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

Final Report

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Morton Z. Hoffman
Department of Chemistry
Boston University
Boston, Massachusetts 02215

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Abstract

The techniques of continuous photolysis and pulsed laser flash photolysis, continuous and pulse radiolysis, fast-scan cyclic voltammetry, and time-resolved fluorimetry have been used to examine intramolecular electron transfer within the solvent quenching cage, photodynamics of quenching of the excited states of transition-metal photosensitizers, the properties of excited states and one-electron reduced forms, ground- and excited-state interactions with solutes, and photoinduced oxidations of organic solutes in aqueous solution. The following specific areas were examined: 1) the parameters that govern the yields of redox products from excited-state electron-transfer quenching reactions; 2) the mediation of the properties of excited states and one-electron reduced forms by the ligands and the solution medium; 3) the effect of the interactions between the ground state of the complex and the solution components on the behavior of the excited state; 4) the yields of singlet oxygen from excited-state energy-transfer quenching by O_2 ; 5) the oxidations of solutes by singlet oxygen, excited-state electron-transfer quenching, and free radicals.

Reprints removed for separate processing

Publications (1986-1997)

1. D.R. Prasad and M.Z. Hoffman, "Photodynamics of the Tris(2,2'-bipyrazine)ruthenium-(2+)/Methylviologen/EDTA System," *J. Am. Chem. Soc.*, **108**, 2568-2573 (1986).
2. M.Z. Hoffman and A.B. Ross, "Bibliographies on Radiation Chemistry: IX. Metal Ions and Complexes. Part A: Cobalt, Rhodium, Iridium," *Radiat. Phys. Chem.*, **27**, 477-487 (1986).
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11. Q.G. Mulazzani, M. Venturi, and M.Z. Hoffman, "Interaction of Tris(2,2'-bipyrazine)-ruthenium(2+) Ion with Radiolytically-Generated Radicals in Aqueous Solution. Reactivity of $\text{Ru}(\text{bpz})_3^+$ Toward Electron Relays," *Radiat. Phys. Chem.*, 32, 71-78 (1988).
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Evaluation of Progress (Abstracts of Publications)

1. D.R. Prasad and M.Z. Hoffman, "Photodynamics of the Tris(2,2'-bipyrazine)ruthenium-(2+)/Methylviologen/EDTA System," *J. Am. Chem. Soc.*, **108**, 2568-2573 (1986).

Luminescence quenching and flash photolysis (pulsed laser and conventional) techniques have been employed to study the photodynamics of the $\text{Ru}(\text{bpz})_3^{2+}/\text{MV}^{2+}/\text{EDTA}$ system in aqueous solution (bpz = 2,2'-bipyrazine; MV^{2+} = methylviologen). The quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ by EDTA in alkaline solution via Stern-Volmer kinetics ($k_q = 6.9 \times 10^8$ and $7.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at pH 8.7 and 11.0, respectively) generates $\text{Ru}(\text{bpz})_3^+$ which reacts with MV^{2+} ($k = 4.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) to yield $\text{MV}^{+\bullet}$; the reducing EDTA radical, formed from the irreversible transformation of the species obtained from the oxidation of EDTA, reacts with MV^{2+} ($k = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) to yield a second equivalent of $\text{MV}^{+\bullet}$. At pH 4.7, the quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$ by EDTA does not follow Stern-Volmer kinetics; k_q approaches $\sim 2 \times 10^8$ and $\sim 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ in the limits of low and high $[\text{EDTA}]$, respectively. The quantum yields of $\text{MV}^{+\bullet}$ in acidic solution are dramatically lower than in neutral and alkaline solution due to the lower efficiencies of the quenching and cage release processes and the decreased reactivities of the protonated forms of $\text{Ru}(\text{bpz})_3^+$ and reducing EDTA radicals toward $\text{MV}^{+\bullet}$.

2. M.Z. Hoffman and A.B. Ross, "Bibliographies on Radiation Chemistry: IX. Metal Ions and Complexes. Part A: Cobalt, Rhodium, Iridium," *Radiat. Phys. Chem.*, **27**, 477-487 (1986).

The one-electron oxidation and reduction of metal ions and complexes can yield species in unusual oxidation states, and ligand-radicals coordinated to the central metal. These often unstable species can be mechanistically important intermediates in thermal, photochemical, and electrochemical reactions involving metal-containing substances. Their generation via radiolysis provides an alternate means of characterizing them using kinetic and spectroscopic techniques. We hope these bibliographies on the radiation chemistry of metal ions and complexes, presented according to periodic groups, will prove useful to researchers in metallo-redox chemistry.

3. D.R. Prasad, M.Z. Hoffman, Q.G. Mulazzani, and M.A.J. Rodgers, "Pulsed-Laser Flash and Continuous Photolysis of Aqueous Solutions of Methylviologen, Oxalate, and Their Ion-Pair Complexes," *J. Am. Chem. Soc.*, **108**, 5135-5142 (1986).

MV^{2+} forms a 1:1 ion-pair complex ($K_{\text{eq}} = 21 \text{ M}^{-1}$) with $\text{C}_2\text{O}_4^{2-}$ in aqueous solution at natural pH (7.1) that exhibits an enhanced tail absorption in the 310–400-nm region; at $\lambda < 310 \text{ nm}$, the apparent molar absorptivity of the complex is approximately the same as that of the uncomplexed

MV^{2+} . The continuous photolysis of deaerated solutions of MV^{2+} and $C_2O_4^{2-}$ at 254–380 nm generates MV^+ initially linearly with increasing irradiation time from which values of $\Phi(MV^+)$ are obtained. $\Phi(MV^+)$ is a function of the excitation wavelength and the fraction of light absorbed by the complex and the uncomplexed substrates; there is no evidence that light absorbed by uncomplexed MV^{2+} and $C_2O_4^{2-}$ results in any net photochemistry. Inasmuch as the oxidation of $C_2O_4^{2-}$ yields strongly reducing $CO_2^{\cdot-}$ (via the decarboxylation of ephemeral $C_2O_4^{\cdot-}$), which generates a second equivalent of MV^+ , η_{cr} , the efficiency of release of redox products from the initially populated charge-transfer excited state, can be calculated; η_{cr} exhibits a long-wavelength plateau (0.12 at 340–380 nm) and rises smoothly to 0.25 at 254 nm. Pulsed-laser excitation of $C_2O_4^{2-}$ at 266 nm produced e_{aq}^- via multiphoton processes; excitation of the complex generates MV^+ within the laser pulse, followed by the formation of the second equivalent. At 355 nm, where higher concentrations of MV^{2+} are required (>1 mM), the initial transient absorption generated by the laser pulse is not that of free MV^+ ; its enhanced absorption in the 450–500-nm region is reminiscent of that displayed by reduced-viologen dimers and aggregates. The conversion of the initial absorption to that of free MV^+ occurs via $[MV^{2+}]$ -independent first-order kinetics; k_{obsd} decreases with increasing $[C_2O_4^{2-}]$. Under these conditions, MV^{2+} can be visualized as existing as an aggregate surrounded by $C_2O_4^{2-}$; excitation of an ion pair eventually results in the existence of two MV^+ species within a "pseudomicelle". The final absorption change represents the formation of MV^+ in its equilibrated state in bulk solution.

4. K.D. Whitburn, M.Z. Hoffman, N.V. Brezniak, and M.G. Simic, "Mechanisms of Ligand-to-Metal Intramolecular Electron Transfer in Cobalt(III)-Amine Complexes Containing a Coordinated Radical", *Inorg. Chem.*, **25**, 3037-3043 (1986).

The one-electron reduction of Co(III) complexes containing nitrophenylligands possessing differing lead-in and bridging groups by radiolytically generated $\cdot CO_2^-$ and $\cdot C(CH_3)_2OH$ radicals in neutral and acidic aqueous solution results in the formation of coordinated nitrophenyl ligand radicals. The UV-visible absorption spectra, the acid-base properties, and the decay kinetics of the transient intermediates were examined by pulse radiolysis. In neutral solution, the coordinated ligand radicals decay via intramolecular electron-transfer from the coordinated nitrophenyl radical donor to the Co(III) acceptor. The values of the intramolecular electron-transfer rate constants depend on the isomeric position of the nitro group on the phenyl moiety, the structure of the bridging molecule between the redox sites, and the nature of the lead-in group to the metal center. Bridging structures between the initial radical site and the metal center of varying length, flexibility, and π -conjugation are incorporated into the 18 complexes studied. Correlation of the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of electron transfer with the structural relationship of the donor and acceptor sites leads to the proposition that four different mechanisms of intramolecular electron transfer operate in

these complexes: through chain, direct and indirect ligand bypass, and nonadiabatic transfer. Protonation of the coordinated nitro radical greatly diminishes the rate of intramolecular electron transfer in the nitrophenyl carboxylato complexes; in most cases, protonation affects only the driving force for electron transfer while leaving the mechanism unchanged.

5. Q.G. Mulazzani, M. D'Angelantonio, M. Venturi, M.Z. Hoffman, and M.A.J. Rodgers, "Interaction of Formate and Oxalate Ions with Radiation-Generated Radicals in Aqueous Solution. Methylviologen as a Mechanistic Probe," *J. Phys. Chem.*, **90**, 5347-5352 (1986).

The reduction of methylviologen (MV^{2+}) to $MV^{\bullet+}$ by species arising from the interaction of radiation-generated radicals with formate and oxalate ions in aqueous solution has been studied by using the techniques of continuous and pulse radiolysis. $CO_2^{\bullet-}$, arising from the reaction of H and OH with HCO_2^- , generates $MV^{\bullet+}$ rapidly ($k \sim 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ at zero ionic strength) and quantitatively; $k(CO_2^{\bullet-} + MV^{2+})$ decreases with increasing ionic strength, and $G(MV^{\bullet+})$ increases with increasing $[HCO_2^-]$. The reaction of e_{aq}^- with oxalate ions produces species capable of reducing MV^{2+} , possibly via the intermediacy of $CO_2^{\bullet-}$. The oxidation of $MV^{\bullet+}$ by the radicals resulting from the reaction of OH and oxalate ions, in competition with their rapid ($k = 2 \times 10^6 \text{ s}^{-1}$) conversion into $CO_2^{\bullet-}$, results in a decrease of $G(MV^{\bullet+})$ with increasing radiation dose. The relevance of these observations to the use of oxalate ions as a sacrificial electron donor in photochemical model systems for energy conversion is discussed.

