genuine five-coordinate intermediate in basic solution must be questioned on the basis of our results. It is on the basis of the available data appropriate to think in terms of a more associative process for the reaction of the conjugate base species, and a type of interchange mechanism would account best for the observed effects. This would require the introduction of an ICB (interchange conjugate base) mechanism, in line with our more recent findings for associative character in aquation reactions of pentaamminechromium(III) complexes.[13,17,18] On the other hand, for the methylamine complex steric hindrance obviously forces the conjugate base species to react in a dissociative way similar to that found for the Co(III) complexes.

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Rate Constants for the Scavenging of $Ru(bpy)_3^{3+}$ by EDTA in Aqueous Solution

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In the model system for the photosensitized reduction of water, containing $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) as the photosensitizer and methylviologen (1,1′-dimethyl-4,4′-bipyridinium dication; MV^{2+}) as the quencher,[1] a sacrificial electron donor, which upon one-electron oxidation transforms rapidly and irreversibly into a species that lacks the ability to oxidize the methylviologen radical cation ($MV^{\bullet +}$), is required to scavenge the $Ru(bpy)_3^{3+}$ generated in the oxidative quenching reaction in order to permit the $MV^{\bullet +}$ to accumulate in solution.[2] In the absence of the sacrificial donor, the rapid and highly exoergic back-electron-transfer reaction between $Ru(bpy)_3^{3+}$ ($E_{red}° = 1.26$ V)[3] and $MV^{\bullet +}$ ($E_{ox}° = 0.45$ V)[4] would annihilate these redox charge carriers.[5]

Because the formation of H_2 from the interaction of $MV^{\bullet +}$ with colloidal metal catalysts is most efficient in mildly acidic solution,[6] the sacrificial donor of choice for this particular application over the past decade has been EDTA (pK_a 0.0, 1.5, 2.0, 2.7, 6.1, 10.2).[7] At pH ~ 5, EDTA exists primarily as a dianion; in increasingly basic solution, first the trianion and then the tetraanion predominate. The one-electron oxidation of EDTA ($>N{-}CH_2{-}CO_2^-$) yields an amine-localized radical ($EDTA_{ox}^{\bullet}$; $>\dot{N}^+{-}CH_2{-}CO_2^-$) that rapidly loses a proton from the carbon atom α to the amine and carboxylate moiety to generate a carbon-localized radical that is a strong reducing agent ($EDTA_{red}^{\bullet}$; $>N{-}\dot{C}H{-}CO_2^-$).[8] Our work with EDTA as an electron donor indicates that the transformation step is very rapid ($k_{tr} > 10^7$ s^{-1}), and independent of pH.[9-12]

The relevant steps in the mechanism that deal with excitation, relaxation, quenching, back electron transfer, and scavenging are shown as reactions 1–5. Reaction 6 describes the overall transformation of $EDTA_{ox}^{\bullet}$ to $EDTA_{red}^{\bullet}$.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \quad (1)$$

$$^*Ru(bpy)_3^{2+} \xrightarrow{k_0} Ru(bpy)_3^{2+} + h\nu' \quad (2)$$

$$^*Ru(bpy)_3^{2+} + MV^{2+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + MV^{\bullet +} \quad (3)$$

$$Ru(bpy)_3^{3+} + MV^{\bullet +} \xrightarrow{k_{et}} Ru(bpy)_3^{2+} + MV^{2+} \quad (4)$$

$$Ru(bpy)_3^{3+} + EDTA \xrightarrow{k_{sc}} Ru(bpy)_3^{2+} + EDTA_{ox}^{\bullet} \quad (5)$$

