Photoinduced Electron Transfer in a Trinuclear Mixed-Valence Chromophore-Quencher Compound

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Introduction

The elaborate energy/electron transfer mechanism which occurs following the absorption of visible light in photosystem II has led to the synthesis of increasingly complex artificial photosynthetic systems which are designed to perform photoinduced vectorial charge transport.[1] Recent studies have focused on supramolecular covalently linked donor−acceptor (CLDA) complexes, in which intramolecular electron transfer occurs following photochemical excitation of the chromophore. Typically, the photoinduced charge-separated state in these supermolecules is detected by time-resolved absorption studies, as back electron transfer is also rapid, particularly due to the fact that the electron donor and acceptor are still covalently linked. To avoid rapid back electron transfer, molecular triads and tetrads have been synthesized, in which the initial photochemically generated charge-separated state is followed by an electron transfer cascade. The larger spatial separation thus achieved decreases the kinetics of electron−hole recombination. Another possible reason for slow back electron transfer in artificial photosynthetic systems is that the thermodynamics of the back electron transfer might lie in the Marcus inverted region.[2] Back electron transfer can also be prevented by the use of a sacrificial donor such as phenothiazine (PTZ), which can be irreversibly oxidized by Re(II)-bpy$^{\bullet-}$ or Ru(III)-bpy$^{\bullet-}$ MLCT excited states.[3] We herein report the synthesis of a trinuclear CLDA complex of the form [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{III}(CN)$_5$]$^+$, where dmb = 4,4′-dimethyl-2,2′-dipyridyl, bpy = 2,2′-bipyridine, and en = ethanediamine. Irradiation of the Re(I) → bpy MLCT band of this complex in the presence of PTZ leads via a series of electron transfer reactions to [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$] and PTZ$^+$. To the best of our knowledge, this compound represents the first electron transfer cascade molecule which utilizes a mixed-valence (MV) compound as the quencher. The stable MV photoproduct is readily detectable because it absorbs light at considerably lower energies than does the unirradiated complex. The proposed photoprocess, however, is also complicated by the presence of competing PTZ $\pi \rightarrow \pi^*$, Ru LF, and CN$^-$ → Fe(III) LMCT absorptions in the same region of the spectrum. The largest competing contribution to the photochemistry originates from photooxidation of PTZ in the presence of Fe(III) to yield the same set of photoproducts.

Experimental Section

Materials. Re(CO)$_5$Cl, K$_3$Fe(CN)$_6$, RuCl$_3$·xH$_2$O, en, anhydrous acetonitrile, and all other reagents were purchased from Aldrich and were used without further purification. [dmbRe(CO)$_3$bpy]PF$_6$ was synthesized by the procedure of Tapolsky[4] and was characterized by NMR spectroscopy. *t*-[Ru(en)$_2$Cl$_2$]Cl was synthesized according to the literature procedure[5] and was characterized by IR and UV/vis spectroscopy.

Synthesis of K$_2$[ClRu^{III}(en)$_2$(μ-CN)Fe^{II}(CN)$_5$]. *t*-[Ru(en)$_2$Cl$_2$]Cl (0.100 g, 0.305 mmol) was suspended in 30 mL of water, reduced with zinc amalgam under an Ar atmosphere, and then filtered into 15 mL of an aqueous solution of K$_3$Fe(CN)$_6$ (0.0998 g, 0.305 mmol). The solution changed color from yellow to green-blue in a matter of minutes, and a blue precipitate developed on standing. The precipitate was collected by vacuum filtration and washed with two 5-mL portions of cold deionized water, followed by two 5-mL portions of diethyl ether. Yield: 0.120 g, 0.219 mmol, 72.0%.