6. M. Venturi, Q.G. Mulazzani, M. Ciano, and M.Z. Hoffman, "Radiolytic and Electro-chemical Reduction of $Ru(bpz)_3^{2+}$ in Aqueous Solution. Stability, Redox, and Acid-Base Properties of $Ru(bpz)_3^+$," *Inorg. Chem.*, **25**, 4493-4498 (1986).

The reduction of $Ru(bpz)_3^{2+}$ in aqueous solution has been investigated by using radiolytic and electrochemical techniques. The one-electron reduction of $Ru(bpz)_3^{2+}$ by e_{aq}^- , $CO_2^{\bullet-}$, and $\bullet C(CH_3)_2OH$ radicals is rapid ($k = (5-9) \times 10^{10}$, 1.3×10^{10} , and $3.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively) and quantitative; the products of these reactions are $Ru(bpz)_3^+$, which can be represented as $Ru(bpz)_2(bpz^{\bullet-})^+$ in alkaline solution and its conjugate acid $Ru(bpz)_2(bpzH^{\bullet})^{2+}$ ($pK_a = 7.1 \pm 0.3$) in acidic solution. In the absence of oxygen, $Ru(bpz)_3^+$ is stable; in the presence of MV^{2+} , an equilibrium is established with $k(Ru(bpz)_3^+ + MV^{2+}) = 1.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, $k(Ru(bpz)_3^{2+} + MV^{\bullet+}) = 1.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, and $K_{eq} = 7.6$. From these data and from cyclic voltammetric measurements a value of $E^0(Ru(bpz)_3^{2+/+}) = -0.50 \text{ V}$ has been derived for alkaline aqueous solution. When the pH of the solution is changed from alkaline to acidic, E_{pc} shifts toward less negative potentials by about 170 mV. Accordingly, $Ru(bpz)_2(bpzH^{\bullet})^{2+}$ is unable to reduce MV^{2+} ; it is unstable ($t_{1/2} \sim 20 \text{ s}$), presumably toward a disproportionation reaction leading to the starting material and to the

doubly reduced species $\text{Ru}(\text{bpz})_2(\text{bpzH}_2)^{2+}$. The latter is also generated by controlled-potential electrolysis of $\text{Ru}(\text{bpz})_3^{2+}$ in acidic solution; it can be electrochemically oxidized back to $\text{Ru}(\text{bpz})_3^{2+}$, or it can generate $\text{Ru}(\text{bpz})_2(\text{bpz}^{\cdot-})^+$ slowly ($t_{1/2} \sim 1$ h) upon reaction with OH^- under oxygen-free conditions.

7. D.R. Prasad and M.Z. Hoffman, "Pulsed-Laser Flash and Continuous Photolysis of Ion-Pair Complexes of Methylviologen and EDTA in Aqueous Solution," *J. Chem. Soc., Faraday Trans. 2*, **82**, 2275-2289 (1986).

Methyl viologen (MV^{2+}) and EDTA form ion-pair complexes in aqueous solution that exhibit enhanced tail absorption in the u.v.-visible spectral region. Continuous photolysis of the system yields $\text{MV}^{\cdot+}$ with values of $\Phi(\text{MV}^{\cdot+})$ that are dependent on pH, the concentrations of the various species in solution, temperature, and the wavelength of excitation. Pulsed-laser excitation at 355 nm generates initially a spectrum that is not that of free $\text{MV}^{\cdot+}$; its enhanced absorption in the 440–540 nm region is reminiscent of that displayed by reduced viologen dimers and aggregates. The conversion of the initial absorption to that of free $\text{MV}^{\cdot+}$ occurs via $[\text{MV}^{2+}]$ -independent first-order kinetics in the μs time frame; k_{obs} increases as $[\text{EDTA}]$ is decreased and the pH of the solution is increased. It is suggested that the ion-pair complexes of MV^{2+} exist as "pseudo-micellar" aggregates, so that the absorption of light generates $\text{MV}^{\cdot+}$ and an oxidized EDTA radical, with the electron localized on an amine moiety, within the aggregate. The reducing EDTA radical, formed via the deprotonation of the extremely strong carbon-acid radical *alpha* to the amine radical site and a carboxylate group, causes the generation of another equivalent of $\text{MV}^{\cdot+}$ within the aggregate in competition with the decay modes of the radical; the $\text{MV}^{\cdot+}$ species therein are ultimately released into bulk solution as the aggregate structure equilibrates; the rate of equilibration depends on $[\text{EDTA}]$ in bulk solution and the degree of repulsion among the anionic species in the outer hydrophilic sheath of the "pseudo-micelle". The observed values of $\Phi(\text{MV}^{\cdot+})$ reflect the competition with the aggregates between geninate-pair back electron transfer (radiationless deactivation in photophysical terms) and radical degradation processes.

8. M.Z. Hoffman, "Pulse Radiolysis," in *Inorganic Reactions and Methods*, J.J. Zuckerman, ed., Vol. 15, VCH Publishers, Deerfield Beach, FL, 1986, pp 272-297.

Pulse radiolysis is the radiation chemical analogue of flash photolysis. It is a fast-kinetics technique that enables transitory processes, initiated by the absorption of ionizing radiation, to be observed in time frames as short as the submicrosecond region. It permits the detection and characterization of short-lived intermediates, the determination of the kinetics of their decay, and a probing of reaction mechanisms. The technique finds use in the study of radiation effects on

materials, and as a tool for the examination of mechanistic details. For inorganic systems, pulse radiolysis is used to characterize metal complexes in unusual oxidation states, to examine the kinetics and rates of ligand-labilization reactions, and to elucidate the mechanism of electron transfer.

9. V. Novakovic and M.Z. Hoffman, "Kinetics of the Thermal Reduction of Methylviologen in Alkaline Aqueous and Methanolic Solutions," *J. Am. Chem. Soc.*, **109**, 2341-2346 (1987).

Methylviologen (MV^{2+}) is reduced to $MV^{\bullet+}$ in alkaline aqueous and methanolic solutions in the absence of air. In aqueous solution, the initial rate of $MV^{\bullet+}$ formation (R_i) obeys the following rate law: $R_i = k_{\text{obsd}}[MV^{2+}]^2[OH^-]^2$; $k_{\text{obsd}} = 0.12 \text{ M}^{-1}\text{min}^{-1}$ at 25.0°C with $E_a = 58 \text{ kJ mol}^{-1}$. A mechanism is proposed whereby the initial phase of the reaction occurs via the successive attack of OH^- on the 2- and 2'-positions of the aromatic rings, followed by the reduction of MV^{2+} by the electron-rich double pseudobase. In methanolic solution, the rate law is $R_i = k_{\text{obsd}}[MV^{2+}]^{1/2}[CH_3O^-]^2$; $k_{\text{obsd}} = 4.9 \times 10^2 \text{ M}^{-3/2}\text{min}^{-1}$ at 25.0°C with $E_a = 95 \text{ kJ mol}^{-1}$. It is suggested that MV^{2+} exists in methanolic solution at the concentrations employed mainly as a dimeric aggregate, $(MV^{2+})_2$. The proposed mechanism involves an equilibrium between MV^{2+} and $(MV^{2+})_2$, with only MV^{2+} being reactive toward the formation of the pseudobase with CH_3O^- . Exposure of $MV^{\bullet+}$ to O_2 results in the formation of luminescent ($\lambda_{\text{em}} 525 \text{ nm}$) and absorbing ($\lambda_{\text{max}} \sim 380 \text{ nm}$) species via secondary reactions involving H_2O_2 , which is formed slowly from the disproportionation of $O_2^{\bullet-}$.

10. M.Z. Hoffman and D.R. Prasad, "Photoinduced Charge Separation in Ion-Pair Electron Donor-Acceptor Aggregates," in *Supramolecular Photochemistry*, V. Balzani, ed., Reidel Publishing Company, Dordrecht, Holland, 1987, pp 153-165.

Methylviologen (MV^{2+}) forms ion-pair electron donor-acceptor complexes in aqueous solution with $C_2O_4^{2-}$ and EDTA. From the results of pulsed laser excitation at 355 nm, a model is proposed in which the ion-pair complexes of MV^{2+} exist as "pseudo-micelle" aggregates; absorption of light generates $MV^{\bullet+}$ and an oxidized-donor radical within the aggregate. The irreversible conversion of the oxidized radical to a reducing radical, in competition with geminate pair back electron-transfer, leads to the formation of a second equivalent of $MV^{\bullet+}$ within the aggregate structure; the $MV^{\bullet+}$ species are ultimately released into bulk solution as the aggregate structure equilibrates. The values of $\Phi(MV^{\bullet+})$ from continuous photolysis are a measure of the dependence of the rate of geminate pair back electron-transfer on the structure of the aggregate, state of protonation of the species, and the states populated in the light-absorption process.

11. Q.G. Mulazzani, M. Venturi, and M.Z. Hoffman, "Interaction of Tris(2,2'-bipyrazine)-ruthenium(2+) Ion with Radiolytically-Generated Radicals in Aqueous Solution. Reactivity of $\text{Ru}(\text{bpz})_3^{2+}$ Toward Electron Relays," *Radiat. Phys. Chem.*, **32**, 71-78 (1988).

