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Photodynamics of the Tris(2,2′-bipyrazine)ruthenium(2+)/Methylviologen/EDTA System in Aqueous Solution

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

The most popular and best-studied model system for the photosensitized reduction of water has been the one containing $\mathrm{Ru(bpy)_3^{2+}}$ (bpy = 2,2′-bipyridine) as the photosensitizier, methylviologen (1,1′-dimethyl-4,4′-bipyridinium dication; $\mathrm{MV^{2+}}$) as the electron relay, and EDTA or triethanolamine (TEOA) as the sacrificial electron donor.[1] The oxidative quenching of $\mathrm{{*}Ru(bpy)_3^{2+}}$ by $\mathrm{MV^{2+}}$ yields the methylviologen radical cation ($\mathrm{MV^{+}\cdot}$) which can interact with colloidal metal redox catalysts to generate $\mathrm{H_2}$. The role of the sacrificial donor is to scavenge $\mathrm{Ru(bpy)_3^{3+}}$ before annihilation of $\mathrm{MV^{+}\cdot}$ occurs via back electron transfer; oxidation of the donor results in its irreversible degradation.[2] In the case of EDTA, the oxidized amine radical species ($\mathrm{EDTA_{ox}^{+}}$) undergoes irreversible transformation, resulting in the formation of a carbon-centered reducing radical (EDTA′); the interaction of EDTA′ with $\mathrm{MV^{2+}}$ results in the formation of a second equivalent of $\mathrm{MV^{+}\cdot}$.[3] The ability of EDTA to act as a reducing agent toward $\mathrm{Ru(bpy)_3^{3+}}$, the transformation of $\mathrm{EDTA_{ox}^{+}}$ to EDTA′, and the stability of the radicals toward degradative processes (e.g., decarboxylation) are pH-dependent; however, the system is virtually free of complexities in neutral and alkaline solution. As a result, the quantum yield of $\mathrm{MV^{+}\cdot}$ formation ($\Phi(\mathrm{MV^{+}\cdot})$) is a plateau under those conditions and falls off strongly in acidic solution; the dependence of $\Phi(\mathrm{MV^{+}\cdot})$ on $[\mathrm{MV^{2+}}]$ is predictable on the basis of the competition between the quenching of $\mathrm{{*}Ru(bpy)_3^{2+}}$ and its natural decay.[4-6] The ion pairing of EDTA with the cationic species in solution[7-10] results in a dependence of $\Phi(\mathrm{MV^{+}\cdot})$ on [EDTA] and $[\mathrm{Ru(bpy)_3^{2+}}]$ in alkaline solution.[4-6] Despite the ion-pairing interaction of EDTA and $\mathrm{Ru(bpy)_3^{2+}}$, there is no evidence for the reductive quenching of $\mathrm{{*}Ru(bpy)_3^{2+}}$ by EDTA.

In an attempt to improve the performance of the photosensitization system with regard to the quantum yield of the high-energy redox products, many new Ru(II) photocatalysts have been introduced that possess substituted poly(pyridine) or other nitrogen heterocyclic ligands. One such complex, which has been regarded as superior to $\mathrm{Ru(bpy)_3^{2+}}$ for the photoproduction of $\mathrm{MV^{+}\cdot}$,[11] is $\mathrm{Ru(bpz)_3^{2+}}$ (bpz = 2,2′-bipyrazine). The reduction potentials of $\mathrm{Ru(bpz)_3^{2+}}$ and $\mathrm{Ru(bpz)_3^{3+}}$ (−0.68 and 1.98 V, respectively) are more than 0.5 V more positive than those of $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{Ru(bpy)_3^{3+}}$.[11-14] As a result, $\mathrm{{*}Ru(bpz)_3^{2+}}$ is a stronger oxidant ($E° = 1.40$ V), but a poorer reductant ($E° = -0.10$ V), than is $\mathrm{{*}Ru(bpy)_3^{2+}}$. Unlike $\mathrm{{*}Ru(bpy)_3^{2+}}$, $\mathrm{{*}Ru(bpz)_3^{2+}}$ is reductively quenched by TEOA and EDTA[11,15-17] but is not oxidatively quenched by $\mathrm{MV^{2+}}$; the resulting $\mathrm{Ru(bpz)_3^{+}}$ would be expected to reduce $\mathrm{MV^{2+}}$ ($E° = -0.44$ V). The absorption and emission spectra of $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{Ru(bpz)_3^{2+}}$ are virtually the same; the reported lifetime of $\mathrm{{*}Ru(bpz)_3^{2+}}$ is 0.75–1.04 μs, depending on the solution medium.[11-19] Because each coordinated bpz ligand can be protonated at two nitrogen sites, the ground and excited states of the complex exhibit acid–base behavior. The first and second pK_a's and pK_a*'s of the complex occur at −2.2 and −3.0 and 2.0 (3.8 calcd) and −2.4, respectively.[18] As a result, in alkaline and neutral solution, the ground and excited states exist in their deprotonated form; in acidic solution, the ground state is deprotonated but the excited state can be protonated. Single protonation shortens the lifetime of the excited state to 50 ns, diminishes its capacity to act as an oxidant or a reductant, and, as a result, lowers its quenching rate constants.[19]

Indeed, the reported values of $\Phi(\mathrm{MV^{+}\cdot})$ for $\mathrm{Ru(bpz)_3^{2+}}$ are higher than those for $\mathrm{Ru(bpy)_3^{2+}}$ under similar photochemical conditions. Crutchley and Lever,[11] using TEOA as the quencher, obtained a value of 0.77 for $\mathrm{Ru(bpz)_3^{2+}}$ compared to 0.19 for $\mathrm{Ru(bpy)_3^{2+}}$; Kitamura et al.[16] reported values of 0.98 and 0.22, respectively, for essentially the same conditions. Dürr et al.[15]