Synthesis of [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$]. *t*-[Ru(en)$_2$Cl$_2$]Cl (0.0660 g, 0.201 mmol) was suspended in 15 mL of water, and [dmbRe(CO)$_3$bpy]PF$_6$ (0.152 g, 0.201 mmol) dissolved in 30 mL of methanol was added with stirring. The mixture was reduced with zinc amalgam under an Ar atmosphere for 15 min, during which time its color changed from pale yellow to red-purple (λ_{max} = 530 nm). This solution was then filtered into 10 mL of an aqueous solution containing K$_3$Fe(CN)$_6$ (0.0663 g, 0.201 mmol). The filtrate slowly darkened in color, and a green precipitate formed. The precipitate was filtered by vacuum and washed with two 5-mL portions of cold deionized water, two 5-mL portions of cold acetone, and an excess of diethyl ether. Yield: 0.161 g, 0.156 mmol, 77.3%.

Synthesis of [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{III}(CN)$_5$]Br. [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$] was suspended in CH$_3$CN and oxidized with an excess of bromine for a period of ~20 min. The excess bromine was then displaced by gently heating the mixture while bubbling argon through it. After evaporation of the solvent, a tan-orange precipitate of the product remained.

Instrumentation and Techniques. Infrared absorption spectra (KBr pellets) were collected as the average of 16 scans by using a Perkin-Elmer 1600 series FTIR with 2-cm^{-1} resolution. Electronic absorption spectra were collected in 1-cm quartz cuvettes at room temperature by using a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrometer with 1-nm resolution. Cyclic voltammograms were collected by using a standard three-electrode configuration and an EG&G PAR model 264A polarographic analyzer/stripping voltammeter. The potentiostat was coupled to a Power Macintosh computer running the LabVIEW program written by National Instruments. A gold button electrode was used as the working electrode, a Pt wire as the counter electrode, and a saturated silver/silver ion electrode (SSE) as the reference electrode. The accuracy of the reference electrode was checked by obtaining the cyclic voltammogram of ferrocene in a 0.1 M TBAH/CH$_3$CN electrolyte solution. Cyclic voltammograms were recorded for each complex in 0.1 M TBAH/CH$_3$CN electrolyte solutions at scan rates ranging from 20 to 500 mV/s.

The photoaction spectrum was collected by using the lamp of a Spex Fluorolog 2 fluorimeter with the excitation monochromator slits removed. Acetonitrile solutions which were 70 μM in [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{III}(CN)$_5$]$^+$ and 7.0 mM in PTZ were irradiated for 45 min at the following wavelengths: 254, 297, 313, 334, 365, 405, 436, 468, 480, 509, 546, and 578 nm. After irradiation, the solutions were quantitatively diluted with acetonitrile so that they were

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Table 1. Selected UV/Vis, IR (KBr Pellet), and Electrochemistry Data for $[dmbRe^{I}(CO)_3\text{-}bpy\text{-}Ru^{III}(en)_2NCFe^{III}(CN)_5]Br$ and Its Mononuclear Components[a]

compound	UV/vis peaks (nm)	selected IR peaks (cm^{-1})	$E_{1/2}$ (V vs SSE)
$[dmbRe^{I}(CO)_3\text{-}bpy{-}Ru^{III}(en)_2NCFe^{III}(CN)_5]Br$	219, 278, 310, 390, 415, 468 (623)[b]	3440,[b] 3239,[b] 2091,[b] 2020,[b] 1885[b]	1.47,[c] 0.40, −0.49, −1.14,[c] −1.32[c]
$[dmbRe^{I}(CO)_3bpy](PF_6)$	246, 306, 318, 340	ν(CO): 2030, 1913	−1.08,[c] −1.34[c]
$t\text{-}[Ru^{III}(en)_2Cl_2]Cl$	272, 296, 343	ν(NH): 3346, 3298, 3239	−0.27[d]
$K_3[Fe^{III}(CN)_6]$	220,[d] 286,[d] 303,[d] 320,[d] 420[d]	ν(CN): 2045[e]	0.16[d]

[a] The solvent is acetonitrile unless otherwise indicated. [b] These peaks are for the form of the complex in which the Fe is reduced. [c] Electrochemically irreversible. [d] Aqueous solution. [e] Bridging cyanide absorptions are generally shifted to higher energies.[15]