The one-electron reduction of $\text{Ru}(\text{bpz})_3^{2+}$ by $\cdot\text{C}(\text{CH}_3)_2\text{OH}$ is rapid ($k = 3.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and quantitative. The product of the reaction, which possesses a ligand-radical coordinated to a Ru(II) center, can be written generically as $\text{Ru}(\text{bpz})_3^+$, and represented as $\text{Ru}(\text{bpz})_2(\text{bpz}^{\cdot-})^+$ in alkaline solution and its conjugate acid $(\text{Ru}(\text{bpz})_2(\text{bpzH}^{\cdot+}))^{2+}$; $\text{p}K_a = 7.1$ in acidic solution. The reaction of $\text{Ru}(\text{bpz})_3^{2+}$ with $\cdot\text{OH}$ ($k = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) yields the OH-adduct to the ring system of the ligands; $\text{Ru}(\text{bpz})_2(\text{bpzOH}^{\cdot+})^{2+}$ is unstable toward bimolecular decay ($k \sim 4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). Reaction with $\text{H}^{\cdot}$ ($k = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) results in hydrogenation at a ring-carbon; this product is unstable in the time frame of seconds. No reaction is observed between $\text{Ru}(\text{bpz})_3^{2+}$ and $\text{Cl}_2^{\cdot-}$. $\text{Ru}(\text{bpz})_2(\text{bpz}^{\cdot-})^+$ reduces $\text{Co}(\text{sep})^{3+}$ ($k = 3.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) at pH 10, but there is no reaction at pH 4. However, $\text{Ru}(\text{bpz})_2(\text{bpzH}^{\cdot+})^{2+}$ establishes an electron-transfer equilibrium ($K_{\text{eq}} = 7$) with $\text{Cr}(\text{bpy})_3^{3+}$ at pH 3.

12. M.Z. Hoffman, "Cage Escape Yields from the Quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by Methylviologen in Aqueous Solution," *J. Phys. Chem.*, **92**, 3458-3464 (1988).

The primary quantum yield of formation of $\text{Ru}(\text{bpy})_3^{3+}$ and methylviologen radical cation ($\text{MV}^{\cdot+}$), ϕ , resulting from the oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen (MV^{2+}) in aqueous solution, has been determined by the use of pulsed-laser flash photolysis ($\lambda_{\text{exc}} = 532 \text{ nm}$; $\lambda_{\text{mon}} = 450 \text{ nm}$) as a function of $[\text{MV}^{2+}]$, ionic strength, and pH in the absence and presence of Na_2SO_4 , $\text{C}_2\text{O}_4^{2-}$ (Na^+ or K^+ salt), and ethylenediaminetetraacetate (EDTA). Inasmuch as $\phi = \eta_q \eta_{\text{ce}}$, where η_q is the efficiency of the quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ ($= k_q[\text{MV}^{2+}]/(k_o + k_q[\text{MV}^{2+}])$) and η_{ce} is the cage escape efficiency of the geminate redox pair, values of η_{ce} are easily calculated. The values of η_{ce} are a complex function of the solution medium parameters, reflecting the self-aggregation of MV^{2+} , the presence of ion-pair aggregates of MV^{2+} and EDTA, and the effect of the ionic strength of the solution on the rate constant of the cage escape reaction. Values range from ~ 0.45 in the limit of zero ionic strength at $[\text{MV}^{2+}] \geq 5 \text{ mM}$ to ~ 0.10 at high ionic strength (3.0 M) in the presence of Na_2SO_4 and $\text{C}_2\text{O}_4^{2-}$; η_{ce} follows an empirical relationship as a function of μ : $\eta_{\text{ce}} = (2.22 + 3.81\mu^{1/2})^{-1}$. For solutions containing 0.010–0.10 M EDTA, η_{ce} is generally lower than that predicted by the empirical relationship, indicating the existence of a specific effect for that reagent due, perhaps, to the presence of ion-paired aggregates of MV^{2+} and EDTA. The results obtained here compare very well with values of η_{ce} reported by other investigators for similar solution medium conditions, when due account is taken of the differences in the ϵ -values of the various species used in the calculations. The implications of the dependence of η_{ce} on solution

medium are explored for the model photochemical system containing $\text{Ru}(\text{bpy})_3^{2+}$, MV^{2+} , and a sacrificial donor.

13. M.Z. Hoffman, "Rate Constants for the Scavenging of $\text{Ru}(\text{bpy})_3^{3+}$ by EDTA in Aqueous Solution," *Inorg. Chem.*, **28**, 978-980 (1989).

The rate constants for the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with EDTA were measured as a function of pH, [EDTA], $[\text{MV}^{2+}]$, and ionic strength; $\text{Ru}(\text{bpy})_3^{3+}$ was generated in the oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} . The value of k is in the 10^6 – $10^8 \text{ M}^{-1}\text{s}^{-1}$ range, and is strongly dependent on pH and ionic strength. The value of the one-electron oxidation potential of EDTA is estimated to be $\sim -1.5 \text{ V}$.

14. M.Z. Hoffman, F. Bolletta, L. Moggi, and G.L. Hug, "Rate Constants for the Quenching of Excited States of Metal Complexes in Fluid Solution," *J. Phys. Chem. Ref. Data*, **18**, 219-534 (1989).

The rate constants for the quenching of the excited states of metal ions and complexes in homogeneous fluid solution are reported in this compilation. Values of k_q for dynamic, collisional processes between excited species and quenchers have been critically evaluated, and are presented with the following information, among others, from the original publications, when available: description of the solution medium, temperature at which k_q was determined, experimental method, range of quencher concentration used, lifetime of the excited state in the absence of quencher, activation parameters, quenching mechanism. Data collection is complete through the end of 1986, and covers the coordination compounds of 26 metals, including the ions and complexes of the inner- and outer-transition metals, and porphyrin complexes of nontransition metals. Data for 261 excited states quenched by more than 400 inorganic quenchers and 600 organic quenchers have been extracted from almost 500 publications. The introduction to the work contains a discussion of the conceptual background to quenching, including a general treatment of the kinetics, and explanation of the tables, and a list of recent review articles. Uncommon kinetics mechanisms and equations, used to obtain the reported values of k_1 , are discussed in detail as part of the notes to the tables. Indexes of excited states, quenchers, and authors are appended.

15. 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).

The photodynamics of aqueous solutions containing $\text{Ru}(\text{bpz})_3^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine) and reductive quenchers ($\text{D} = \text{EDTA}$ (ethylenediaminetetraacetic acid), $\text{C}_2\text{O}_4^{2-}$, TEOA (triethanolamine), ascorbate ion, and thiols (RS^-), e.g., cysteine and glutathione) in the presence and absence of MV^{2+} (methylviologen) have been evaluated by the use of time-resolved spectrofluorimetry and pulsed laser flash photolysis as a function of pH, $[\text{D}]$, and $[\text{MV}^{2+}]$; as well, we have determined $\Phi(\text{MV}^{+\bullet})$ from the continuous photolysis of these systems. Values of k_q are dependent on pH due to the acid-base properties of the quenchers and range from $\sim 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for ascorbate ion and deprotonated thiols to $\sim 1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for $\text{C}_2\text{O}_4^{2-}$. The oxidized radicals ($\text{D}_{\text{ox}}^\bullet$) of EDTA, $\text{C}_2\text{O}_4^{2-}$, and TEOA can undergo irreversible transformation into reducing radicals ($\text{D}_{\text{red}}^\bullet$) within the quenching solvent cage in competition with geminate-pair back electron transfer; the efficiencies of escape of the redox products ($\text{Ru}(\text{bpz})_3^+$ and $\text{D}_{\text{ox}}^\bullet$) into the bulk solution (η_{ce}) for these sacrificial quenchers are very high. (≥ 0.5). Thiols are semisacrificial quenchers; their oxidized radicals ($\text{RS}^\bullet$) must escape from the quenching cage before conversion to $\text{D}_{\text{red}}^\bullet$ ($\text{RSSR}^\bullet$) can occur; $\eta_{\text{ce}} \leq 0.03$. Ascorbate ion is a nonsacrificial quencher; its oxidized radical reacts rapidly and quantitatively with $\text{Ru}(\text{bpz})_3^+$ in bulk solution. In the absence of MV^{2+} , $\text{D}_{\text{red}}^\bullet$ from sacrificial and semisacrificial quenchers reacts rapidly ($k > 10^9 \text{ M}^{-1}\text{s}^{-1}$) with $\text{Ru}(\text{bpz})_3^{2+}$, generating a second equivalent of the reduced complex. In the presence of MV^{2+} , both $\text{Ru}(\text{bpz})_3^+$ and $\text{D}_{\text{red}}^\bullet$ produce $\text{MV}^{+\bullet}$ rapidly ($k = 10^8\text{--}10^9 \text{ M}^{-1}\text{s}^{-1}$). $\text{Ru}(\text{bpz})_3^+$ engages in an acid-base equilibrium ($\text{p}K_a = 7.1$); the conjugate acid is a poorer reducing agent by $\sim 0.2 \text{ V}$ than is the basic form and is unable to reduce MV^{2+} . As a result, the generation of $\text{MV}^{+\bullet}$ in acidic solution is pH- and $[\text{MV}^{2+}]$ -dependent. The values of $\Phi(\text{MV}^{+\bullet})$ from the continuous photolysis correlate very well with the rate constants and efficiencies of the various steps in the mechanism according to the following expression: $\Phi(\text{MV}^{+\bullet}) = \eta_* \eta_q \eta_{\text{ce}} (\eta_{\text{red}} + \eta_{\text{red}}')$, where η_* is the efficiency of population of $^*\text{Ru}(\text{bpz})_3^{2+}$, η_q is the efficiency of quenching of $^*\text{Ru}(\text{bpz})_3^{2+}$, and η_{red} and η_{red}' are the efficiencies of the reactions of $\text{Ru}(\text{bpz})_3^+$ and $\text{D}_{\text{red}}^\bullet$ with MV^{2+} , respectively. Values of $\Phi(\text{MV}^{+\bullet})$ as high as 1.2 have been obtained at pH 4.5 in solution containing 0.10 M MV^{2+} and 0.26 M $\text{C}_2\text{O}_4^{2-}$.

16. 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).

