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

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Projects Undertaken

Excited state absorption spectrum of $\text{Ru}(\text{bpy})_3^{2+}$. Three pulsed laser techniques were 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 gave 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 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.

Solvent cage model for electron transfer quenching. A re-evaluation of the commonly invoked solvent cage model for electron transfer quenching of the luminescent excited states of $\text{Ru}(\text{II})$ complexes was made on the basis of two sets of experimental results. Firstly, the cage escape yields (η_{ce}) for the reductive quenching of the excited states on an homologous series of $\text{Ru}(\text{II})$ complexes that contain 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2'-bipyrazine ligands by TEOA were 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 $^*\text{Ru}(\text{II})$ 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} were determined as a function of temperature for the oxidative quenching of the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ 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.

Reductive quenching of $^*\text{Cr}(\text{III})$ complexes. The kinetics of reductive quenching of bpy and phen complexes of $\text{Cr}(\text{III})$ (and their substituted analogues) by oxalate ion, EDTA, TEOA, ascorbate ion, and DNA bases were studied by luminescence and laser flash photolysis techniques; in addition, the absorption spectra and reduction potentials of the excited states were determined. The quenching rate constants depended on the ionic strength and pH of the solution and the reducing ability of the quencher. Values of η_{ce} range from 0.6 and 0.3 for quenching by oxalate ion and EDTA, respectively, to <0.001 for TEOA and DNA bases. The dependence of η_{ce} of ΔG° of the back electron transfer reaction between $\text{Cr}(\text{II})$ and the oxidized quencher was very weak. Values of η_{ce} as a function of temperature were determined for the quenching by ascorbate ion; η_{ce} increases with increasing temperature. The approach is to interpret the results in terms of the conventional cage escape model, and to make modifications to the model as necessary. When Fe^{2+} is used as the reductive quencher for $^*\text{Cr}(\text{bpy})_3^{3+}$, η_{ce} varies from 0.2 to 0.9, depending on the concentrations of the species present, especially the nature of the anion. The results are interpreted in terms of ion-pair equilibria and aggregation, and the complexities of the events within the solvent cage.

Solution medium effects in the oxidative quenching of $^*\text{Ru(II)}$ complexes. Values of k_q for the quenching of $^*\text{Ru(bpy)}_3^{2+}$ by MV^{2+} , k_{et} for the electron transfer reaction between Ru(bpy)_3^{2+} and MV^+ , and η_{ce} for the efficiency of generation of the redox pair in bulk solution were determined as a function of ionic strength and the nature of the added electrolyte. Large specific anion dependencies were observed for the rate constants in accord with the Olson-Simonson effect. The rate constants at a constant ionic strength *increase* in the order $\text{H}_2\text{PO}_4^- \sim \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{ClO}_4^-$; values of η_{ce} *decrease* in the same order. Variation of the cation had no effect on the rate constants. The effective charges of the reacting species were calculated by fitting the ionic strength dependencies of the rate constants to the extended Debye-Hückel equation. The results can be interpreted in terms of the orbitals involved in the quenching and electron transfer reactions.

Photosensitized oxidation of phenol in aqueous solution. $^*\text{Cr(bpy)}_3^{3+}$ and $^*\text{Ru(bpz)}_3^{2+}$ are good excited-state oxidants with standard reduction potentials in water of 1.44 V and 1.68 V vs NHE, respectively; $^*\text{Ru(bpy)}_3^{2+}$ is a weaker oxidant with $E^\circ = 0.93$ V. $^*\text{Cr(bpy)}_3^{3+}$ and $^*\text{Ru(bpz)}_3^{2+}$ are quenched by phenol with $k_q = 8.0 \times 10^6$ and 3.7×10^8 ($2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ at pH 11), respectively; $^*\text{Ru(bpy)}_3^{2+}$ is not quenched. The three excited states are quenched by O_2 with k_q values of 1.7×10^7 , 5.1×10^8 , and $3.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively with the formation of $^1\text{O}_2$. The continuous photolysis of air-saturated acidic solutions of Cr(bpy)_3^{3+} and phenol yielded $\text{Cr(bpy)}_2(\text{OH}_2)_2^{3+}$ and 1,4-benzophenone as the only photoproducts, as determined by HPLC; quantum yields were of the order of 10^{-3} and 10^{-4} , respectively. In the absence of air, only the aquation of the photosensitizer was manifest; no Cr(bpy)_3^{2+} was detected in pulsed-laser flash photolysis, indicating that the cage escape yield (η_{ce}) for the electron transfer quenching is < 0.01 . For $^*\text{Ru(bpz)}_3^{2+}$, η_{ce} for the formation of Ru(bpz)_3^+ and the phenoxyl radical is 0.48, and the products of the reaction in the absence of air are hydroxyphenyl dimers. With $^*\text{Ru(bpy)}_3^{2+}$ as the photosensitizer, the only product in the presence of air is 1,4-benzoquinone. We conclude that 1,4-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.

Quenching of Ru(II) complexes by oxygen. The quenching by O_2 of the excited states of Ru(II) complexes that contain 2,2'-bipyridine, 2,2'-bipyrimidine, and 2,2'-bipyrazine ligands was investigated using the techniques of laser flash photolysis, time-resolved and steady-state near-infrared emission spectrophotometry. Values of k_q were determined in H_2O and D_2O , and range between 5.1×10^8 and $3.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The quantum yields (Φ_Δ) of singlet molecular oxygen, $\text{O}_2(^1\Delta_g)$, 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 Ru(bpy)_3^{2+} and ~ 1 for all the other complexes. It was established that for Ru(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 Ru(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 bpz ligand decrease with increasing driving force, indicating that the process is in the Marcus inverted region.

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