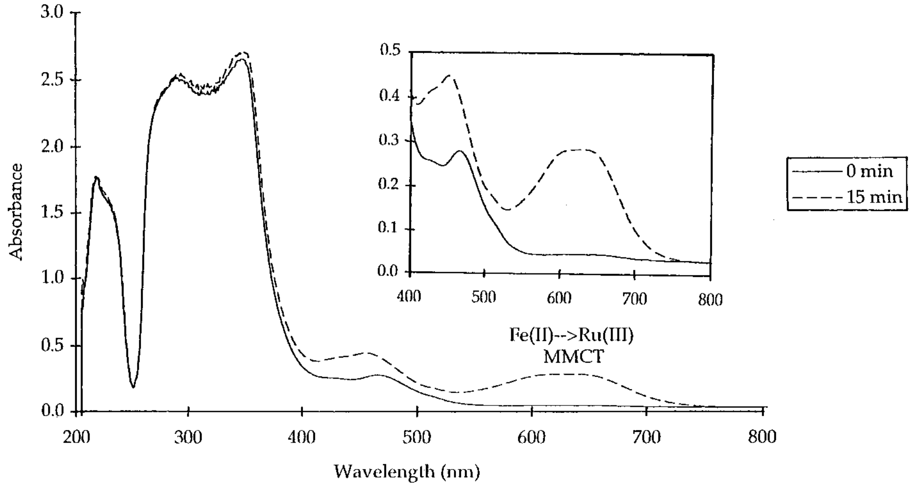

Figure 1. Absorption spectrum of $[dmbRe^{I}(CO)_3\text{-}bpy\text{-}Ru^{III}(en)_2NCFe^{III}(CN)_5]Br$ in acetonitrile with 100 equiv of PTZ before and after irradiation at 390 nm.

optically dilute; and their UV/vis spectra were collected. The molar absorptivity of the photoproduct at 633 nm was determined by irradiating a known concentration of sample until no further changes occurred in the UV/vis spectrum and assuming 100% conversion. The photoaction spectrum was corrected for the lamp intensity by ferrioxalate actinometry according to the literature procedure.[6] The dependence of the quantum efficiencies on the concentration of added PTZ was determined at 457 nm by irradiating 1-mL samples with a Coherent Innova 70 argon ion laser (expanded beam) for 15 min and monitoring the growth of the MMCT band at 633 nm. The incident light intensity was measured with a calibrated Newport Research model 815 power meter using the expanded laser beam.

Results and Discussion

Synthesis and Characterization. The synthesis of $K_2[ClRu^{III}(en)_2(\mu\text{-}CN)Fe^{II}(CN)_5]$ exploits the well-documented lability of $t\text{-}[Ru(en)_2Cl_2]Cl$ when its oxidation state is reduced from +3 to +2. The reduced Ru complex is then capable of undergoing an inner-sphere electron transfer reaction with ferricyanide to form the cyanide-bridged mixed valence complex. The IR spectrum of $K_2[ClRu^{III}(en)_2(\mu\text{-}CN)Fe^{II}(CN)_5]$ contains both NH stretches from the en ligand on Ru at 3412 and 3254 cm^{-1} and a broad CN stretch at 2078 cm^{-1}, indicating that both metals are present in the resulting dinuclear complex. The energy of the cyanide stretch is intermediate between that of ferrocyanide (~2045 cm^{-1}) and other bridging Fe(II) cyano complexes (~2125 cm^{-1}).[7] Bridging and nonbridging Fe(III) CN stretches typically occur at least 50−70 cm^{-1} higher than their Fe(II) counterparts. Therefore, the broad peak at 2078 cm^{-1} in this complex is assigned as a mixture of bridging and nonbridging Fe(II) cyanides, confirming the +2 oxidation state of iron. The UV/vis spectrum of the resulting Ru(III)−Fe(II) mixed-valence compound has only a single new absorption at 971 nm which cannot be attributed to a peak from either of its reactants. On the basis of the oxidation states of the two metals, this band is assigned as a MMCT band from Fe(II) → Ru(III). By comparison, the MMCT band occurs at 975 nm in aqueous solution for $[(NH_3)_5Ru^{III}NCFe^{II}(CN)_5]^{-}$.[8]