$$EDTA_{ox}^{\bullet} \xrightarrow{k_{tr}} EDTA_{red}^{\bullet} \quad (6)$$

The ultimate yield of $MV^{\bullet +}$ is dictated by the efficiencies of quenching ($\eta_q = k_q[MV^{2+}]/(k_q[MV^{2+}] + k_0)$), cage escape of the redox products in reaction 3 (η_{ce}), and scavenging ($\eta_{sc} = k_{sc}[EDTA]/(k_{sc}[EDTA] + k_{et}[MV^{\bullet +}])$), as well as those of the secondary reduction steps; knowledge of the kinetic details of the mechanism is required for the most efficacious use of the model photochemical system and for the design of better systems. Values of k_0 (1.6×10^6 s^{-1}), k_q (~10^9 M^{-1} s^{-1}, depending on [EDTA], pH, μ), η_{ce} (0.1–0.3, depending on [MV^{2+}], [EDTA], and μ), and k_{et} (>10^9 M^{-1} s^{-1}, depending on μ), as well as the rate constant for reaction 7 ($k_{red} = 10^6$–10^9 M^{-1} s^{-1} at pH 4.7–11), have been extensively reported.[5,9,10,13,14] Interestingly, despite the obvious importance of knowing the value of k_{sc} under photochemically relevant conditions, there have been very few direct determinations of that quantity, which still remains somewhat in doubt. As a result, a complete kinetic understanding of this model photochemical system, with an eye toward the maximization of the yields of charge-separated redox products, has not yet been achieved.

$$EDTA_{red}^{\bullet} + MV^{2+} \xrightarrow{k_{red}} MV^{\bullet +} + \text{products} \quad (7)$$

Sutin[15] first reported a value for k_{sc} of 2×10^6 M^{-1} s^{-1} at pH 8.2; unfortunately, experimental details were not given in this review article. From the [EDTA]-dependent recovery of the bleaching of $Ru(bpy)_3^{2+}$ upon pulsed-laser flash photolysis, Keller et al.[8] obtained a value of 1.1×10^8 M^{-1} s^{-1} for solutions containing 0.5–5 mM MV^{2+} at pH 5 in 0.5 M acetic acid/acetate buffer; the range of [EDTA] for these experiments was not specifically given. By using the stopped-flow technique to effect the direct reaction of $Ru(bpy)_3^{3+}$ with EDTA, Miller and McLendon[16] determined k_{sc} as a function of pH: 8×10^3, 7×10^4, and 2×10^6 M^{-1} s^{-1} at pH 3, 5, and 7, respectively. They noted that the deprotonation of the acidic forms of EDTA would render the species a stronger reductant, thereby accounting for their observed "titration curve" of the rate constants. However, the details of the exact composition of the solutions, especially regarding the ionic strength, were not given.

Because of these very different values of k_{sc}, Orellana et al.[17] made a redetermination. They obtained a value of 1.7×10^8 M^{-1} s^{-1} from a pulsed-laser flash photolysis study on a solution containing 25 mM MV^{2+} at pH 5 in 0.05 M potassium hydrogen phthalate buffer; apparently, only one concentration of EDTA

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(0.050 M) was used. These authors expressed surprise that the rate constant of reaction 5 between oppositely and highly charged ions is much smaller than that of reaction 4 between positively charged species.

Clearly, the Sutin–Miller and Keller–Orellana values are internally consistent, although, as a group, they are quite discordant. The research described in this paper responds to the need to know k_{sc} over a wide range of solution medium conditions. It is to be expected that k_{sc} would be a function of ionic strength and pH; the highest values of k_{sc} should occur in alkaline solution at low μ. Although k_{sc} should be independent of [MV^{2+}], it could be a function of [EDTA] due to the ion-pairing of $Ru(bpy)_3^{3+}$ with that species. It should be noted that $Ru(bpy)_3^{2+}$ and EDTA form a 1:1 complex with a formation constant of 115 ± 18 M^{-1};[18] the oxidized photosensitizer would be expected to ion pair even more strongly.

Experimental Section

Materials and procedures were used as described recently.[14] Laser flash photolysis experiments (Nd:YAG Q-switched laser at 532 nm) and the computer analysis of the data were performed at The Center for Fast Kinetics Research (CFKR), University of Texas, Austin TX. Solutions were deaerated and continuously mixed with a stream of N_2. Data were collected and averaged for 5–10 shots.

Results

When monitored at 450 nm, the absorption maximum of $Ru(bpy)_3^{2+}$ ($\epsilon_{max} = 1.46 \times 10^4$ M^{-1} cm^{-1}), the flash excitation of the $Ru(bpy)_3^{2+}/MV^{2+}$ system, in the absence or presence of EDTA, initially causes the bleaching of the ground state and the formation of an equivalent amount of $^*Ru(bpy)_3^{2+}$ ($\epsilon_{450} = 7.0 \times 10^3$ M^{-1} cm^{-1}),[19] resulting in an absorbance that is less than that of the starting solution. The competition between reactions 2 and 3 results in a first-order recovery of the absorbance in the 0.2–2-μs time frame; the exact profile of this pseudo-first-order process is dependent, of course, on the value of [MV^{2+}]. The absorbance of the solution after the quenching reaction is still negative relative to that of the original solution because of the presence of $Ru(bpy)_3^{3+}$ ($\epsilon_{450} = 1.5 \times 10^3$ M^{-1} cm^{-1})[20] and $MV^{\bullet+}$ ($\epsilon_{450} = 6.1 \times 10^3$ M^{-1} cm^{-1})[21] and the absence of an equivalent amount of ground-state complex.

