of the redox pair in bulk solution from the quenching process, the high sensitivity of the subsequent steps to the presence of radicals makes it possible to observe polymerization.

We then turned our attention to the general problem of the generation of radicals that could initiate polymerization from the electron-transfer quenching of excited

states of metal complexes. Because the oxidation of phenol produces the phenoxyl radical ($\text{PhO}^\bullet$), which is a good oxidizing agent and H-atom acceptor, we undertook an examination of this process when photosensitized by $\text{Cr}(\text{bpy})_3^{3+}$. In the continuous photolysis in aerated acidic aqueous solution, where $^*\text{Cr}(\text{bpy})_3^{3+}$ is quenched by phenol with $k_q = 8.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, the only organic product is 1,4-benzoquinone; in the absence of air, only the aquation of the photosensitizer is manifest. However, the yield of $\text{Cr}(\text{bpy})_3^{2+}$ in flash photolysis is so low that it cannot be measured, raising the question as to whether the product arises from electron transfer or via the intermediacy of $^1\text{O}_2$ from the quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ by O_2 [12].

In order to establish the mechanism of the photooxidation of phenol, we turned to $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpz})_3^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine) as sensitizers, the excited states of which are quenched by O_2 , generating $^1\text{O}_2$, possibly in different yields. However, $^*\text{Ru}(\text{bpz})_3^{2+}$ is quenched efficiently by phenol, forming the reduced photosensitizer and the $\text{PhO}^\bullet$ with a yield of 40%, while $^*\text{Ru}(\text{bpy})_3^{2+}$, an insufficiently strong oxidizing agent, is not quenched at all. As in the case of $^*\text{Cr}(\text{bpy})_3^{3+}$, the only product formed when $\text{Ru}(\text{bpy})_3^{2+}$ is the photosensitizer is 1,4-benzoquinone; with $\text{Ru}(\text{bpz})_3^{2+}$, phenol dimers were produced. We have completed all the flash photolysis experiments, and have good values of k_q , cage escape and $^1\text{O}_2$ yields, and the rate constants for the various radical combination reactions. Quantitative measurement of the quantum yields from continuous photolysis are currently underway as a function of $[\text{phenol}]$ and $[\text{O}_2]$, and in D_2O (where the lifetime of $^1\text{O}_2$ is a factor of ten longer than in H_2O). When all the experiments have been completed, we will use the continuous and flash photolysis data to rationalize the overall mechanism in a quantitative manner.

Interaction with Bio-organic Molecules. Because of its strength as an oxidizing agent, $^*\text{Ru}(\text{bpz})_3^{2+}$ is readily quenched by good bio-organic reducing agents, such as tryptophan and tyrosine, and others that contain indolic and phenolic moieties. Phenylalanine, histidine, and methionine are not effective quenchers; we had already demonstrated the effectiveness of thiolic compounds, such as cysteine and reduced

glutathione [1]. We have determined k_q and η_{ce} as a function of pH and μ , and have examined the formation and decay of transient intermediates for these quenchers. We extended the work to include the free base components of RNA and DNA; k_q for adenine is $\sim 10^7 \text{ M}^{-1}\text{s}^{-1}$, at least an order of magnitude higher than for cytosine, thymine, guanine, and uracil. In addition, η_{ce} for adenine and the adenosine nucleotide was 0.45, indicating that the generation of the charge separated products is quite efficient. Inasmuch as Ru(II) complexes are known to intercalate into the DNA structure and cut the chain, we currently are examining the interactions of $\text{Ru}(\text{bpz})_3^{2+}$ with single-strand DNA in the presence and absence of light and O_2 , in collaboration with Professor Robert Davenport of this department. Preliminary results show that damage occurs upon photolysis in the presence of O_2 ; whether a complete strand cut or a nick takes place, and whether the damage is induced by electron-transfer at adenine sites or via attack by $^1\text{O}_2$ remains to be seen.