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determined the quantum yields of H_2 formation (expressed as $\Phi(^1/_2H_2)$) for EDTA as the quencher in the presence of colloidal Pt catalyst at pH 5; they were 0.243 and 0.085 for Ru(bpz)$_3^{2+}$ and Ru(bpy)$_3^{2+}$, respectively. Recently, we determined $\Phi(MV^{+}\cdot)$ for the Ru(bpz)$_3^{2+}$/MV^{2+}/EDTA system as a function of pH.[20] The value of 1.4 for $\Phi_0(MV^{+}\cdot)$, the limiting quantum yield at infinite quencher concentration, that was obtained in neutral and alkaline solutions (pH 6–11) is the highest yet reported for a photochemical system consisting of a Ru(II)–poly(pyridyl) complex, viologen electron relay, and sacrificial electron donor; however, at pH < 6, the value of $\Phi(MV^{+}\cdot)$ decreases dramatically with decreasing pH. We concluded that compared to Ru(bpy)$_3^{2+}$, Ru(bpz)$_3^{2+}$ is a superior photosensitizer because its excited state favors reductive quenching by sacrificial electron donors, the oxidized forms of which can undergo rapid irreversible transformation within the solvent cage, resulting in large values of the cage release yield of redox products.

The Ru(bpz)$_3^{2+}$/MV^{2+}/EDTA photochemical system and its reductive quenching mechanism are of potential importance to the development of further models for the photochemical storage of radiant energy. In this paper, the examination of the photodynamics of the system through the use of luminescence quenching and flash photolysis (pulsed laser and conventional) techniques is described.

Experimental Section

Materials. Methylviologen dichloride (B.D.H.) was recrystallized several times from methanol and dried at 70 °C under vacuum for more than 24 h. Na$_2$EDTA and Na$_2$SO$_4$ (Baker Analyzed Reagent) were used without further purification. Ru(bpz)$_3^{2+}$, as the Cl$^-$ salt, was obtained from Prof. A. B. P. Lever; it was recrystallized by dissolution in water, precipitated by the addition of a 1:2 ethanol:propanol mixture, and vacuum-dried at 40 °C. [Ru(bpz)$_3$](PF$_6$)$_2$ was prepared by the method of Rillema et al.;[14] both samples exhibited the same behavior. Distilled water was further purified by passage through a Millipore purification train.

Apparatus. Luminescence quenching measurements were made by using a Perkin-Elmer MPF-2A spectrofluorimeter set at 440 nm for excitation and 603 nm for emission. Excited-state lifetime measurements were made by using a Nd:YAG pulsed laser system with excitation at 355 nm; the right-angle emission was focused onto the entrance slit of an Instruments SA H-20 monochromator set at 603 nm. The output of the RCA 4840 photomultiplier from 50 8-ns laser pulses was averaged by using a Kinetic Systems CAMAC crate and associated PDP-11/23 computer.[21] Laser flash photolysis experiments were performed at the Center for Fast Kinetics Research (CFKR), University of Texas, Austin; 12-ns pulses at 355 nm were provided by a Nd:YAG Q-switched laser. Conventional flash photolysis was used to probe slower kinetics. Continuous photolyses were performed by using a Bausch & Lomb high-intensity monochromator in conjunction with a 200-W super-pressure Hg lamp.

Procedures. Solutions for the excited-state lifetime measurements, conventional flash photolysis experiments, and continuous photolyses were contained in a 1-cm cuvette provided with a Teflon stopcock; the solutions could be deaerated before excitation with a stream of Ar. Luminescence quenching measurements were performed using air-equilibrated solutions contained in 1-cm cuvettes. Solutions for laser flash photolysis were contained in a 1 × 0.5 cm cuvette, excited along the larger dimension and probed by the analyzing light along the smaller one. They were deaerated and continuously mixed with a stream of N$_2$ and could also be saturated with O$_2$.

Results

Ru(bpz)$_3^{2+}$. The absorption and emission spectra of the complex in water were identical with those reported by Lever;[18] the lifetimes of the unquenched emission in deaerated (τ_0) and air-saturated solutions (τ_0^{air}) containing 50 μM Ru(bpz)$_3^{2+}$ and 0.33 M Na$_2$SO$_4$ at natural pH were 0.82 and 0.60 μs, respectively.

Solutions containing 50 μM Ru(bpz)$_3^{2+}$ in the absence of MV^{2+} and EDTA showed long-term thermal and photochemical stabilizies. The absorption spectrum of the complex did not change over a period of 3 h at pH 6.0, 9.0, and 11.0; the continuous irradiation (λ_{exc} = 440 nm; $I_a = 3 \times 10^{-6}$ einstein min^{-1}) of deaerated solutions at pH 4.7 (containing 0.33 M Na$_2$SO$_4$), 8.7, and 11.0 for 2 h also resulted in no spectral change.

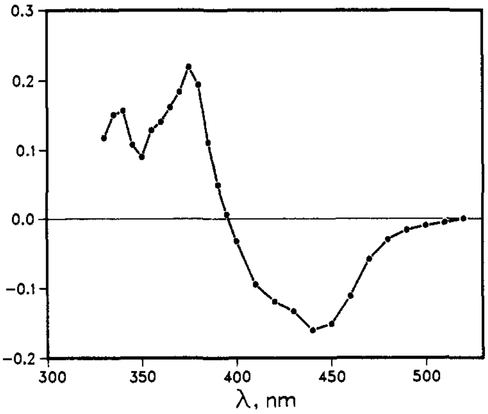

Figure 1. Instantaneous spectral changes resulting from the 355-nm laser flash photolysis of N$_2$-purged solutions containing 50 μM Ru(bpz)$_3^{2+}$ at natural pH.