In the absence of EDTA, the loss of $MV^{\bullet+}$ (monitored at 605 nm; $\epsilon_{605} = 1.37 \times 10^4$ M^{-1} cm^{-1})[22] and the recovery of $Ru(bpy)_3^{2+}$ at 450 nm follow second-order kinetics in the 1–100-μs time frame; the exact time frame is dependent on the initial concentrations of the reactants in reaction 4, which, in turn, are controlled by the intensity of the absorbed light (intensity of the laser pulse, [$Ru(bpy)_3^{2+}$]) and η_q ([MV^{2+}]).

In the presence of high concentrations of EDTA, such that reaction 5 kinetically overwhelms reaction 4, the re-formation of the ground-state absorption at 450 nm follows good first-order kinetics, and $MV^{\bullet+}$ is stable. However, at intermediate concentrations of EDTA, the re-formation follows mixed first- and second-order kinetics, and some of the $MV^{\bullet+}$ is destroyed. The extent of destruction of $MV^{\bullet+}$ is a function of [EDTA], being greatest at low [EDTA]. If the recovery of the absorbance at 450 nm is fitted to first-order kinetics in the mixed-order regime, the rate constant that is obtained becomes smaller as [EDTA] is lowered and the second-order component becomes increasingly more dominant at the early part of the reaction; such a treatment yields anomalously high values for k_{sc}. Instead, a computer deconvolution of the mixed-order trace must be performed in order to extract the rate constant of the first-order component. Those conditions that maximize the rate of reaction 5 (high [EDTA] but low ionic strength) and minimize the rate of reaction 4 (low η_q and low I_a, consistent with the obtaining of usable signals) enhance the temporal separation of the kinetic components; however, a low value of η_q also causes the kinetics of reactions 3, 4, and 5 to merge. In addition, the formation of a second equivalent of $MV^{\bullet+}$ via reaction 7, which is enhanced at high [MV^{2+}], can occur in the same time frame as reactions 4 and 5.

Table I. First-Order Component of the Recovery of the Absorption at 450 nm from the Reaction of $Ru(bpy)_3^{3+}$ with EDTA

[EDTA], M	[MV^{2+}], mM	μ,[a] M	k_I, s^{-1}
pH 4.7			
0.0010	10	0.033[b]	8.2×10^4
0.010	10	0.060[b]	1.7×10^5
0.070	2.0	0.21[b]	9.2×10^4
0.080	1.0	0.24[b]	8.8×10^4
0.080	10	0.27[b]	1.4×10^5
0.095	0.50	0.29[b]	5.4×10^4
0.10	2.0	0.30[b]	1.3×10^5
0.0010	2.0	1.0	1.8×10^3
0.0050	2.0	1.0	1.3×10^4
0.010	2.0	1.0	1.3×10^4
0.020	2.0	1.0	2.7×10^4
0.050	2.0	1.0	5.2×10^4
0.10	20	1.0	1.2×10^5
pH 8.7			
0.0010	0.50	0.60	5.2×10^4
0.0010	1.0	0.60	5.7×10^4
0.0010	2.0	0.60	5.9×10^4
0.010	0.50	0.60	4.7×10^5
0.010·	1.0	0.60	4.5×10^5
0.010	2.0	0.60	4.2×10^5
pH 11.0			
0.0010	0.50	1.0	5.5×10^4
0.0010	1.0	1.0	6.2×10^4
0.0010	2.0	1.0	6.7×10^4
0.010	0.50	1.0	4.6×10^5
0.010	1.0	1.0	5.0×10^5
0.010	2.0	1.0	5.0×10^5

[a] Controlled with Na_2SO_4, unless otherwise indicated. [b] Ambient ionic strength; no Na_2SO_4 added.