The reduction of $\text{Ru}(\text{bpm})_3^{2+}$ in aqueous solution has been investigated by use of photochemical, radiation chemical, and electrochemical techniques. The luminescent excited state of the substrate, $^*\text{Ru}(\text{bpm})_3^{2+}$, has a lifetime (τ_0) of 0.081 μs and a standard reduction potential of $\sim 1.2 \text{ V}$; it is quenched by electron donors (D) such as ethylenediaminetetraacetic acid (EDTA),

triethanolamine (TEOA), ascorbate ion, deprotonated cysteine, and reduced glutathione with values of k_q that depend on the pH of the solution and the reducing ability of the quencher. The one-electron reduced species, $\text{Ru}(\text{bpm})_3^+$, is formed in the quenching reaction; it is also produced electrochemically and from the reaction of radiolytically generated $\text{CO}_2^{\cdot-}$ with $\text{Ru}(\text{bpm})_3^{2+}$ ($k = 6.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). $\text{Ru}(\text{bpm})_3^+$ is a good reducing agent ($E_{\text{ox}}^0 = 0.73 \text{ V}$) and reduces MV^{2+} (methylviologen) to $\text{MV}^{\cdot+}$ ($k = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). $\text{Ru}(\text{bpm})_3^+$ also undergoes protonation; its acidic form ($\text{p}K_a$ 6.3) is a milder reducing agent ($E_{\text{ox}}^0 = 0.50 \text{ V}$) but is still capable of reducing MV^{2+} ($k = 1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). Both forms of $\text{Ru}(\text{bpm})_3^+$ are unstable with respect to long-term storage; it is likely they engage in disproportionation and/or reaction with the solvent. The continuous photolysis of a solution containing $\text{Ru}(\text{bpm})_3^{2+}$, MV^{2+} , and a sacrificial reductive quencher (EDTA, TEOA) generates $\text{MV}^{\cdot+}$. The values of $\Phi(\text{MV}^{\cdot+})$ correlate very well with the rate constants and efficiencies of the various steps in the mechanism according to the following expression: $\Phi(\text{MV}^{\cdot+}) = \eta_* \eta_q \eta_{\text{ce}} (\eta_{\text{red}} + \eta_{\text{red}}')$, where η_* is the efficiency of population of $^*\text{Ru}(\text{bpm})_3^{2+}$, η_q is the efficiency of quenching of $^*\text{Ru}(\text{bpm})_3^{2+}$, η_{ce} is the efficiency of escape of the redox products into the bulk solution, and η_{red} and η_{red}' are the efficiencies of the reactions of $\text{Ru}(\text{bpm})_3^+$ and $\text{D}_{\text{red}}^{\cdot}$, the reducing radical from the irreversible transformation of the initially formed oxidized-quencher radical, respectively, with MV^{2+} . Values of η_{ce} of 0.64 and ~ 0.7 for TEOA and EDTA, respectively, in alkaline solution have been obtained. For $\text{D} = \text{TEOA}$, evidence is cited indicating that the back electron transfer between the geminate pair ($\text{Ru}(\text{bpm})_3^+$ and the oxidized-TEOA radical) within the solvent cage occurs in the "inverted Marcus" region. The absorption spectra of $^*\text{Ru}(\text{bpm})_3^{2+}$ and the acid-base forms of $\text{Ru}(\text{bpm})_3^+$ are also characterized.

17. 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.

The focus of our research over the past several years has been the evaluation of the kinetics of light-induced processes involving transition-metal coordination complexes, with an eye toward an understanding of the detailed mechanisms of the reactions. Through the use of the fast kinetics techniques of conventional and pulsed-laser flash photolysis, the temporal changes in the emission spectra of excited complexes, and in the absorption spectra of excited- and ground-state transient species, such as free radicals, coordinated radicals, and complexes in unusual oxidation states, have been examined. In this review paper, some of the fundamental photophysics and photochemistry of coordination complexes will be described in general terms after which the dynamics of systems involving $\text{Cr}(\text{III})$ -polypyridyl complexes will be examined in more detail. Because the

fast kinetics technique of pulse radiolysis is used to examine specific aspects of excited-state electron-transfer reactions, the principles of that technique will be reviewed.

18. M.Z. Hoffman and D. Prasad, "Oxalate Ion as a Sacrificial Electron Donor in the Ru(bpy)₃²⁺-Methylviologen Model Photochemical System, *J. Photochem. Photobiol., A: Chem.*, **54**, 197-204 (1990).

Oxalate ion (C₂O₄²⁻) reduces Ru(bpy)₃³⁺ (bpy = 2,2'-bipyridine) in aqueous solution, albeit with rather small rate constants ($k = (1.0 \pm 0.3) \times 10^5$ and $(3 \pm 1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for $\mu = 0.30$ – 1.0 and 2.1 – 3.0 M , respectively). As a result, the scavenging by C₂O₄²⁻ of photochemically-generated Ru(bpy)₃³⁺ ($E_{\text{red}}^0 = 1.3 \text{ V}$) from the oxidative quenching (by methylviologen; MV²⁺) of the lowest electronically excited state of Ru(bpy)₃²⁺ cannot compete satisfactorily with the electron transfer reaction between Ru(bpy)₃³⁺ and MV⁺•, the reduced methylviologen cation radical ($k \approx 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Thus, the quantum yields of MV⁺• formation in the continuous photolysis of the Ru(bpy)₃²⁺-MV²⁺-C₂O₄²⁻ photochemical system are no higher than approximately 0.02, even under optimized conditions.

19. 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," *Molec. Cryst. Liq. Cryst.*, **194**, 141-150 (1991).

The yield of oxidized and reduced products released into the bulk solution upon electron-transfer quenching is the critical parameter governing the efficacy of a redox photosensitizer. The cage escape efficiency (η_{ce}) is a measure of the competition between back electron transfer (k_{bt}) and diffusional separation (k_{ce}) of the geminate redox pair formed within the solvent cage in the quenching act. Values of η_{ce} have been obtained for the sacrificial reductive quenching of the excited states of homo- and heteroleptic Ru(II)-diimine complexes of bpy (2,2'-bipyridine), bpz (2,2'-bipyrazine), and bpm (2,2'-bipyrimidine) by TEOA and EDTA. The values of η_{ce} vary with the ground-state reduction potentials of the complexes, describing a strong U-shaped dependence for EDTA, but a much weaker dependence for TEOA. Plots of $\log(k_{\text{bt}}/k_{\text{ce}})$ vs. ΔG_{bt}^0 exhibit well-defined bell-shaped curves, indicating that k_{bt} traverses the "normal" and "inverted Marcus" regions if k_{ce} has a constant value for all the one-electron reduced photosensitizers.

20. 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).

The rate constants for the reduction of RuL^{2+} (where RuL^{2+} represents ten complexes of the general formula $\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z^{2+}$, $\text{bpy} = 2,2'$ -bipyridine, $\text{bpm} = 2,2'$ -bipyrimidine, $\text{bpz} = 2,2'$ -bipyrazine, m and $z = 0,1,2,3$ and $m + z \leq 3$) to RuL^+ by $\text{CO}_2^{\cdot-}$ radicals and the rate constants for the reactions between the couples $\text{RuL}^{2+}/\text{RuL}^+$ or $\text{RuL}^{2+}, \text{H}^+/\text{RuLH}^{2+}$ and the couple $\text{MV}^{2+}/\text{MV}^{\cdot+}$ ($\text{MV}^{2+} = 1,1'$ -dimethyl-4,4'-bipyridinium dication) have been measured in aqueous solution using pulse radiolysis methods. The kinetic data, interpreted with use of Marcus electron-transfer theory, have generated the following parameters 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 that of the intrinsic barrier $\Delta G^\ddagger(0)$ is 57.3 kJ mol^{-1} . For the $\text{CO}_2/\text{CO}_2^{\cdot-}$ self-exchange electron-transfer reaction, values of $\Delta G^\ddagger(0) = 97.0 \text{ kJ mol}^{-1}$ and $k_{\text{se}} = 1.4 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ have been derived. For the electron-transfer reactions involving the $\text{MV}^{2+}/\text{MV}^{\cdot+}$ 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 acid solution, respectively, by assuming adiabatic behaviour, *i.e.*, $k = 1$; the difference between these two values is attributed to an additional intrinsic barrier associated with the protonation/deprotonation process.

21. T. Ohno, A. Yoshimura, D.R. Prasad, and M.Z. Hoffman, "A Weak ΔG^0 -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).

The oxidative quenching by MV^{2+} of the lowest luminescent excited states of nine Ru^{II} -diimine complexes in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ was studied by pulsed laser flash photolysis. From a knowledge of the spectral characteristics of the excited states, the fraction of the excited states quenched, and the yield of $\text{MV}^{\cdot+}$ generated in the flash, the efficiency of escape of the redox products into bulk solution (η_{ce}) was calculated; values of η_{ce} were also obtained for a variation of the composition of the mixed solvent, for changes in the ionic strength, and for quenching by $\text{Rh}(\text{phen})_3^{3+}$. From the values of η_{ce} were calculated $k_{\text{bet}}/k_{\text{dis}}$ ratios, where k_{bet} is the rate constant of back electron transfer between the geminate redox pair ($\text{Ru}^{\text{III}}\cdots\text{MV}^{\cdot+}$) within the solvent cage and k_{dis} is the rate constant of escape of the redox pair out of the cage. By assuming that k_{dis} is a constant value for these identically charged species, the variation of k_{bet} was found to be weakly dependent on ΔG^0 of the back electron-transfer reaction (-1.4 to -2.0 eV) within the "inverted Marcus" region. For those 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 that would increase the intrapair distance and decrease the value of k_{dis} . Possible origins of the weak dependence of k_{bet} on ΔG^0 are discussed.

22. M. Venturi, M. D'Angelantonio, M. Ciano, Q.G. Mulazzani, and M.Z. Hoffman, "One-Electron Reduction of Ru(II)-Diimine Complexes. Characterization of Reduced Species Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine in Aqueous Solution," *J. Phys. Chem.*, **95**, 5121-5129 (1991).