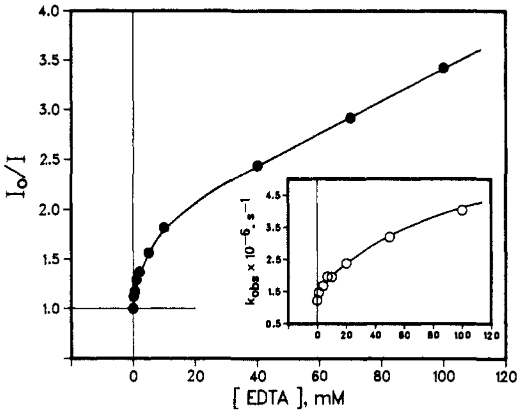

Figure 2. Plot of I_0/I and k_{obsd} for the luminescence intensity and lifetime quenching of *Ru(bpz)$_3^{2+}$ by EDTA at pH 4.7. Measurements of I (●) and k_{obsd} (○) were made with air-saturated and deaerated solutions, respectively, containing 50 μM Ru(bpz)$_3^{2+}$; ionic strength = 1.0 M (Na$_2$SO$_4$).

The laser flash photolysis of a deaerated solution containing 50 μM Ru(bpz)$_3^{2+}$ at natural pH results in transient absorption at λ < 395 nm and transient bleaching at λ > 395 nm. The difference spectrum, obtained from an extrapolation of the first-order kinetic decay to $t = 0$, is shown in Figure 1. This transient spectrum, monitored at 375 and 440 nm, decays completely with a lifetime of 0.89 μs.

Ru(bpz)$_3^{2+}$/EDTA. The emission from and the lifetime of *Ru(bpz)$_3^{2+}$ are quenched by EDTA. At pH 8.7 and 11.0, plots of both I_0/I and τ_0/τ as a function of [EDTA] (0.10 mM–0.10 M) are linear and yield values of the quenching rate constants (k_q) at a constant ionic strength (1.0 M with Na$_2$SO$_4$) of 6.9 × 10^8 and 7.7 × 10^8 M^{-1} s^{-1}, respectively. However, the plot of I_0/I and k_{obsd} vs. [EDTA] at pH 4.7 is not linear (Figure 2). No quenching of the emission from *Ru(bpz)$_3^{2+}$ by 0.020 M MV^{2+} in the absence of EDTA was observed.

At pH 8.7 and 11.0, the laser flash photolysis of deaerated solutions containing 50 μM Ru(bpz)$_3^{2+}$ and EDTA (0.010–0.50 M) results in the immediate formation of absorption maxima at 360 and 490 nm and bleaching at 400–460 nm (Figure 3). In the course of the next several hundred microseconds, this difference spectrum continues to grow. At pH 11.0, the secondary growth represents 40–50% of the total absorption or bleaching, while at pH 8.7 the fraction is 30–40%, with the larger fraction observed at lower laser intensities; the extent of secondary growth is independent of [EDTA]. The kinetics of this secondary formation are complex, being incapable of resolution into simple first- or second-order behavior. A pH- and [EDTA]-independent first-

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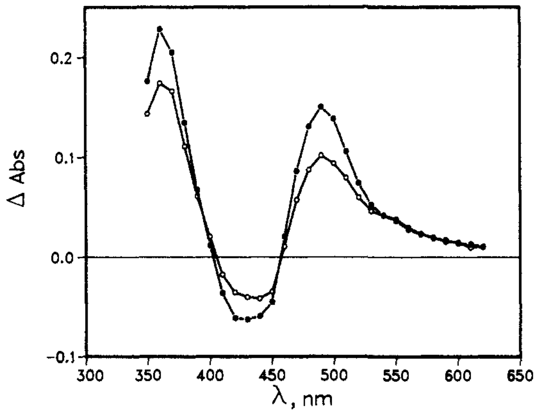

Figure 3. Spectral changes resulting from the 355-nm laser flash photolysis of N_2-purged solutions containing 50 μM $Ru(bpz)_3^{2+}$ and 0.10 M EDTA at pH 11.0. Time after the flash: 5.0 μs (○), 0.67 ms (●).

Table I. Kinetics Parameters from the 355-nm Laser Flash Photolysis of the $Ru(bpz)_3^{2+}$/EDTA System at pH 4.7[a]

	k (s^{-1})[b] at [EDTA] (M)		
	0.010	0.050	0.10
decay of emission at 600 nm			
N_2-purged	2.3×10^6	3.9×10^6	5.1×10^6
O_2-saturated	3.1×10^6		
decay of $^*Ru(bpz)_3^{2+}$ at 375 nm			
N_2-purged		4.0×10^6	4.5×10^6
formation of 490-nm absorption			
N_2-purged	2.3×10^6	3.8×10^6	5.0×10^6
O_2-saturated	3.1×10^6	4.3×10^6	5.0×10^6
spectral changes (N_2-purged)			
390 nm	1.2×10^4	9.0×10^3	8.7×10^3
430 nm	1.3×10^4	9.7×10^3	8.1×10^3
spectral changes (O_2-saturated)			
490 nm	1.8×10^4	1.5×10^4	1.5×10^4
430 nm			1.5×10^4

[a] $[Ru(bpz)_3^{2+}]$ = 50 μM. [b] Computer-averaged from 4–10 individual shots.

order component during the latter stages of the reaction can be resolved with $k \sim 2 \times 10^4$ s^{-1}. In the presence of O_2, the initial transient spectrum is quenched via clean first-order kinetics with $k = 7.6 \times 10^5$ s^{-1}; only a very small permanent change in the base line at 360, 430, and 490 nm is observed.