Photochemistry of Ion-Pair Electron Donor-Acceptor Complexes

Several years ago, we studied the photochemistry of charge-transfer complexes between MV^{2+} and $\text{C}_2\text{O}_4^{2-}$ or EDTA as a function of concentration, pH, excitation wavelength, and temperature. The ion-pair complexes exhibited enhanced tail absorption in the uv-visible spectral region, and yielded MV^{++} as a stable product upon continuous photolysis in the absence of air. Their excitation can be visualized as resulting in redox geminate pair species within the solvent cage, thereby providing a model for the cage escape and back electron-transfer processes in quenching reactions. However, pulsed-laser excitation revealed an initial transient absorption that was not that of free MV^{++} , but did, rather, resemble that of reduced viologen dimers and aggregates. We proposed that ion-pair complexes of MV^{2+} can exist as pseudo-micelle aggregates; absorption of light generates MV^{++} and the oxidized donor radical, which transforms irreversibly into a reducing radical capable of generating another equivalent of MV^{++} within the aggregate structure. We interpreted the observed values of

• $\Phi(MV^{**})$ as reflecting the competition within the aggregates between geminate-pair back electron transfer and radical degradation processes.

MV^{2+}/α -Hydroxycarboxylates. In this study, we chose donors of the form $R_1R_2C(OH)CO_2^-$ ($R = H, CH_3, C_6H_5$); oxidation of the carboxylate would be expected to generate a radical, which, upon rapid and irreversible decarboxylation, would produce the strongly reducing R_1R_2COH radical. For $R_1 = R_2 = H$ and $R_1 = H, R_2 = CH_3$, no absorbance changes were observed that could be attributed to charge-transfer complexes with MV^{2+} ; the expected tail absorption of any complex is probably hidden under that of the MV^{2+} . For the other carboxylates at pH 10, $\epsilon_{350} = 50$ -200 $M^{-1}cm^{-1}$ and $K_{eq} = 1$ -10 M^{-1} . Upon continuous photolysis at 350 nm, MV^{**} is formed linearly with irradiation time; $\Phi(MV^{**})$ increases as the initial concentration of MV^{2+} is increased at constant excess [donor], approaching a limiting value (0.30 and 1.3 for $R_1 = R_2 = CH_3$ and C_6H_5 , respectively).

Flash photolysis revealed the formation of MV^{**} within the time of the laser pulse, followed by a secondary time-resolved generation that, under some circumstances, appears to be very similar to that observed earlier for $C_2O_4^{2-}$ and EDTA. The results suggest that MV^{**} dimers may be formed due to the decarboxylation of the oxidized donors within carboxylate pseudo-micelles. The generality of this phenomenon is under current investigation. If pseudo-micelle aggregation is implicated here and in other systems, the mechanisms detailing the events in the solvent cage, and the quantitative relationships of quantum yield and the rate constants for the mechanistic steps will have to be dramatically modified [18].

Personnel

Senior Collaborators:

Professor Takeshi Ohno - Department of Chemistry, College of General Education, Osaka University, Osaka, Japan.

Dr. Quinto G. Mulazzani - Istituto di Fotochimica e Radiazioni d'Alta Energia (FRAE), Consiglio Nazionale delle Ricerche (CNR), Bologna, Italy.

Dr. Michele Bolte - Laboratoire de Photochimie, Universite Blaise Pascal, Clermont-Ferrand, France.

Postdoctoral Associates:

Dr. Mikhael Georgopoulos

Dr. Gilda Neshvad

Dr. Dasari R. Prasad

Dr. Akio Yoshimura

Graduate Students:

Catherine Clark (Ph.D. candidate)

Jerusha Kinraide (M.A. candidate)

Hai Sun (Ph.D. candidate)

Lu Zhang (Ph.D. candidate)

Liwen Zou (Ph.D. candidate)

Undergraduate Students:

Jerusha Kinraide (B.A., 1991)

Lesley Litt (B.A., 1992)

Michelle O'Brien (B.A., 1990)

Timothy Warner (B.A., 1990)