The one-electron reductions of ten Ru(II)-diimine complexes of the general formula $\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z^{2+}$ (bpy = 2,2'-bipyridine, bpm = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine, m and z = 0,1,2,3 and $m + z \leq 3$), generically indicated as RuL^{2+} , have been investigated in aqueous solution by the use of radiation chemical and electrochemical techniques, leading to the characterization of the one-electron reduced products (RuL^+) and their conjugate acids (RuLH^{2+}). Because the ease of reduction of the ligands follows the trend $\text{bpz} > \text{bpm} > \text{bpy}$, the electron added to RuL^{2+} is localized on the ligand that is most easily reduced. The E^0 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 unique 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 $E^0(\text{RuL}^{2+}/\text{RuL}^+)$, with separate lines for bpz and bpm acceptor ligands. From the values of pK_a and $E^0(\text{RuL}^{2+}/\text{RuL}^+)$, $E^0(\text{RuL}^{2+}, \text{H}^+/\text{RuLH}^{2+})$ are obtained. The rate constants for the following electron-transfer reactions have been measured or calculated and have been correlated with the values of ΔG^0 and other kinetic parameters by use of the Marcus theory: $\text{RuL}^{2+} + \text{CO}_2^{\cdot-} \rightarrow \text{RuL}^+ + \text{CO}_2$, $\text{RuL}^{\cdot+} + \text{MV}^{2+} \rightarrow \text{RuL}^{2+} + \text{MV}^{\cdot+}$ and its reverse reaction, and $\text{RuLH}^{2+} + \text{MV}^{\cdot+} \rightarrow \text{RuL}^{2+} + \text{MV}^+ + \text{H}^+$ and its reverse reaction. The relevance of the results to the use of the complexes as electron-transfer photosensitizers is discussed.

23. 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).

Continuous and pulsed laser flash photolysis techniques have been used to determine the efficiency (η_{ce}) with which the redox products are released into bulk upon the oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} in the absence and presence of TEOA as a sacrificial electron donor in aqueous solution. The value of η_{ce} is diminished as the ionic strength (μ) of the solution increases, although the extent of the effect depends on whether or not TEOA is present: in the absence of TEOA, $\eta_{\text{ce}} = (3.8 + 4.8\mu^{1/2})^{-1}$; in the presence of 0.1 M TEOA in alkaline solution, η_{ce}

$= (3.8 + 9.0\mu^{1/2})^{-1}$. TEOA is an effective scavenger of $\text{Ru}(\text{bpy})_3^{3+}$ at concentrations of ≥ 0.05 M and in the pH 8.5–11.5 range. In less alkaline solution, its protonation diminishes its reducing ability; in more alkaline solution, reactions between its degradation products and MV^{2+} yield additional equivalents of MV^{+} . The value of η_{ce} is also a function of $[\text{Ru}(\text{bpy})_3^{2+}]$ with a transition at 20–50 μM between upper and lower plateau values.

24. C. Pizzocaro, M. Bolte, and M.Z. Hoffman, " $\text{Cr}(\text{bpy})_3^{3+}$ -Sensitized Photooxidation of Phenol in Aqueous Solution," *J. Photochem. Photobiol. A: Chem.*, **68**, 115-119 (1992).

In the presence of air the 365 nm irradiation of mildly acidic aqueous solutions of $\text{Cr}(\text{bpy})_3^{3+}$ and phenol yields 1,4-benzoquinone (BQ) as the only organic product; the aquation photoproduct $\text{Cr}(\text{bpy})_2(\text{OH})_2^{3+}$ is also produced. Although $^*\text{Cr}(\text{bpy})_3^{3+}$ is quenched by phenol ($k_q = 8.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$), there is no evidence of redox products. The results suggest that singlet oxygen, generated in the quenching of $^*\text{Cr}(\text{bpy})_3^{3+}$ by O_2 , is the mediator of the formation of BQ.

25. A. Yoshimura, M.Z. Hoffman, and H. Sun, "An Evaluation of the Excited-State Absorption Spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ in Aqueous and Acetonitrile Solutions," *J. Photochem. Photobiol. A: Chem.*, **70**, 29-33 (1993).

Three pulsed laser techniques have been used to evaluate the absorption spectrum of $^*\text{Ru}(\text{bpy})_3^{2+}$ in H_2O , CH_3CN , and $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ mixtures: complete conversion of the ground state, energy transfer to anthracene, and benzophenone actinometry. The three techniques give reliable and reproducible values of $\epsilon_{450} = 4.6(\pm 0.4) \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, independent of the solution medium. The ground state spectrum is virtually the same in H_2O and CH_3CN with $\epsilon_{452} = 1.46 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$; the value of $\Delta\epsilon_{450}$, the difference in the ϵ values of the excited and the ground states at 450 nm, is $-1.0(\pm 0.09) \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. $\text{Ru}(\text{bpy})_3^{2+}$ can serve as a reliable actinometer for the 532 nm frequency doubled Nd:YAG pulsed laser line and, with appropriate corrections for the inner filter effect, for the 355 nm frequency tripled line.

26. 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," *J. Phys. Chem.*, **97**, 5014-5018 (1993).

The apparent pK_a^* values and the rate constants for the quenching by H^+ of the excited states of nine homo- and heteroleptic complexes of Ru(II) that contain bpm (2,2'-bipyrimidine), bpz (2,2'-bipyrazine), and bpy (2,2'-bipyridine) as ligands were determined in aqueous solution; the excited state can be described as a one-electron reduced ligand that is coordinated to a Ru(III)

center with the electron localized on the most easily reduced ligand ($\text{bpz} > \text{bpm} > \text{bpy}$). As is the case with the one-electron reduced bpm and bpz complexes, which exhibit $\text{p}K_a$ values in the range from 6.3 to 9.2, the excited states can be protonated, resulting in spectral shifts and marked lowering of the lifetime and emission intensity. Where luminescence from the monoprotonated excited state is observable, the lifetimes and $\text{p}K_a^*$ values can be directly determined; in the other cases, estimates of the deprotonation rate constants can be made. The relationship $\text{p}K_a - \text{p}K_a^* = 4.8$ is obtained from the data. Correlations with the values of E_{red}^0 show that protonation occurs on the uniquely reduced ligand and that the bpm and bpz ligands can be distinguished. Values of $\text{p}K_a^*$ for $\text{Ru}(\text{bpz})_3^{2+}$ were determined as a function of temperature; activation energies for the protonation and deprotonation reactions, as well as thermodynamic parameters, were obtained from the data.

27. C. Pizzocaro, M. Bolte, and M.Z. Hoffman, "Polymerization of Acrylamide Photosensitized by Tris(2,2'-bipyridine)chromium(III) Ion in Aqueous Solution," *Polyhedron*, **12**, 855-858 (1993).

The 365 nm continuous irradiation of acidic aqueous solutions of $\text{Cr}(\text{bpy})_3^{3+}$ and acrylamide yields polyacrylamide; the $\text{Cr}(\text{bpy})_2(\text{OH}_2)_2^{3+}$ aquation product is also produced. Upon pulsed-laser excitation, no chromium(II) product is observed, likely due to the low rate constant for the quenching of thermally-equilibrated $^2T_1/{}^2E$ excited states of the photosensitizer by acrylamide and the low cage-escape yield of redox products. Nevertheless, $\text{Cr}(\text{bpy})_3^{3+}$ is a suitable photosensitizer even for excitation with visible light up to 450 nm. The positive dependence of the rate of polymerization on the intensity of absorbed light and $[\text{monomer}]^2$ and the inverse dependence on $[\text{Cr}(\text{bpy})_3^{3+}]$ suggest that the termination step of the chain reaction involves the oxidative scavenging of the macro-radicals by the photosensitizer.

28. H. Sun and M.Z. Hoffman, "Photophysics of Ruthenium(II)-Diimine Complexes in H_2O - CH_3CN Mixed Solvents," *J. Phys. Chem.*, **97**, 11956-11959 (1993).

The photophysical properties of $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{bpz})_3^{2+}$, and $\text{Ru}(\text{bpz})_2(\text{bpm})^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{bpz} = 2,2'$ -bipyrazine, $\text{bpm} = 2,2'$ -bipyrimidine) have been studied in neat and mixed CH_3CN - H_2O solutions. The temperature-dependent lifetimes, and room-temperature emission spectra and quantum yields were determined for the complexes; the rate constants and activation parameters for the various photophysical pathways were calculated from the data. Shifts of the emission energy (E_{em}) as a function of solvent composition suggest that the excited states are preferentially solvated by water molecules. Although radiative decay is relatively insensitive to the change of solution medium, nonradiative decay (k_{nr}) and the temperature-dependent thermal

population of the metal centered d-d state, which account for more than 90% of the decay of the emitting MLCT state, are strongly dependent on solvent and temperature; the observed phenomena can be well understood on the basis that the energy level of the MLCT state, which possesses a static dipole moment, is sensitive to the polarity change of the solution medium. At lower temperatures, nonradiative decay is the dominant process, and the overall deactivation of the emitting state is faster in water-rich than in acetonitrile-rich solutions; at higher temperatures, the thermal population of the d-d state is the dominant process, and the overall decay is slower in water-rich solvents. The nonlinear correlations between $\ln k_{nr}$ and E_{em} in these solvents are qualitatively explained by the energy gap law for the radiationless transition, and support the argument that water molecules provide an unusually high solvent reorganization energy for the decay of the MLCT excited states.

29. H. Sun and M.Z. Hoffman, "Photoinduced Charge Separation by Ruthenium(II) Photosensitizers," *Proc. Indian Acad. Sci., Chem. Sci.*, **105**, 487-494 (1993).