The system is more complex at pH 4.7 when monitored by laser flash photolysis. In the first place, the quenching of $^*Ru(bpz)_3^{2+}$ by EDTA is significantly slower than in alkaline solution. As a result, emission from $^*Ru(bpz)_3^{2+}$ is detected at 600 nm, and the initial transient absorption also seen in the absence of EDTA is observed; these decay via clean first-order kinetics in deaerated solution with rate constants that change only slightly with a 10-fold variation in [EDTA] (Table I). Within that time frame, essentially the same spectrum as observed in alkaline solution grows in, but with an absorbance approximately 3 times less intense; over the course of the next several hundred microseconds, it transforms slightly into a new spectrum (Figure 4) via first-order kinetics. In the presence of O_2, the difference spectrum after the decay of $^*Ru(bpz)_3^{2+}$ is virtually the same as in N_2-purged solutions; this transient decays with significant absorbance change (Figure 5) via first-order kinetics (Table I).

Deaerated $Ru(bpz)_3^{2+}$/EDTA solutions are photosensitive at pH 4.7, 8.7, and 11.0. Continuous photolysis at 440 nm results in the development of a new absorption band at 420 nm with increased tail absorptions at <380 nm and >450 nm and the diminution of the 440-nm band of $Ru(bpz)_3^{2+}$; the spectral changes appear to be the same at all pHs. When a deaerated solution containing 32 μM $Ru(bpz)_3^{2+}$ and 0.10 M EDTA at pH 4.7 is flashed once through a Pyrex filter, the absorption spectrum of the solution changes as shown in Figure 6. Time resolution of the changes at 500 nm reveals that the formation of a strong absorbance at that wavelength occurs during the time of the flash; the subsequent diminution of the absorbance occurs slowly in the 1–2-min time frame. Further flashing of the solution causes the tail absorption in the UV–vis to grow, with the almost total elimination of discernible visible bands.

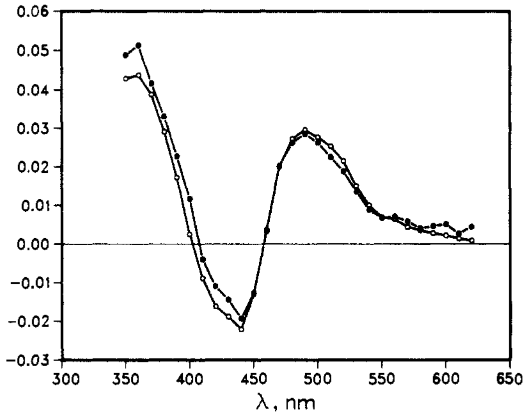

Figure 4. Spectral changes resulting from 355-nm laser flash photolysis of N_2-purged solutions containing 50 μM $Ru(bpz)_3^{2+}$ and 0.10 M EDTA at pH 4.7. Time after the flash: 5.0 μs (○), 0.67 ms (●).

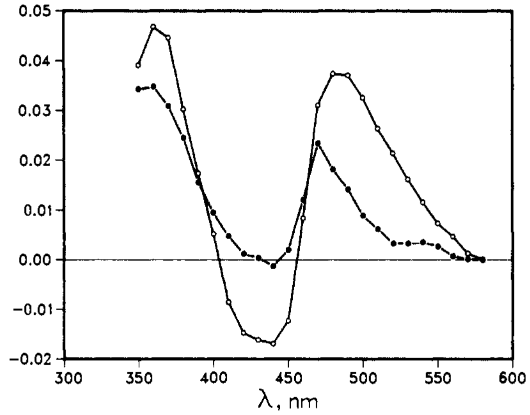

Figure 5. Spectral changes resulting from the 355-nm laser flash photolysis of O_2-saturated solutions containing 50 μM $Ru(bpz)_3^{2+}$ and 0.10 M EDTA at pH 4.7. Time after the flash: 5.0 μs (○), 0.67 ms (●).

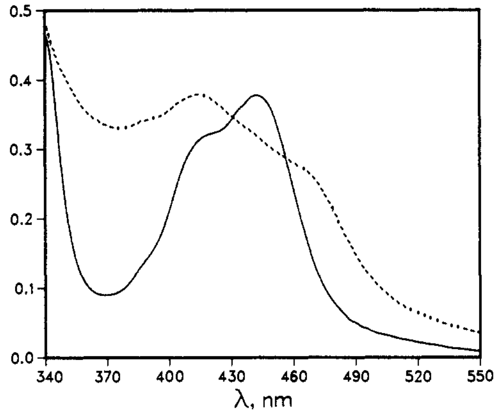

Figure 6. Spectral changes resulting from the conventional flash photolysis of deaerated solutions containing 32 μM $Ru(bpz)_3^{2+}$ and 0.10 M EDTA at pH 4.7: (—) before the flash; (---) after the flash.

$Ru(bpz)_3^{2+}$/MV^{2+}/EDTA. The laser flash photolysis of deaerated solutions yields the same initial spectrum as observed in the absence of MV^{2+} (Figure 3); the formation is within the time resolution of the instrumentation at pH 8.7 and 11.0 in 0.10 M EDTA but occurs with a rate constant of 4.0×10^6 s^{-1} at pH 4.7 in 0.070 M EDTA. At pH 8.7 and 11.0, the absorption band at 490 nm decays via a single $[MV^{2+}]$-dependent first-order process; bands at 395 and 605 nm, representing $MV^{+\cdot}$,[22] form via two $[MV^{2+}]$-dependent first-order components (Table II). At pH 11.0, the faster component (k_1) represents 50% of the total