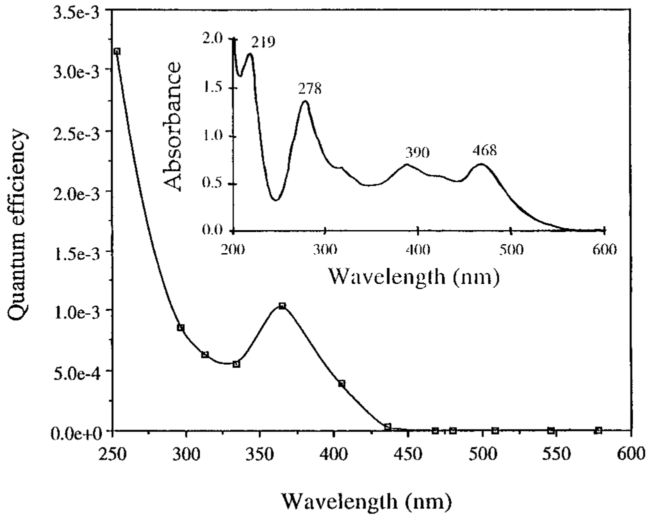

Figure 2. Photoaction spectrum of $[dmbRe^{I}(CO)_3\text{-}bpy\text{-}Ru^{III}(en)_2\text{-}NCFe^{III}(CN)_5]Br$ in acetonitrile with 100 equiv of PTZ. The quantum efficiencies were corrected for the lamp intensity by using ferrioxalate actinometry. The inset shows the UV/vis spectrum of the complex in acetonitrile.

$[dmbRe^{I}(CO)_3(\mu\text{-}bpy)Ru^{III}(en)_2(\mu\text{-}NC)Fe^{II}(CN)_5]$ was synthesized by reducing $t\text{-}[Ru(en)_2Cl_2]Cl$ in the presence of

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(6) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968; pp 208−214.

(7) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1986; pp 272−280.

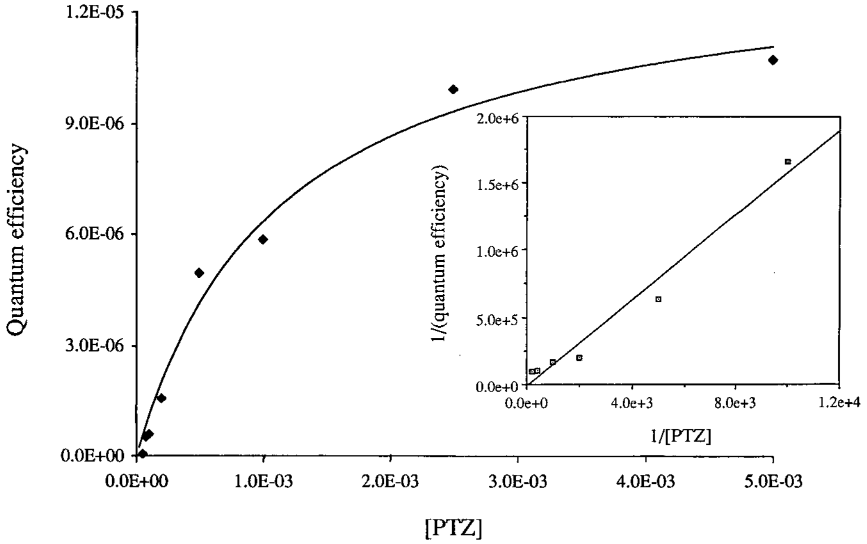
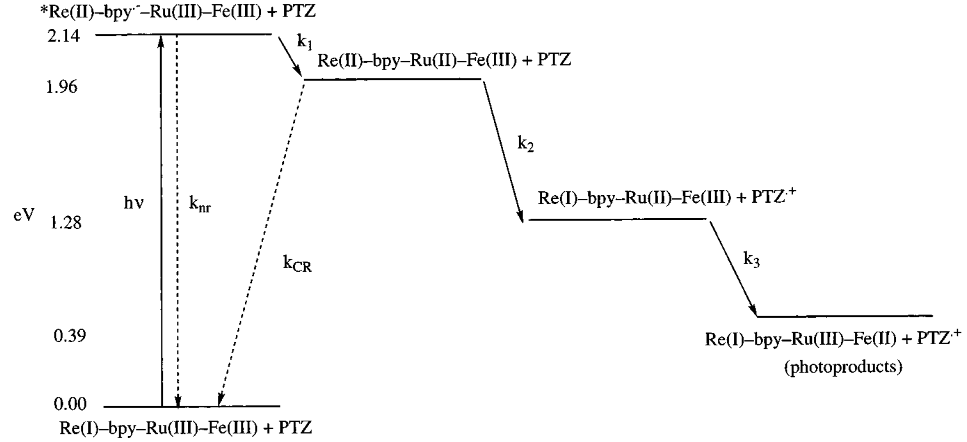