The values of the cage escape yields of redox products (η_{ce}) were determined for the reductive quenching of the excited states of homo- and heteroleptic complexes of Ru(II) and 2,2'-bipyridine (bpy), 2,2'-bipyrimidine (bpm), and 2,2'-bipyrazine (bpz) by triethanolamine (TEOA) as a sacrificial reductive quencher in aqueous, acetonitrile, and propylene carbonate solutions. In aqueous solution, η_{ce} varies with the standard reduction potential (E^0) of the complex, describing a weak dependence. The values of η_{ce} are independent of E^0 in propylene carbonate, but exhibit an inverted dependence in acetonitrile; the values of η_{ce} in acetonitrile are generally higher than those in aqueous and propylene carbonate solutions, due to the higher diffusional rate constant for cage escape of the redox geminate pair in acetonitrile. The variable dependences of η_{ce} in the different solvents on the driving force of back electron transfer requires that the conventional model be modified to account for the reorientation of the geminate pair within the solvent cage.

30. Q.G. Mulazzani, H. Sun, M.Z. Hoffman, W.E. Ford, and M.A.J. Rodgers, "Quenching of the Excited States of Ru(II)-Diimine Complexes by Oxygen," *J. Phys. Chem.*, **98**, 1145-1150 (1994).

The quenching by O_2 of the MLCT excited states of ten Ru(II)-diimine complexes (RuL^{2+}) of the form $Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z^{2+}$ ($bpy = 2,2'$ -bipyridine, $bpm = 2,2'$ -bipyrimidine, $bpz = 2,2'$ -bipyrazine, m and $z = 0,1,2,3$ and $m + z \leq 3$) in aqueous solution has been investigated using the techniques of laser flash photolysis and time-resolved and steady-state near-infrared emission spectrophotometry. Values of k_q have been determined in H_2O and D_2O , and range between 5.1×10^8 and $3.4 \times 10^9 M^{-1}s^{-1}$. The quantum yields (Φ_Δ) of singlet molecular oxygen, $O_2(^1\Delta_g)$,

originating from the energy transfer quenching of $^*\text{RuL}^{2+}$ by O_2 , and determined in D_2O by comparison with Φ_Δ from the excited state of tetrakis(4-sulfonatophenyl)porphine (TPPS^{4-}), are 0.5 for $\text{Ru}(\text{bpy})_3^{2+}$ and ~ 1 for all the other complexes. It has been established that for $\text{Ru}(\text{bpy})_3^{2+}$ and, presumably, all the other complexes, the yield of electron transfer products, RuL^{3+} and O_2^- , in bulk solution, is negligibly small. The lower value of Φ_Δ for $\text{Ru}(\text{bpy})_3^{2+}$ is attributed to competitive charge transfer quenching, followed by efficient back electron transfer within the solvent cage. The values of the rate constants of energy transfer for the six complexes that contain at least one bpy ligand decrease with increasing driving force.

31. H. Sun, A. Yoshimura, and M.Z. Hoffman, "Oxidative Quenching of the Excited State of Tris(2,2'-bipyridine)ruthenium(2+) Ion by Methylviologen. Effect of Solution Medium and Temperature," *J. Phys. Chem.*, **98**, 5058-5064 (1994).

The rate constant (k_q) for the quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen (MV^{2+}) has been determined as a function of the mole fraction of CH_3CN (X_{AN}) in aqueous mixtures; k_q goes through a minimum at $X_{\text{AN}} \sim 0.4$, which is suggested to occur because of the dynamic solvent effect for the electron transfer reaction in the mixed solvents, whereby the relaxation dynamics of the solvent is a strong function of its composition. The cage escape yield (η_{ce}) for the release of the redox products into bulk solution has been determined as a function of ionic strength, temperature and X_{AN} ; the apparent activation energy for the back electron transfer (E_{bt}) between the geminate redox pair, $\text{Ru}(\text{bpy})_3^{3+}$ and MV^+ , within the solvent cage produced upon quenching is obtained from the data through the application of the simple cage model. E_{bt} is independent of ionic strength in aqueous solutions, but is strongly dependent on solvent composition in mixed solvents. However, E_{bt} decreases smoothly from 9.6 kJ mol^{-1} in aqueous solution to -5.5 kJ mol^{-1} in CH_3CN -rich solvents as X_{AN} is increased, requiring that a modification of the simple model be made. The concept of a kinetically important reorientation of the geminate redox pair is introduced to account for the experimental observations; the simple solvent cage model can be viewed as a limiting case in the modified model.

32. H. Sun, M.Z. Hoffman, and Q.G. Mulazzani, "Properties of Excited States and One-Electron Reduced Forms of Ruthenium(II)-Diimine Photosensitizers," *Res. Chem. Intermed.*, **20**, 735-754 (1994).

In this review, we compare the spectral, acid-base, electrochemical, and kinetic properties of the excited states and one-electron reduced forms of homo- and heteroleptic $\text{Ru}(\text{II})$ -diimine photosensitizers that contain 2,2'-bipyridine, 2,2'-bipyrazine, and 2,2'-bipyrimidine ligands. These species, represented as $^*(\text{Ru}^{\text{III}}\text{L}^-)^{2+}$ and $(\text{Ru}^{\text{II}}\text{L}^-)^+$, respectively, are orbital analogues in

that the intra- or intermolecularly transferred electron resides on the same uniquely reduced ligand. The variations in the properties of these species, resulting from changes in the coordinating ligands, permit the fine-tuning of photochemical systems.

33. C. Pizzocaro, M. Bolte, H. Sun, and M.Z. Hoffman, "Metal Complex Sensitized Photo-oxidation of Phenol in Aqueous Solution," *New J. Chem.*, **18**, 737-743 (1994).

The luminescent excited states of $\text{Cr}(\text{bpy})_3^{3+}$ ($\text{bpy} = 2,2'$ -bipyridine) and $\text{Ru}(\text{bpz})_3^{2+}$ ($\text{bpz} = 2,2'$ -bipyrazine) are good oxidants with E° values in water of 1.44 and 1.68 V, respectively; $^*\text{Ru}(\text{bpy})_3^{2+}$ is a weaker oxidant with $E^\circ = 0.93$ V. $^*\text{Cr}(\text{bpy})_3^{3+}$ and $^*\text{Ru}(\text{bpz})_3^{2+}$ are quenched by phenol; $^*\text{Ru}(\text{bpy})_3^{2+}$ is not. The three excited states are quenched by O_2 with the formation of $^1\text{O}_2$. The continuous photolysis of air-saturated acidic solutions of $\text{Cr}(\text{bpy})_3^{3+}$ and phenol yields $\text{Cr}(\text{bpy})_2(\text{OH}_2)_2^{3+}$ and 1,4-benzoquinone as the only photoproducts as determined by HPLC. In the absence of air, only the aquation of the photosensitizer is manifest. No $\text{Cr}(\text{bpy})_3^{2+}$ is detected in pulsed-laser flash photolysis, indicating that the cage escape yield (η_{ce}) for the electron transfer reaction is < 0.01 . For $^*\text{Ru}(\text{bpz})_3^{2+}$, η_{ce} for the formation of $\text{Ru}(\text{bpz})_3^+$ and the phenoxyl radical is 0.48, and the products of the reaction in the absence of air are hydroxyphenyl dimers. With $^*\text{Ru}(\text{bpy})_3^{2+}$ as the photosensitizer in aerated solution, the product is benzoquinone. We conclude that benzoquinone is generated via a $^1\text{O}_2$ pathway, while the hydroxyphenyl dimers arise via redox quenching. The results demonstrate how the products of the photosensitization reaction can be fine-tuned through the utilization of alternative mechanisms that take advantage of the excited state properties of the coordination complex.

34. H. Sun and M.Z. Hoffman, "Reductive Quenching of the Excited States of Ruthenium(II) Complexes Containing 2,2'-Bipyridine, 2,2'-Bipyrazine, and 2,2'-Bipyrimidine Ligands," *J. Phys. Chem.*, **98**, 11719-11726 (1994).

The reductive quenching of the luminescent excited states of $\text{Ru}(\text{II})$ complexes of the general formula $\text{Ru}(\text{bpy})_{3-m-z}(\text{bpm})_m(\text{bpz})_z^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{bpm} = 2,2'$ -bipyrimidine, $\text{bpz} = 2,2'$ -bipyrazine, m and $z = 0, 1, 2, 3$ and $m + z \leq 3$) by aromatic amines and methoxybenzenes as non-sacrificial electron donors, and by $\text{C}_2\text{O}_4^{2-}$, EDTA, and TEOA as sacrificial donors in aqueous, acetonitrile, and propylene carbonate solution was examined by continuous and pulsed laser flash photolysis techniques. From k_{q} , a value of E° for the irreversible oxidation of TEOA (-0.84 ± 0.12 V vs. NHE) in acetonitrile was obtained. Values of the cage escape yield of redox products (η_{ce}) showed weak or no dependencies on the driving forces of back electron transfer within the geminate redox pair in the solvent cage ($\Delta G_{\text{bt}}^\circ$), suggesting that the simple model of competition between cage escape and back electron transfer may be inadequate to describe the results. A

modification of the simple model, in which is introduced a kinetically important reorientation of the geminate redox pair, is proposed.

35. H. Sun and M.Z. Hoffman, "Re-evaluation of the Solvent Cage Model for Electron Transfer Quenching of the MLCT Excited States of Ru(II) Complexes," *J. Photochem. Photobiol., A: Chem.*, **84**, 97-99 (1994).

A re-evaluation of the commonly invoked solvent cage model for electron transfer quenching of the luminescent excited states of Ru(II) complexes is presented on the basis of two sets of experimental results. Firstly, the cage escape yields (η_{ce}) for the reductive quenching of the excited states of an homologous series of Ru(II) complexes that contain 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2'-bipyrazine ligands by triethanolamine have been determined in aqueous, acetonitrile and propylene carbonate solutions. Weak or no dependencies of η_{ce} on the driving force for the back electron transfer reaction between the redox pair within the solvent cage were found, which is in sharp contrast to the well defined "bell-shaped" curves for the reductive quenching of $^*Ru(II)$ complexes by aromatic amines and methoxybenzenes as reported in the literature; weak dependencies have also been reported in other oxidative and reductive systems. Secondly, values of η_{ce} have been determined as a function of temperature for the oxidative quenching of the excited state of $Ru(bpy)_3^{2+}$ by methylviologen in H_2O-CH_3CN solutions; application of the conventional model gives rise to *negative* activation energies for the back electron transfer reaction within the solvent cage in CH_3CN -rich solvents. A modification of the simple model, in which the concept of a kinetically important reorientation of the geminate redox pair is introduced, is proposed to account for the experimental observations; the simple solvent cage model can be viewed as a limiting case in the new model.