Table II. Kinetics Parameters from the 355-nm Laser Flash Photolysis of the Ru(bpz)$_3^{2+}$/MV^{2+}/EDTA System[a]

pH	[EDTA], M	[MV^{2+}], mM	λ_{mon}, nm	$k_{\rm I}$, s^{-1}	$k_{\rm II}$, s^{-1}
11.0	0.10	0.50	395	8.5×10^5	1.7×10^5
			605	8.8×10^5	1.6×10^5
			490[b]		1.6×10^5
		1.0	395	1.7×10^6	3.6×10^5
			605	1.7×10^6	3.6×10^5
			490[b]		3.7×10^5
		5.0	395	*c*	2.6×10^6
			605	*c*	2.5×10^6
			490[b]		2.1×10^6
8.7	0.10	0.50	395	7.4×10^5	1.7×10^5
			605	7.4×10^5	1.8×10^5
			490[b]		1.6×10^5
		1.0	395	1.3×10^6	3.2×10^5
			605	1.2×10^6	3.8×10^5
			490[b]		3.6×10^5
		5.0	395	*c*	2.6×10^6
			605	*c*	2.6×10^6
			490[b]		2.3×10^6
4.7[d]	0.070	0.50	395	6.5×10^2	
			605	5.3×10^2	
		1.0	395	1.1×10^3	
			605	1.1×10^3	
		5.0	395	3.4×10^3	
			605	3.3×10^3	

[a] Computer-averaged from 4–10 individual shots. [b] One first-order process; $k_{\rm II}$. [c] Too fast to be resolved. [d] One first-order process; $k_{\rm I}$.

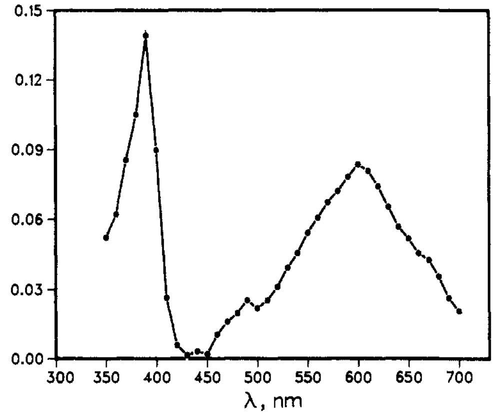

Figure 7. Spectral changes resulting from the 355-nm laser flash photolysis of N$_2$-purged solutions containing 50 μM Ru(bpz)$_3^{2+}$, 5.0 mM MV^{2+}, and 0.10 M EDTA at pH 4.7. Time after the flash = 6.7 ms.

absorption, independent of [MV^{2+}] (0.50–5.0 mM); at pH 8.7, the fraction is 37%, 44%, and 50% at [MV^{2+}] = 0.50, 1.0, and 5.0 mV, respectively. At pH 4.7, MV$^{+}\cdot$ forms slowly via a single [MV^{2+}]-dependent first-order process (Table II); the initial absorption band at 490 nm exhibits virtually no change (Figure 7). The final yield of MV$^{+}\cdot$ at pH 4.7 is approximately 20% of that in alkaline solution.

Discussion

Excitation of Ru(bpz)$_3^{2+}$. The absorption band of Ru(bpz)$_3^{2+}$ centered around 400 nm has been assigned,[11] by analogy to Ru(bpy)$_3^{2+}$, as belonging to a d$\pi \rightarrow \pi^*$ charge-transfer transition (reaction 1); in simplest terms, *Ru(bpz)$_3^{2+}$ can be visualized as

$$\mathrm{Ru(bpz)_3^{2+}} \xrightarrow{h\nu} \mathrm{{}^*Ru(bpz)_3^{2+}} \qquad (1)$$

possessing a one-electron-reduced ligand radical coordinated to the Ru(III) center: *[Ru$^{\rm III}$(bpz)$_2$(bpz$^-\cdot$)]$^{2+}$. The differential absorption spectrum obtained immediately after the laser pulse (Figure 1) is virtually identical with that obtained[23] for Ru(bpy)$_3^{2+}$, reflecting the lower absorption in the visible region exhibited by Ru(III)–poly(pyridyl) complexes[24] and the very intense absorption of free bpy$^-\cdot$ in aqueous solution;[25] it is anticipated that free bpz$^-\cdot$ would show a similar spectrum.

The average lifetime of *Ru(bpz)$_3^{2+}$ in deaerated aqueous solution reported here (0.86 ± 0.04 ns) lies well within the range of literature values;[11-19] τ_0 is somewhat larger in CH$_3$CN than in water, a phenomenon also noted for *Ru(bpy)$_3^{2+}$.[1a] Inasmuch as the relative emission intensity from *Ru(bpz)$_3^{2+}$ is independent of pH above 4.5,[18] the independence of τ_0 in that pH range can be assumed (reaction 2).

$$\mathrm{{}^*Ru(bpz)_3^{2+}} \rightarrow \mathrm{Ru(bpz)_3^{2+}} + h\nu' \qquad (2)$$

Quenching of *Ru(bpz)$_3^{2+}$ by EDTA and the Formation of Ru(bpz)$_3^{+}$. The quenching of *Ru(bpz)$_3^{2+}$ by EDTA (reaction 3) results in the formation of Ru(bpz)$_3^{+}$, the absorption spectrum of which is observed easily by flash photolysis; the spectrum we

$$\mathrm{{}^*Ru(bpz)_3^{2+}} + \mathrm{EDTA} \rightarrow \mathrm{Ru(bpz)_3^{+}} + \mathrm{EDTA_{ox}^{+}} \qquad (3)$$

observe is the same as that reported by Crutchley and Lever[11] which, in turn, is virtually identical with that of Ru(bpy)$_3^{+}$.[26] Under all the conditions investigted by us, the rates of decay of *Ru(bpz)$_3^{2+}$ and formation of Ru(bpz)$_3^{+}$ are identical.