Figure 3. Observed quantum efficiencies at 457 nm for the photolysis of 0.10 mM [dmbRe^{I}(CO)$_3$-bpy-Ru^{III}(en)$_2$NCFe^{III}(CN)$_5$]Br in acetonitrile as a function of added PTZ, along with their fits to a Michaelis–Menten kinetic model. The inset shows the double-reciprocal plot of the data.

Scheme 1



[dmbRe(CO)$_3$bpy]PF$_6$. The chloride ligand on the reduced Ru complex is substituted by the nitrogen lone pairs on the bpy ligand to form a Ru(II)–bpy–Re(I) bridged species. The formation of this bridged intermediate is supported by the UV/vis spectrum of the reacting mixture, which contains a new peak at ~530 nm (not present in either of the initial reagents). This peak is assigned as MLCT from Ru(II) → bpy by analogy to the 510-nm MLCT band in [Ru(NH$_3$)$_5$bpy]$^{2+}$ measured in 2:1 (v:v) CH$_3$OH/H$_2$O solution. The Ru(II)–bpy–Re(I) complex is then rapidly combined with ferricyanide in an inner-sphere electron transfer reaction analogous to the one above for K$_2$[ClRu^{III}(en)$_2$(μ-CN)Fe^{II}(CN)$_5$] to yield the mixed-valence product [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$]. The IR spectrum of this complex supports the presence of all three metal centers with NH stretches at 3440 and 3239 cm^{-1}, a CN stretch at 2091 cm^{-1}, and CO stretches at 2020 and 1885 cm^{-1} (Table 1). The energy of the broad CN stretch supports its assignment as a mixture of bridging and nonbridging Fe(II) cyanide stretches, confirming the +2 oxidation state of iron. The UV/vis spectrum of [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$] contains a new low-energy absorption at 623 nm, which is assigned as MMCT from Fe(II) → Ru(III). The absence of this band in the oxidized complex, [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{III}(CN)$_5$]Br, supports its assignment as MMCT. The UV/vis spectrum of [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$] also contains a new absorption at 435 nm, which is tentatively assigned as bpy → Ru(III) LMCT since it is present in both this and the oxidized trinuclear complex, but is absent in K$_2$[ClRu^{III}(en)$_2$(μ-CN)Fe^{II}(CN)$_5$].