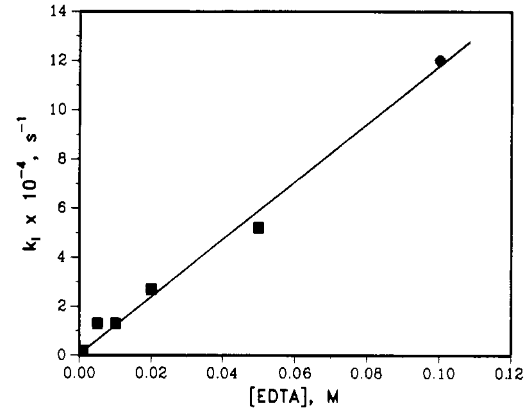

Figure 1. Plot of k_I vs [EDTA] for pH 4.7 and μ = 1.0 M: (■) 2.0 mM MV^{2+}; (●) 20 mM MV^{2+}.

The net result of these kinetic complications is that it was only possible to extract the rate constant of the first-order component (k_I) with the computer treatment at CFKR for a relatively restricted set of solution medium conditions. Table I presents those values of k_I.

Discussion

The anticipated dependence of k_{sc} on μ requires that any comparison of the experimental k_I values be conducted for solutions with the same ionic strength. For the data at pH 4.7 at μ = 1.0 M, a plot of k_I vs [EDTA] is linear (Figure 1), yielding a value for k_{sc} of 1.2×10^6 M^{-1} s^{-1}.

Because of the linearity of the plot, demonstrating that k_{sc} is not a function of [EDTA] under these conditions, the values of k_I at ambient and varying ionic strengths can be converted directly

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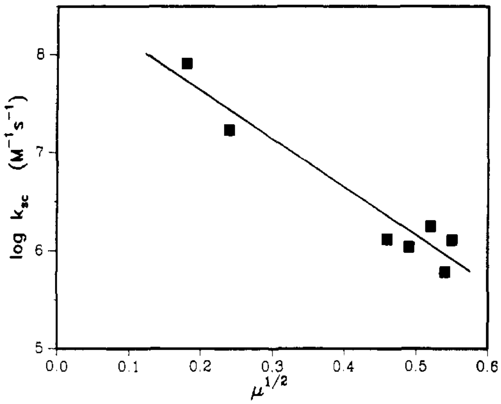

Figure 2. Plot of log k_{sc} vs $\mu^{1/2}$ for pH 4.7.

into k_{sc} by dividing by [EDTA]. This results in values of k_{sc} that range from $\sim 10^8$ to $\sim 10^6$ M^{-1} s^{-1} with increasing μ. A straight line can be forced through the points of a plot of log k_{sc} vs $\mu^{1/2}$ (Figure 2), showing that k_{sc} does, as expected, decrease with increasing ionic strength. Although this treatment is not valid in a quantitative sense at these relatively high ionic strengths, being well beyond the point where the Debye–Hückel limiting law can be applied and a linear plot expected, the slope of the line (−5) is amazingly consistent with the product of the charges of the reacting species. At the same time it must be noted that the value of k_{sc} at $\mu = 1.0$ M is approximately the same as those at $\mu \sim 0.3$, indicating that k_{sc} ceases to be a function of μ in that range, and/or that the presence of SO_4^{2-} changes the dynamics of the reaction due to a change in the ionic atmosphere surrounding the $Ru(bpy)_3^{3+}$.

The data for pH 8.7 at $\mu = 0.60$ M and pH 11.0 at $\mu = 1.0$ M yield values of k_{sc} of 4.6×10^7 and 5.0×10^7 M^{-1} s^{-1}, respectively, and demonstrate that they are not a function of [MV^{2+}]. Although the dependence of k_{sc} on μ was not studied at alkaline pH, it is safe to assume that it would show the same general trend as in acidic solution and may have a value $\sim 10^9$ M^{-1} s^{-1} at $\mu = 0$.

Comparison of the values of k_{sc} at high ionic strengths for acidic and basic solutions shows that the rate constant is more than an order of magnitude larger in alkaline medium, consistent with the increasing reducing power of EDTA as it undergoes deprotonation. However, the fact that k_{sc} is $\sim 10^8$ M^{-1} s^{-1} at pH 4.7 and low ionic strengths underscores the necessity of comparing rate constants under the same solution medium conditions.