The values of k_q at 8.7 and 11.0 reported here (6.9×10^8 and 7.7×10^8 M^{-1} s^{-1}, respectively), based on liner Stern–Volmer plots of I_0/I and τ_0/τ for the quenching of *Ru(bpz)$_3^{2+}$ by EDTA (pK_a 0.0, 1.5, 2.0, 2.7, 6.1, and 10.2),[27] are considerably higher than the one (3.9×10^7 M^{-1} s^{-1}) obtained by Dürr et al.[17] at pH 5 in 0.1 M KH-phthalate buffer by lifetime quenching; these authors also obtained a value of 9.4×10^7 M^{-1} s^{-1} by luminescence quenching using τ_0 = 0.75 μs but did not report any nonlinear Stern–Volmer behavior. The fall off of the quenching effect at pH 4.7 with increasing [EDTA] is also observed in the laser flash photolysis experiments in the decays of emission at 600 nm and absorption at 375 nm due to *Ru(bpz)$_3^{2+}$ and growth of absorption at 490 nm due to Ru(bpz)$_3^{+}$ (Table I). It should be noted that in the absence of any disparity between I_0/I and τ_0/τ values, or upward curvature of the Stern–Volmer plots, no evidence is presented for static quenching involving the anticipated ion pairs between cationic *Ru(bpz)$_3^{2+}$ and anionic EDTA in acidic or alkaline medium.

Figure 2 shows that the observed value of k_q at pH 4.7 decreases sharply as [EDTA] is increased, approaching $\sim 2 \times 10^8$ and $\sim 2 \times 10^7$ M^{-1} s^{-1} in the limits of low and high [EDTA], respectively. In addition, the linear region of the plot at high [EDTA] extrapolates to a value of k_0 that is approximately twice the observed value in the absence of EDTA. These results can be explained if the increased extent of the ion pairing of *Ru(bpz)$_3^{2+}$ and EDTA as [EDTA] is increased causes a small increase in the value of pK_a* so that the protonated form of the excited state, which exhibits a shorter lifetime and smaller quenching rate constants than does the unprotonated form,[19] is in greater abundance than in the absence of EDTA. This analysis predicts that the acid–base behavior of the excited-state parameters of Ru(bpz)$_3^{2+}$ will be dependent on the nature and extent of its ion pairing; of course, what has been observed here is a composite of effects. As a result, we do not know, at this point, the extent to which the initially generated excited state in acidic solution is partitioned between its ion-paired acid-base forms, the values of their quenching rate constants, nor the magnitude of the cage release yield of redox products.

In alkaline solution, the initial formation of Ru(bpz)$_3^{+}$ in the quenching reaction is followed by a secondary growth of that species and further bleaching of the substrate. This process can

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be attributed to the reduction of $Ru(bpz)_3^{2+}$ by EDTA′ (reaction 5); this latter species is formed by the rapid deprotonation of the carbon atom adjacent to the nitrogen radical site of $EDTA_{ox}^+$ (reaction 4), a process that could occur within the solvent cage of reaction 3. As a result of reactions 1 and 3, the concentration of $Ru(bpz)_3^{2+}$ at the time of reaction 5 is unknown and considerably less than its initial value of 50 μM. As a result, reaction 5 occurs in competition with the other modes of decay of EDTA′. It appears certain, from pulse radiolytic studies,[3,28] that EDTA′ undergoes numerous first- and second-order processes involving disproportionation (reaction 6) and decarboxylation (reaction 7), among others. Inasmuch as EDTA′ will exhibit acid–base behavior,[29] it is clear that the rate constants of these reactions will be pH-dependent; there is evidence[3] that the decarboxylation reaction is considerably accelerated by acid. Thus, the kinetics of the secondary formation of $Ru(bpz)_3^+$ will be complex, depending on pH and laser intensity. Nevertheless, as pointed out above, a pH- and [EDTA]-independent first-order component can be resolved during the latter stages of the reaction with $k \sim 2 \times 10^4\ s^{-1}$. If one assumes that ~90% of the $Ru(bpz)_3^{2+}$ initially present has been bleached, a not unreasonable estimate based on benzophenone actinometry, then a value of k_5 of $\sim 4 \times 10^9\ M^{-1}\ s^{-1}$ is obtained. Thus, reaction 5 is very fast and occurs at or near the diffusion-controlled limit; this fact, and the lack of reaction between EDTA′ and $Ru(bpy)_3^{2+}$, implies that $E°$ for EDTA′ in alkaline solution is of the order of −0.8 to −1.0 V, consistent with the reducing abilities of other carbon-based radicals.[30] Indeed, it should be noted that $Ru(bpz)_3^{2+}$, but not $Ru(bpy)_3^{2+}$, is reduced by radiation-generated $CO_2^{-}\cdot$ radicals.[31]

$$EDTA_{ox}^+ \rightarrow EDTA' + H^+ \qquad (4)$$

$$Ru(bpz)_3^{2+} + EDTA' \rightarrow Ru(bpz)_3^+ + \text{products} \qquad (5)$$

$$2EDTA' \rightarrow \text{products} \qquad (6)$$

$$EDTA' \xrightarrow{H^+} \text{decarboxylation} \qquad (7)$$

In the presence of O_2 in alkaline solution, the amounts of $^*Ru(bpz)_3^{2+}$ and $Ru(bpz)_3^+$ generated are less than under N_2 purge due to the competitive quenching of the excited state. The rate constant for this reaction is estimated to be $\sim 2 \times 10^9\ M^{-1}\ s^{-1}$, based on our observed values of τ_0 and τ_0^{air} and the concentration of O_2 (0.25 mM) in air-saturated solution; a corresponding value for the oxidative quenching of $^*Ru(bpy)_3^{2+}$ by O_2 is $3.3 \times 10^9\ M^{-1}\ s^{-1}$.[32] With $[O_2] = 1.3$ mM in O_2-saturated solution, the reaction of $Ru(bpz)_3^+$ with O_2, which is most likely electron transfer in nature (reaction 8), occurs with $k = 5.8 \times 10^8\ M^{-1}\ s^{-1}$. The very small permanent change in the spectrum after the decay of $Ru(bpz)_3^+$ can be attributed to subsequent reactions of the resultant highly reactive oxygen species and their products.