The [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{II}(CN)$_5$] complex exhibits irreversible reduction peaks at −1.32 and −1.14 V vs SSE which are assigned as reduction of dmb and bpy, respectively, to radical anions, by analogy to the reductions at −1.34 and −1.08 V for [dmbRe(CO)$_3$bpy]PF$_6$.[4] Two quasireversible peaks are also observed in the acetonitrile CV of the trinuclear complex, one occurring at −0.49 V vs SSE and assigned to the Ru$^{III/II}$ couple (−0.27 V in aqueous solution for *t*-[Ru(en)$_2$Cl$_2$]Cl) and another at +0.40 V vs SSE and assigned to the Fe$^{III/II}$ couple (+0.16 V in aqueous solution for K$_3$Fe(CN)$_6$). An irreversible oxidation wave at +1.47 V vs SSE was observed and is attributed to the Re$^{I/II}$ couple. The cyclic voltammetric data further support the presence of all three metal centers in the complex.

Photochemistry. When a 70 μM acetonitrile solution of [dmbRe^{I}(CO)$_3$(μ-bpy)Ru^{III}(en)$_2$(μ-NC)Fe^{III}(CN)$_5$]Br is irradiated for several hours by a xenon lamp with no filters in place, no major changes in the UV/vis spectrum occur. However, if the same complex is irradiated in the presence of a 7.0 mM PTZ

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solution, a broad absorption centered at 633 nm gradually grows in with time (Figure 1) and the solution changes from a pale yellow to a dark green color. The photoaction spectrum for the production of this photoproduct is shown in Figure 2. It consists of two peaks at ~250 and ~365 nm, with quantum efficiencies of 3.2×10^{-3} and 1.0×10^{-3}, respectively. The latter peak corresponds to the energy of the Re(I) → bpy MLCT absorption at 390 nm in the UV/vis spectrum of $[\mathrm{dmbRe^{I}(CO)_3}$-$(\mu$-bpy$)\mathrm{Ru^{III}(en)_2}(\mu$-NC$)\mathrm{Fe^{III}(CN)_5}]$Br (Figure 2, inset), although Ru LF and $\mathrm{CN^-}$ → Fe(III) LMCT absorptions also occur in this region.

We attempt to explain the observed photochemistry of the Re(I)−bpy−Ru(III)−Fe(III) complex in the presence of PTZ by using the potential energy diagram proposed in Scheme 1. Photoexcitation into the Re(I) → bpy MLCT band at ~365 nm produces an excited state which is ~2.14 eV above the ground state, as estimated by the emission energy of $[\mathrm{dmbRe(CO)_3bpy}]\mathrm{PF_6}$ in acetonitrile. The Re(I) → bpy and Re(I) → dmb MLCT transition energies are very similar in the model compound and are both temperature- and solvent-dependent, with the Re(I) → bpy excited state 0.2 eV lower in energy at room temperature in acetonitrile solution.[4b] Since the bpy ligand is bridged in the trinuclear complex, it is unclear whether the Re(I)→bpy or Re(I)→dmb excited state is actually lower in energy. Nevertheless, the emission of this MLCT band is completely quenched in the trinuclear complex, presumably by an intramolecular oxidative electron transfer to Ru(III), indicating that k_1 is faster than $2.9 \times 10^{6}\ \mathrm{s^{-1}}$ (the reciprocal of the radiative lifetime reported for $[\mathrm{dmbRe(CO)_3bpy}]\mathrm{PF_6}$ in acetonitrile).[4] The energy at which the Re(II)−bpy−Ru(II)−Fe(III) + PTZ intermediate lies below the initial excited state is calculated from the difference in the excited state oxidation potential and $E°$ for the Ru component. Once the excited electron in Re(II)−bpy−Ru(II)−Fe(III) has reached this point, charge recombination (k_{CR}) can occur to re-form the ground state of the triad or a second intramolecular electron transfer, k_{f} (from Ru(II) to Fe(III)), can take place. In the absence of PTZ, $k_{\mathrm{CR}} > k_{\mathrm{f}}$ since the Re(I)−bpy−Ru(III)−Fe(II) MV photoproduct is not observed. However, in the presence of added PTZ, the PTZ can be irreversibly oxidized by Re(II) with rate constant k_2 to yield a Re(I)−bpy−Ru(II)−Fe(III) + $\mathrm{PTZ^{\bullet +}}$ intermediate, which is lower in energy (based on the difference in oxidation potentials between $\mathrm{Re^{I/II}}$, 1.47 V, and $\mathrm{PTZ^{0/+}}$, 0.79 V). Charge recombination is thereby prevented, and the electron transfers from Ru(II) to Fe(III) with rate constant k_3 to yield the final photoproducts. Supporting this mechanism was the observation of the $\mathrm{PTZ^{\bullet +}}$ radical cation ($\lambda_{\max} = 514$ nm) in several of the photolysis solutions before it underwent subsequent decomposition.[9]