36. M. Sarakha, V. Portal, M. Bolte, and M.Z. Hoffman, "Polymerization of Acrylamide Photoinitiated by $Co(NH_3)_5N_3^{2+}$ with Long-Wavelength Visible Light in Aqueous Solution," *J. Photochem. Photobiol. A: Chem.*, **91**, 165-70 (1995).

The 546-nm continuous irradiation of acidic aqueous solutions of $Co(NH_3)_5N_3^{2+}$ and acrylamide (AA) results in the formation of polyacrylamide. Excitation of $Co(NH_3)_5N_3^{2+}$ yields Co_{aq}^{2+} and $N_3^{\bullet}$ radicals; the latter species initiate the free-radical chain reaction via oxidative electron- and/or H-atom transfer with the monomer. The positive dependence of the rate of polymerization on the square root of the absorbed light intensity and [AA] suggests that the termination step of the chain reaction involves the mutual annihilation of the macroradicals. ESR spin trapping experiments demonstrate unequivocally that $N_3^{\bullet}$ radicals are present in the system.

$\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ is a suitable photosensitizer for the initiation of free-radical polymerization with visible light.

37. C.D. Clark and M.Z. Hoffman, "Temperature and Specific Anion Effects in Photoinduced Intermolecular Electron-Transfer Reactions," *Proc. Indian Acad. Sci. (Chem. Sci.)*, **107**, 769-777 (1995).

The rate constants for the bimolecular oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen (k_q) and the electron-transfer recombination (k_{rec}) reaction of the redox products were determined as a function of the ionic strength and temperature in aqueous solution. At 25 °C for Na^+ salts at constant μ , k_q and k_{rec} are in the order $\text{H}_2\text{PO}_4^- < \text{CH}_3\text{CO}_2^- \sim \text{HPO}_4^{2-} \sim \text{SO}_4^{2-} \ll \text{ClO}_4^-$; activation energies are independent of μ and the anion (~ 16 kJ/mol), except for ClO_4^- , where E_a is $\sim 30\%$ lower. The trends in k_q and k_{rec} are attributed to the existence of ion-paired aggregates of the cationic reactants and anions; correlations with the sizes and hydration enthalpies of the anions can be made. It is suggested that ClO_4^- , with the smallest hydration radius and the least negative hydration enthalpy, is more closely ion-paired within the $\text{Ru}(\text{bpy})_3^{2+}$ (or $\text{Ru}(\text{bpy})_3^{3+}$) interligand pockets, "tethering" the MV^{2+} (or $\text{MV}^{\bullet+}$) into closer proximity, thereby lowering the activation barrier and increasing the rate of electron transfer.

38. C.D. Clark and M.Z. Hoffman, "Ion-Pairing Control of Excited-State Electron-Transfer Reactions. Quenching, Charge Recombination, and Back Electron Transfer," *J. Phys. Chem.*, **100**, 7526-7532 (1996).

The rate constants for the oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} (k_q) and the charge recombination reaction between $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{MV}^{\bullet+}$ in bulk solution (k_{rec}), and the cage escape yields of the redox products (η_{ce}) were determined as a function of added electrolytes (Na^+ salts of oxyanions and halides) and temperature (10-60 °C) in aqueous solution. At 25 °C and constant [anion], k_q and k_{rec} are a function of the specific anion, decreasing in the order $\text{ClO}_4^- \gg \text{SO}_4^{2-} \sim \text{HPO}_4^{2-} > \text{H}_2\text{PO}_4^- \sim \text{CH}_3\text{CO}_2^-$ and $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. Activation energies for k_q and k_{rec} for ClO_4^- are $\sim 30\%$ lower than the average values for the other salts. Values of η_{ce} show anion-specific trends opposite to those for k_q and k_{rec} . The reactant cations are extensively ion-paired by the dominant anions in bulk solution, and a similar situation is proposed to exist within the quenching solvent cage. The electron transfer component of quenching for ion-paired species (k_{ip}) was extracted from k_q by use of the Olson-Simonson treatment; $\Delta H^\ddagger$ (activation enthalpy) and λ (solvent reorganization energy) were evaluated for k_{ip} and back electron transfer within the solvent cage (k_{bt}), and were found to be smallest for ClO_4^- and I^- . The correlation that exists between k_{ip} or k_{bt} and the standard free energy of hydration ($\Delta G_{\text{hyd}}^\circ$) of the anions indicates that the rates of

electron transfer between the cationic reactants are greatest in the presence of anions that have the most weakly-held hydration sphere and the greatest ability to break the water structure. The rate constants of quenching and charge recombination, and the yields of redox products can be fine-tuned through the variation of the supporting electrolyte as well as the variation of temperature and ionic strength.

39. C.D. Clark and M.Z. Hoffman, "Solvent Reorganization Energy in Excited-State Electron-Transfer Reactions. Quenching and Geminate Pair Back Electron Transfer," *J. Phys. Chem.*, **100**, 14688-14693 (1996).

The temperature dependencies of the quenching rate constants (k_q) and cage escape yields of the redox products (η_{ce}) from the electron-transfer reaction of $^*\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) with nine aromatic amines in deaerated 1:1 (v/v) $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solutions have been determined. Values of λ , the solvent reorganization energy for electron transfer quenching and back electron transfer within the solvent cage, have been extracted from plots of $\log(k_q T^{1/2})$ vs. $1/T$ and $\log((\eta_{ce}^{-1} - 1)T^{1/2})$ vs. $1/T$, respectively. For the quenching process, λ is not a constant value for the series of quenchers; in general, higher values of λ are exhibited by primary amines and lower values by tertiary amines. The structure and size of the quenchers, and nature of the ring substituents contribute to the value of λ . For the back electron-transfer reaction within the geminate redox pair formed in the quenching process, the more sterically hindered two-ring amines exhibit a higher value of λ (1.1 ± 0.08 eV) than do the majority of the one-ring amines (0.82 ± 0.04 eV). A Marcus plot of $\log(\eta_{ce}^{-1} - 1)$ vs. ΔG_{bt}^0 shows a correlation within only the inverted region for systems with the same λ ; the earlier identification of the results for the same photosensitizer and quenchers as a bell-shaped curve is due to the coincidental overlap of two independent segments within the inverted region.

40. C.D. Clark and M.Z. Hoffman, "Does Back Electron Transfer Within Geminate Redox Pairs Formed in Bimolecular Quenching Follow a Marcus Bell-Shaped Energy-Gap Dependence?" *J. Photochem. Photobiol. A: Chem.*, **99**, 9-11 (1996).

We conclude that the earlier identification of the results for the $\text{Ru}(\text{bpy})_3^{2+}$ -aromatic amine systems as a bell-shaped curve is due to the coincidental overlap of two independent segments within the inverted region; the earlier analysis of the data was based on the premise that λ for all the quenchers is the same, a situation that clearly is not the case. It is imperative in studies of this type that reaction rates be measured as a function of temperature in order to confirm suspected Marcus behavior. Investigations of the dependence of rate constants of electron transfer on the driving force must include the careful choice of a truly homologous series of reactants, since differences in

the structure and nature of the reactants can result in different values of λ , resulting in data that lie on different Marcus curves.

41. F. Casalboni, Q.G. Mulazzani, C.D. Clark, M.Z. Hoffman, P.L. Orizondo, M.W. Perkovic, and D.P. Rillema, "Acid-Base and Electrochemical Properties of the MLCT Excited States and One-Electron Reduced Forms of Ru(II) Complexes Containing 2-(2'-Pyridyl)pyrimidine and 2,2'-Bipyridine in Aqueous Solution," *Inorg. Chem.*, **36**, 2252-2257 (1997).

The acid-base and electrochemical properties of the MLCT excited states and the one-electron reduced forms of the three $\text{Ru}(\text{bpy})_3\text{-p}(\text{pypm})_p^{2+}$ complexes, where bpy = 2,2'-bipyridine and pypm = 2-(2'-pyridyl)pyrimidine and $p = 1,2,3$, have been examined in aqueous solution; a determination has been made of the ground- and excited state electrochemical potentials, the values of the $\text{p}K_a$ and deprotonation rate constants of the conjugate acids of the excited states and the one-electron reduced complexes, and the kinetics of the second-order decays of the reduced species. Comparison is made with the behavior of the analogous ten complexes of the form $\text{Ru}(\text{bpy})_3\text{-m-z}(\text{bpm})_m(\text{bpz})_z^{2+}$, where bpm = 2,2'-bipyrimidine and bpz = 2,2'-bipyrazine, m and $z = 0,1,2,3$, and $m + z \leq 3$, which have been studied in detail before.

42. C.D. Clark and M.Z. Hoffman, "Effect of Solution Medium on the Rate Constants of Excited-State Electron-Transfer Reactions of Ruthenium(II)-Diimine Photosensitizers," *Coord. Chem. Rev.*, **159**, 359-373 (1997).