$$Ru(bpz)_3^+ + O_2 \rightarrow Ru(bpz)_3^{2+} + O_2^{-}\cdot \qquad (8)$$

The initial spectrum at pH 4.7 (Figure 4) is essentially the same as that generated in alkaline solution (Figure 3) but is approximately 3 times less intense; the laser pulse intensities and solution absorbances in these experiments were kept relatively constant. Unlike the situation in alkaline solution, no secondary formation of $Ru(bpz)_3^+$ is observed at pH 4.7. The very slight spectral shift that occurs would have to be the result of a relatively slow reaction of $Ru(bpz)_3^+$ that exhibits first-order kinetics ($k \sim 1 \times 10^4\ s^{-1}$) which are only mildly retarded as [EDTA] is increased by a factor of 10 (Table I). Inasmuch as $Ru(bpz)_3^+$, by analogy with $Ru(bpy)_3^+$,[33] exists as a reduced bpz ligand coordinated to the Ru(II) center $(Ru^{II}(bpz)_2(bpz^{-}\cdot)^+)$, it can be visualized as existing in its protonated form in acidic solution; one would expect its pK_a to be higher than that of $^*Ru(bpz)_3^{2+}$ (vide supra). The slow process that is observed in the 0.1-ms time frame is certainly not protonation reaction 9; this slow process could be the first step in the ultimate degradation of the reduced species to the final, but unknown, Ru(II) products (reaction 10); the conventional flash photolysis results, supported by those from pulse radiolysis,[31] demonstrates that the reaction is very complex and probably leads to many Ru(II) species with highly modified ligands. The absence of any secondary formation of $Ru(bpz)_3^+$ indicates that reaction 5 is not operative in acidic solution under laser flash photolysis conditions; its rate constant would be expected to be considerably lower than in alkaline solution due to the diminished reducing ability of protonated EDTA′. Thus, reactions 7 and 8 predominate.

$$Ru(bpz)_2(bpz^{-}\cdot)^+ + H^+ \rightarrow Ru(bpz)_2(\cdot bpzH)^{2+} \qquad (9)$$

$$Ru(bpz)_2(\cdot bpzH)^{2+} \rightarrow Ru(II)\ \text{products} \qquad (10)$$

In O_2-saturated solution at pH 4.7, the decay of $Ru(bpz)_3^+$ is almost 2 orders of magnitude slower than observed in alkaline solution. This observation argues in favor of the existence of $Ru(bpz)_2(\cdot bpzH)^{2+}$, which would be expected to be a much weaker reductant than $Ru(bpz)_2(bpz^{-}\cdot)^+$. In fact, the reaction may very well not be electron transfer in nature at all; O_2 could add to the carbon-localized ligand radical forming a peroxy adduct (reaction 11), the spectrum of which would be recorded in Figure 5. Of course, EDTA′ would be annihilated in the same way by reaction with O_2.

$$Ru(bpz)_2(\cdot bpzH)^{2+} + O_2 \rightarrow Ru(bpz)_2(\cdot OObpzH)^{2+} \qquad (11)$$

Formation of $MV^{+}\cdot$. In alkaline solution containing 0.10 M EDTA, the formation of $MV^{+}\cdot$ occurs via two distinct $[MV^{2+}]$-dependent first-order processes that contribute to the total production (reactions 12 and 13); the observed pseudo-first-order rate constants (k_I and k_{II}; Table II) are virtually the same at pH 11.0 and 8.7. The constant k_{II} can be identified with reaction 12 inasmuch as the disappearance of $Ru(bpz)_3^+$ occurs at the same rate; from the data, $k_{12} = 4.5 \times 10^8\ M^{-1}\ s^{-1}$. By comparison, Sassoon et al.[34] have recently reported a value of $6 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction of $Ru(bpy)_3^+$ with *N,N*′-bis(4-sulfonatotolyl)-4,4′-bipyridiylium to yield the reduced viologen. For reaction 13, the dependence of k_I on $[MV^{2+}]$ yields $k_{13} = 1.5 \times 10^9\ M^{-1}\ s^{-1}$. This latter value compares very well with those for reaction 13 obtained pulse radiolytically:[3] 2.8×10^9 and $7.6 \times 10^8\ M^{-1}\ s^{-1}$ at pH 12.5 and 8.3, respectively. At pH 11.0, the contributions of reactions 12 and 13 to the total yield of $MV^{+}\cdot$ are equal; at pH 8.7, the contribution of reaction 13 decreases with decreasing $[MV^{2+}]$ due to the increased competition of degradative reactions such as (7).

$$Ru(bpz)_3^+ + MV^{2+} \rightarrow MV^{+}\cdot + Ru(bpz)_3^{2+} \qquad (12)$$

$$EDTA' + MV^{2+} \rightarrow MV^{+}\cdot + \text{products} \qquad (13)$$

At pH 4.7 in the presence of 0.070 M EDTA, $MV^{+}\cdot$ forms slowly via a single $[MV^{2+}]$-dependent component, while $Ru(bpz)_3^+$ shows virtually no decay into the millisecond time frame. Thus, reaction 12 is not operative under these laser flash photolysis conditions at low (≤5.0 mM) $[MV^{2+}]$. The value of k_{13}, obtained from the dependence of k_I on $[MV^{2+}]$, equals $5.9 \times 10^5\ M^{-1}\ s^{-1}$, which is more than 10 times lower than the corresponding value reported for pulse radiolysis $(8.5 \times 10^6\ M^{-1}\ s^{-1})^3$. The reason for this discrepancy is not known, although one can speculate that the EDTA′ species formed at this pH by the two techniques are similar, but not identical. Regardless, reaction 13 would occur in competition with the other decay modes of the radical. The net result is that the yield of $MV^{+}\cdot$ in acidic solution is lower than in alkaline solution due to the diminished yield of $Ru(bpz)_3^+$ and its lessened reactivity toward MV^{2+} and the slower reaction of

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EDTA′ with MV^{2+} relative to its other degradative modes.