Publications

1. G. Neshvad and M.Z. Hoffman, "Reductive Quenching of the Luminescent Excited State of Tris(2,2'-bipyrazine)ruthenium(2+) Ion in Aqueous Solution, J. Phys. Chem., 93, 2445-2452 (1989).
2. G. Neshvad, M.Z. Hoffman, Q.G. Mulazzani, M. Venturi, M. Ciano, and M. D'Angelantonio, "One-Electron Reduction of Tris(2,2'-bipyrimidine)ruthenium(2+) Ion in Aqueous Solution. A Photochemical, Radiation Chemical, and Electrochemical Study," J. Phys. Chem., 93, 6080-6088 (1989).
3. M.Z. Hoffman, "Dynamics of Photochemical Processes in Transition Metal Coordination Complexes as Studied by Time-Resolved Spectroscopy," in *Optical Spectroscopy in Chemistry and Biology - Progress and Trends*, D. Fassler, ed., VEB Deutscher Verlag der Wissenschaften, Berlin, DDR, 1989, pp 93-108.
4. M.Z. Hoffman and D.R. Prasad, "Oxalate Ion as a Sacrificial Electron Donor in the $\text{Ru}(\text{bpy})_3^{2+}$ /Methylviologen Model Photochemical System," J. Photochem. Photobiol., 54, 197-204 (1990).
5. H. Sun, G. Neshvad, and M.Z. Hoffman, "Energy Gap Dependence of the Efficiency of Charge Separation upon the Sacrificial Reductive Quenching of the Excited States of Ru(II)-Diimine Photosensitizers in Aqueous Solution," Mol. Cryst. Liq. Cryst., 194, 141-150 (1991).
6. M. Venturi, Q.G. Mulazzani, M. D'Angelantonio, M. Ciano, and M.Z. Hoffman, "Radiation-Induced Electron-Transfer Processes in Ru(II)-Diimine Complexes in Aqueous Solution. An Application of Marcus Electron-Transfer Theory," Radiat. Phys. Chem., 37, 449-456 (1991).
7. M.Z. Hoffman, "Correction: Cage Escape Yields from the Quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by Methylviologen in Aqueous Solution," J. Phys. Chem., 95, 2606 (1991).
8. T. Ohno, A. Yoshimura, Dasari R. Prasad, and M.Z. Hoffman, "A Weak ΔG° -Dependence of Back Electron Transfer within the Geminate Redox Pairs Formed in the Quenching of Excited Ru(II) Complexes by Methylviologen," J. Phys. Chem., 95, 4723-4728 (1991).
9. M. Venturi, M. D'Angelantonio, M. Ciano, Q.G. Mulazzani, and M.Z. Hoffman, "One-Electron Reduction of Ruthenium(II)-Diimine Complexes. Characterization of Reduced Species Containing 2,2'-Bipyridine, 2,2'-Bipyrimidine, and 2,2'-Bipyrazine in Aqueous Solution," J. Phys. Chem., 95, 5121-5129 (1991).
10. M. Georgopoulos and M.Z. Hoffman, "Cage Escape Yields in the Quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by Methylviologen. Presence of Triethanolamine as a Sacrificial Electron Donor," J. Phys. Chem., 95, 7717-7721 (1991).
11. C. Pizzocaro, M. Bolte, and M.Z. Hoffman, " $\text{Cr}(\text{bpy})_3^{3+}$ -Sensitized Photooxidation of Phenol in Aqueous Solution," J. Photochem. Photobiol., in press.
12. A. Yoshimura and M.Z. Hoffman, "An Evaluation of the Excited State Absorption Spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ in Aqueous and Acetonitrile Solution," J. Photochem. Photobiol., under consideration.
13. M. Georgopoulos and M.Z. Hoffman, "Effect of Ionic Strength on the Redox Yields in the $\text{Ru}(\text{bpy})_3^{2+}$ /Methylviologen/EDTA Model Photochemical System," in preparation.

14. T. Ohno, A. Yoshimura, D.R. Prasad, and M.Z. Hoffman, "Effect of Solvent Composition on Cage Escape Efficiencies in the Reductive Quenching of the Luminescent Excited State of Tris(4,4'-Diethoxycarbonyl-2,2'-bipyridine)ruthenium(2+) Ion," in preparation.
15. H. Sun and M.Z. Hoffman, "Sacrificial Reductive Quenching of the Excited States of Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine Ligands in Aqueous Solution," in preparation.
16. A. Yoshimura and M.Z. Hoffman, "Temperature and Solution Medium Dependence of the Cage Escape Yields of Redox Products from the Quenching of $^*Ru(bpy)_3^{2+}$ by Methylviologen," in preparation.
17. H. Sun and M.Z. Hoffman, "Protonation of the Excited States of Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine Ligands in Aqueous Solution," in preparation.
18. D.R. Prasad and M.Z. Hoffman, "Photochemistry of Ion-pairs of Methylviologen and α -Hydroxycarboxylates in Aqueous Solution," in preparation.

END

**DATE
FILMED**

12 / 9 / 92