In this paper, we review the effects of solution medium (pH, solvent, temperature, ionic strength, specific electrolytes) on the oxidative and reductive quenching rate constants (k_q) of the excited states of Ru(II)-diimine photosensitizers. Diffusion of the donor and acceptor species together to form the precursor complex (k_d) and electron transfer within the complex (k_{et}) contribute to the value of k_q . Values of k_d vary with bulk solution properties; variations of k_{et} can be described within the context of Marcus theory, wherein dynamic solvent effects influence the nuclear frequency factor and electronic coupling, and static properties cause changes in the driving force of electron transfer (ΔG_{et}^0) and the reorganization energy (λ). The pH can affect the state of protonation of the excited photosensitizer and/or the quencher, thereby altering k_{et} through changes in ΔG_{et}^0 and k_d through changes in the charges of the reactants. Ionic species are ion-paired by the dominant counterion; the Olson-Simonson treatment allows the electron transfer components of quenching for ion-paired (k_{ip}) and non ion-paired (k_{nip}) species to be extracted. The quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen is used to demonstrate specific salt effects, which result in variations in λ ; λ is lowest, and k_q highest, for the anions with the most weakly-held hydration

spheres and the strongest structure-breaking abilities (*e.g.*, ClO_4^- , I^-). Quenching rate constants can be fine-tuned through the variation of solvent, pH, electrolyte, ionic strength, and temperature.

43. C. Li, H. Sun, and M.Z. Hoffman, "Ground- and Excited-State Interactions Between Tris(2,2'-bipyridine)ruthenium(2+) Ion and Phenol in Aqueous Solution," *J. Photochem. Photobiol. A: Chem.*, **108**, 129-133 (1997).

Although phenol (PhOH) does not quench $^*\text{Ru}(\text{bpy})_3^{2+}$ due to unfavorable energetics, its presence in aqueous solution results in a blue shift in the emission spectrum and a change in the observed lifetime (τ_{obs}). The effect of temperature (5–70 °C) on τ_{obs} and $[\text{PhOH}]$ (0.1–0.7 M) is complex; at low T, where nonradiative decay is the dominant process, τ_{obs} increases with increasing $[\text{PhOH}]$; at high T the opposite effect is seen, reflecting the dominance of the thermal population of the d-d* excited state. The NMR spectra of both $\text{Ru}(\text{bpy})_3^{2+}$ and PhOH are altered in the presence of each other, indicating the existence of ground-state interactions that are, undoubtedly, hydrophobic or π -stacking in nature. The NOE difference spectra show that the H_{3,5} protons of PhOH couple with the H_{4,4'} and H_{6,6'} protons of $\text{Ru}(\text{bpy})_3^{2+}$, indicating the existence of an offset face-to-face orientation.

44. C.D. Clark, M.Z. Hoffman, D.P. Rillema, and Q.G. Mulazzani, "Photophysics of Ruthenium(II) Complexes with 2-(2'-Pyridyl)pyrimidine and 2,2'-Bipyridine Ligands in Fluid Solution," *J. Photochem. Photobiol. A: Chem.*, **110**, 285-290 (1997).

The photophysics of the three complexes of the form $\text{Ru}(\text{bpy})_{3-p}(\text{pypm})_p^{2+}$ (where bpy = 2,2'-bipyridine, pypm = 2-(2'-pyridyl)pyrimidine, and $p = 1, 2, 3$) were examined in H_2O , propylene carbonate, CH_3CN , and 4:1 (v/v) $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$; comparison was made with the well-known photophysical behavior of $\text{Ru}(\text{bpy})_3^{2+}$. The lifetimes of the luminescent metal-to-ligand charge transfer (MLCT) excited states were determined as a function of temperature (between –103 and 90 °C, depending on the solvent), from which were extracted the rate constants for radiative and nonradiative decays and ΔE , the energy gap between the MLCT and metal centered (MC) excited states. The results indicate that $^*\text{Ru}(\text{bpy})_2(\text{pypm})^{2+}$ decays via a higher-lying MLCT state, and that $^*\text{Ru}(\text{pypm})_3^{2+}$ and $^*\text{Ru}(\text{pypm})_2(\text{bpy})^{2+}$ decay predominantly via the MC state.

45. C.D. Clark and M.Z. Hoffman, "Ion-Pairing Control of Excited-State Electron-Transfer Reactions. Effect of Cations on Cationic Reactants," *J. Photochem. Photobiol. A: Chem.*, **000**, 000-000 (1997).

The rate constants for the oxidative quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} (k_q) and the cage escape yields (η_{ce}) of the redox products ($\text{Ru}(\text{bpy})_3^{3+}$ and $\text{MV}^{\bullet+}$) were determined as a function of added electrolytes (Cl^- salts of Li^+ , Na^+ , Cs^+ , Ca^{2+} , La^{3+}) and temperature (10–60 °C) in aqueous solution. At 25 °C and constant $[\text{Cl}^-]$, k_q is independent of the cation. There is, however, a specific cation effect on η_{ce} ($\text{La}^{3+} > \text{Ca}^{2+} \sim \text{Li}^+ > \text{Na}^+ > \text{Cs}^+$), which is attributed to differences in the rate constants of cage escape (k_{ce}) due to variations in the bulk properties of the solution (viscosity, dielectric constant); the rate constants of back electron transfer within the cage are essentially independent of the nature of the electrolyte cation. The reactant cations are extensively ion-paired by Cl^- in bulk solution and within the quenching solvent cage. However, the electrolyte cations do not have any effect on the rates of electron transfer between the cationic species.

46. C. Li and M.Z. Hoffman, "Electron Localization or Delocalization in the MLCT Excited States of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$. Consequences to Their Photochemistry and Photophysics in Fluid Solution," *Inorg. Chem.*, **37**, 0000–0000 (1998).

Turró *et al.* (*Inorg. Chem.* **1996**, *35*, 5104) proposed that the MLCT excited state of $^*\text{Ru}(\text{phen})_3^{2+}$ is delocalized among the phen ligands, whereas $^*\text{Ru}(\text{bpy})_3^{2+}$ is localized on just one bpy ligand. If this were so, one would expect to observe profound differences in the behavior of the lowest energy, thermally equilibrated excited states, which could be described as $(\text{bpy})_2\text{Ru}^{\text{III}}(\text{bpy}^{\bullet-})^{2+}$ and $\text{Ru}^{\text{III}}(\text{phen}^{(-/3)})_3^{2+}$. The luminescence lifetimes of $^*\text{Ru}(\text{bpy})_3^{2+}$ and $^*\text{Ru}(\text{phen})_3^{2+}$ in H_2O , CH_3CN , and their mixtures, and the rate constants for oxidative and reductive quenching by methylviologen dication and phenolate anion, respectively, in H_2O as functions of temperature have been measured; the behavior of both complexes is very similar. The nature of the localization of the electron in the excited states seems to have no significant effect on the observed photophysics and electron-transfer quenching in fluid solution at or near room temperature.

47. A. Rugge, C.D. Clark, M.Z. Hoffman, and D.P. Rillema, "Protonation of the Ground States of Ruthenium(II) Photosensitizers," *Inorg. Chim. Acta*, in press.

$\text{Ru}(\text{II})$ complexes that possess 2,2'-bipyrazine, 2,2'-bipyrimidine, and 2-(2'-pyridyl)-pyrimidine ligands in combination with 2,2'-bipyridine undergo protonation at the basic nitrogen heteroatoms on the periphery of the aromatic rings as the solution is made more acidic, resulting in absorption spectral changes. In this study, the acidity of the solution was controlled with concentrated H_2SO_4 ; titration curves for the first protonations were obtained from plots of absorbance vs. acidity, from which the $\text{p}K_{a1}$ values for the monoprotonated species were

extracted. As has been observed before for the acid-base properties of the excited states and the one-electron reduced forms of the complexes, the pK_{a1} values of the protonated forms of the ground states (-1.6 to -5.0) correlate with their reduction potentials, and demonstrate site selectivity of the protonation process.

48. C. Li and M.Z. Hoffman, "One-Electron Oxidation Potentials of Phenol and Chlorophenols in Aqueous Solution," *J. Phys. Chem.*, under consideration.

The oxidation peak potentials (E_p) of phenolate and 17 chlorophenolate ions were determined as a function of scan rate, substrate concentration, and pH by cyclic voltammetry in aqueous solution. The one-electron reduction potentials ($E_{red}^0 = -E_{ox}^0$) of the phenoxyl radical/phenolate ion couples were calculated from E_p and the rate constants for dimerization of the phenoxyl radicals. The relationships of E_{ox}^0 with pH and E_{ox}^0 in alkaline solution with the pK_a of the phenol are established.

49. C. Li, M.Z. Hoffman, C. Pizzocaro, G. Mailhot, and M. Bolte, "Ground-State Interactions Between Ruthenium(II)-Diimine Complexes and Phenol and Monochlorophenols in Aqueous Solution," *Inorg. Chem.*, under consideration.

Ground-state interactions between $Ru(bpy)_3^{2+}$ ($bpy = 2,2'$ -bipyridine) or $Ru(bpz)_3^{2+}$ ($bpz = 2,2'$ -bipyrazine) and phenol ($PhOH$) or monochlorophenols ($ClPhOH$) have been investigated in aqueous (D_2O) solution by NMR. The upfield shifts of the resonances and the NOE difference spectra of the complexes in the presence of the phenols indicate the presence of offset face-to-face π -stacking interactions between the phenol and the aromatic ligands. Electron withdrawal from the phenol ring by the monochloro substituent and less effective solvation by aqueous (compared to acetonitrile) media favor the interaction. The formation constant for the 1:1 $Ru(bpy)_3^{2+}$ - $PhOH$ complex is estimated to be $\sim 0.01\ M^{-1}$; K is smaller for $Ru(bpz)_3^{2+}$ than for $Ru(bpy)_3^{2+}$, and increases for both complexes in the order $PhOH < 4-ClPhOH < 3-ClPhOH < 2-ClPhOH$.

50. C. Li and M.Z. Hoffman, "Comment on 'Marcus Inverted Region in the Photoinduced Electron Transfer Reactions of Ruthenium(II)-Polypyridine Complexes with Phenolate Ions'," *J. Phys. Chem. A*, under consideration.

A comparison of values of the rate constants for the reductive quenching of $*Ru(II)$ complexes by phenolate ions in aqueous alkaline solution leads to the conclusion that a recent report (*J. Phys. Chem. A* **1997**, *101*, 8195) cannot be taken as an experimental observation of inverted Marcus behavior in intermolecular charge separation reactions.