Photodynamics and $\Phi(MV^{+}\cdot)$. In the continuous photolysis of the $Ru(bpz)_3{}^{2+}/MV^{2+}/EDTA$ system in alkaline solution, the operative reactions are (1)–(5), (12), and (13); bimolecular reaction (6) will not be kinetically significant. In a recent communication on this subject,[20] we reported that $\Phi(MV^{+}\cdot)$ (1.3 ± 0.1) in neutral and alkaline solutions containing 0.10 M EDTA was independent of pH (6–11) and, at pH 8.7 where it was tested, $[MV^{2+}]$ (0.50–40 mM). This result is prefectly understandable in terms of the values of k_{12} and k_{13} and implies that decarboxylation reaction (7) is not an important process at pH 8.7. Thus, in deaerated neutral and alkaline solution, $\Phi(MV^{+}\cdot)$ can be expressed in terms of the efficiencies of formation and quenching of $^{*}Ru(bpz)_3{}^{2+}$ ($\eta_{\bullet}$ and η_q, respectively), and the release of redox products from the solvent cage in which they were formed in reaction 3 (η_{cr}): $\Phi(MV^{+}\cdot) = 2\eta_{\bullet}\eta_q\eta_{cr}$. By analogy to $Ru(bpy)_3{}^{2+}$,[35] $\eta_{\bullet}$ can be taken as unity; $\eta_q = k_3[EDTA]/(k_3[EDTA] + k_2)$, where $k_2 = 1/\tau_0$. From the values of k_3 ($=k_q$) and τ_0 given above, $\eta_q = 0.98$ in 0.1 M EDTA. Therefore, within experimental error, $\eta_{cr} = \Phi/2$; we conclude that the redox products of reaction 3 are released into neutral and alkaline solution with an efficiency of ~0.7.

This value of η_{cr} for the reducting quenching of $^{*}Ru(bpz)_3{}^{2+}$ by EDTA is significantly greater than any reported for the oxidative quenching of $^{*}Ru(bpy)_3{}^{2+}$. It appears secure for this latter complex (from flash photolysis experiments)[36–38] that $\eta_{cr} \sim 0.25$ for MV^{2+} in the absence of other added solutes; recently, a value of ~0.17 from the continuous photolysis of solutions containing 1.0 mM $Ru(bpy)_3{}^{2+}$, 20 mM MV^{2+}, and 0.10 M EDTA at pH 11.0 was reported.[4] Consideration of the electrostatic attaction between the redox partners in reaction 3 would lead one to expect that their separation from each other upon release of the solvent cage would be highly unfavorable compared to the rapid exoergic geminate pair back electron transfer reaction and that η_{cr} should be even smaller than in the case of the quenching of $^{*}Ru(bpy)_3{}^{2+}$ by MV^{2+}. We suggested,[20] and reiterate here, that the surprisingly high value of η_{cr} observed for the quenching of $^{*}Ru(bpz)_3{}^{2+}$ by EDTA in neutral and alkaline solution arises because reaction 4 occurs irreversibly to a large extent within the solvent cage.

At pH 4.7, the yield of $Ru(bpz)_3{}^{+}$ in the laser experiment is approximately one-third that in alkaline solution. From the discussion above regarding the quenching of $^{*}Ru(bpz)_3{}^{2+}$ by EDTA at this pH, we can only conclude that $\eta_{\bullet}\eta_q\eta_{cr} \sim 0.2$, compared to a value of ~0.7 in alkaline solution; unfortunately, the value of η_{cr} is not known independently, although it might be expected to be lower than ~0.7 due to the diminished drive of reaction 4 involving protonated $EDTA_{ox}{}^{+}$ within the solvent cage. Now, for solutions containing 50 μM $Ru(bpz)_3{}^{2+}$, 20 mM MV^{2+}, and 0.10 M EDTA, $\Phi(MV^{+}\cdot) = 0.27$.[20] The expression of $\Phi(MV^{+}\cdot)$ given above can be modified to include η_r and η_t, the efficiencies of formation of $MV^{+}\cdot$ from EDTA′ and $Ru(bpz)_3{}^{+}$, respectively; $\Phi(MV^{+}\cdot) = \eta_{\bullet}\eta_q\eta_{cr}(\eta_r + \eta_t)$. In neutral and alkaline solutions, both η_r and $\eta_t \sim 1$; using the available data, we conclude that $(\eta_r + \eta_t)$ has a value of ~1 in acidic solution, meaning that either or both reactions 12 and 13 are driven by the high concentration of MV^{2+} employed in the continuous photolysis experiments. This analysis predicts that unlike the situation at pH 8.7, $\Phi(MV^{+}\cdot)$ in acidic solution will be a function of $[MV^{2+}]$; experiments are currently in progress to test this prediction.

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Registry No. EDTA, 60-00-4; MV^{2+}, 4685-14-7; MV^{+}, 25239-55-8; $Ru(bpz)_3{}^{2+}$, 75523-96-5; $Ru(bpz)_3$, 75523-97-6; H_2O, 7732-18-5.

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