These factors make it difficult to compare the values of k_{sc} reported here with those in the literature; in fact, they all may be valid for the specific conditions under which they were determined, as long as the reaction was in the domain of strictly first-order kinetics or k_I was extracted from the mixed-order treatment. Nevertheless, there is the strong indication that k_{sc} is a function of the other anions present in the solution.

The important question to address is why k_{sc} is so low, even when account is taken of the effect of ionic strength. Despite the restrictions on the validity of the treatment in Figure 2, extrapolation of the line to $\mu = 0$ yields a lower limit estimate of the value of k_{sc} at pH 4.7; the value of $\sim 4 \times 10^8$ M^{-1} s^{-1} is at least 2 orders of magnitude lower than the diffusion-controlled limit for oppositely and highly charged ions. The result further appears strange if reaction 5 is viewed as being highly exoergic; the reported standard oxidation potentials for EDTA at pH 2 and 9 from polarographic measurements are −0.56 and −0.13 V, respectively.[23]

However, reaction 5 is not highly exoergic; in fact, it may not be exoergic at all. The $E°$ values from polarographic measurements are affected by rapid and irreversible reaction 7, which would make the apparent potential more positive than the reversible one-electron potential. In our recent examination of the reductive quenching of $^*Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) by EDTA,[12] we estimated, from the general correlation of k_q with the driving force of adiabatic excited-state electron-transfer reactions,[24] that $E_{ox}°$ for the one-electron oxidation of EDTA in alkaline solution is ~ -1.5 V, making reaction 5 endoergic by ~ 0.2 V. If the rate constant for self-exchange of EDTA were comparable to that of $Ru(bpy)_3^{3+}$ ($>10^9$ M^{-1} s^{-1}),[25] an application of the free-energy relationships for electron transfer[26] would predict values of k_{sc} that are of the same order of magnitude as reported here.

Regarding the relationship of k_{sc} to the quantum yield of formation of $MV^{\bullet+}$ ($\Phi(MV^{\bullet+})$) in the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA model photochemical system, $\Phi(MV^{\bullet+}) = \eta_{*}\eta_q\eta_{ce}\eta_{sc}(1 + \eta_{red})$, where η_{*} is the efficiency of formation of $^*Ru(bpy)_3^{2+}$ (~ 1),[27] and η_{red} is the efficiency of reduction of MV^{2+} by $EDTA_{red}^{\bullet}$ ($= k_{red}[MV^{2+}]/(k_{red}[MV^{2+}] + k_{dec})$). Reaction 8 and its overall

$$\mathrm{EDTA_{red}}^{\bullet} \xrightarrow{k_{dec}} \text{products} \qquad (8)$$

rate constant (k_{dec}) reflect all the modes of conversion of $EDTA_{red}^{\bullet}$ to unreactive products, especially those that are pH dependent.

In order to optimize the yield of $MV^{\bullet+}$, all the values of η should be maximized. A high concentration of MV^{2+} will maximize η_q and η_{red}; a high concentration of EDTA (but a low ionic strength!) will maximize η_{sc}, but those parameters that enhance reaction 4 (high η_q and I_a) will diminish η_{sc}, especially under laser-flash conditions. Furthermore, η_{ce} is maximized at low [MV^{2+}], [EDTA], and μ.[14] When consideration is given to the prospect that η_{ce} and η_{sc} may be dependent as well on the nature of the solutes used to control μ, one can see that the optimization of the quantum yields of $MV^{\bullet+}$ and the total modeling of the system will require the consideration of the many interlocking relationships that involve the components of the solution medium.

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Synthesis of Tetrakis(trifluoromethyl)lead

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The interesting new compound $Pb(CF_3)_4$ has been prepared by a technique that promises to be a very broadly adaptable route to the synthesis of new σ-bonded metal compounds of relatively low thermal stability. This trifluoromethyl compound is one of the last remaining unsynthesized trifluoromethyl compounds of group IV, and although it is too unstable to be isolated at temperatures required for conventional synthetic methods (>100 °C), it is stable at room temperature when isolated from radiation sources.

We have earlier reported a synthesis of σ-bonded metal compounds based on cocondensation of metal atoms with free radicals[1]

$$M(g) + nR^{\bullet} \xrightarrow{-196\ °C} M(R)_n$$