The quantum efficiency of the 365-nm peak in the photoaction spectrum is dependent on the concentration of PTZ present, indicating that the bimolecular step in the photolysis mechanism, k_2, is rate-determining over the concentration range studied (0.05−5.00 mM). A determination of the exact magnitude of this rate constant was complicated by the fact that other transitions occur in the same region of the electronic spectrum. Phenothiazine itself absorbs to a significant extent at 365 nm in high concentrations. Photooxidation of PTZ in the presence of an electron acceptor such as Fe(III) has been shown to occur.[10] Ligand field excitation of t-$[\mathrm{Ru(en)_2X_2}]^+$ complexes at ~340 nm have also been shown to undergo photochemistry, with halide aquation and stereochemical change.[11] Furthermore, $\mathrm{CN^-}$→Fe(III) LMCT transitions in $\mathrm{K_3[Fe(CN)_6}$ absorb near this region of the electronic spectrum,[12] and the possibility of LMCT photochemistry leading to the formation of an iron(II) adduct must also be considered.[13]

To determine the possible contributions of these other processes to the formation of the photoproduct, the photochemistry of $\mathrm{K[ClRu^{III}(en)_2}(\mu$-NC$)\mathrm{Fe^{III}(CN)_5}]$ in both the absence and the presence of 100 equiv of PTZ was investigated. In the absence of added PTZ, the absorption spectrum was changed by less than 2% even after broad band irradiation by a xenon lamp for 4 h. Furthermore, there was no evidence for the formation of the Ru(III)−Fe(II) mixed-valence product. This would suggest that direct Ru LF and Fe LMCT photochemical processes are not contributing significantly to the observed photochemistry. In the presence of 100 equiv of PTZ, however, the photoaction spectrum has a peak at ~250 nm with a quantum efficiency of 1.5×10^{-3} for the production of the Ru(III)−Fe(II) + $\mathrm{PTZ^{\bullet +}}$ photoproducts, with a smaller broad shoulder at lower energies. This shoulder approaches 0 only at wavelengths longer than 450 nm. The quantum efficiency of this shoulder, when measured at 365 nm, is 6.5×10^{-4}. Just how much the quantum efficiencies for the dinuclear and trinuclear compounds can be correlated is debatable, but it is clear that a direct photoprocess involving PTZ and Fe(III) is also contributing to the formation of the observed photoproducts.

As mentioned above, the concentration of PTZ is critical to the kinetics of the observed photochemistry. Figure 3 shows the dependence of the quantum efficiency for formation of the photoproducts as a function of PTZ concentration, when measured at 457 nm using an argon ion laser as the irradiation source. This wavelength was chosen so as to minimize contributions from processes other than the Re(I)→bpy MLCT induced electron transfer cascade. As shown by the inset in Figure 3, these data can be fitted to a Michaelis−Menten kinetic scheme[14] in which the photochemically generated intermediate is in equilibrium with PTZ to form an activated complex, which then undergoes subsequent electron transfer to yield products. The maximum quantum efficiency at 457 nm was calculated as 1.4×10^{-5}, and the Michaelis constant, k_{M}, was determined to be 1.2×10^{-3}.

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