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SOLUTION MEDIUM CONTROL OF THE $Ru(bpy)_3^{2+}$/METHYL VIOLOGEN/EDTA PHOTOCHEMICAL SYSTEM

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ABSTRACT

The value of $\Phi(MV^{+\cdot})$ from the photolysis of the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA system depends on the pH of the solution and the concentrations of the three components. The pairing of cations with EDTA in alkaline solution, and the formation of larger aggregates at high substrate concentrations, affects the yields of redox products from the excited-state electron-transfer reaction. The degree of linearity of Stern-Volmer luminescence quenching plots, and the values of the quenching rate constants, are functions of solution medium.

INTRODUCTION

The most thoroughly investigated model system for the photochemical conversion and storage of solar energy is the one containing $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) as the photosensitizer, methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dication; MV^{2+}) as the electron relay, and EDTA as the sacrificial electron donor (ref.1). The mechanism of this system has been studied in great detail (ref.2) and involves the oxidative quenching of the luminescent lowest excited state of the photosensitizer, $^*Ru(bpy)_3^{2+}$, by MV^{2+} generating the methyl viologen radical cation, $MV^{+\cdot}$, which, upon interaction with colloidal metal particles such as Pt, yields H_2. The sacrificial electron donor prevents degradative back electron transfer between the redox products of the excited state quenching reaction by reducing $Ru(bpy)_3^{3+}$ to the original substrate; the EDTA, upon oxidation, undergoes conversion to a reducing radical that leads to the formation of a second equivalent of $MV^{+\cdot}$. Ultimately, the irreversible degradation of the EDTA leads to final products (ref.3).

Despite the large number of investigations of the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA system, reported values of $\Phi(MV^{+\cdot})$, the quantum yield of $MV^{+\cdot}$ formation, from the continuous photolysis in the absence of O_2 and metal colloids show a wide range and great disparity (ref.4-8). In particular, the recently reported values of $\Phi(MV^{+\cdot})$ by Nenadovic, *et al.* (ref.8), which range from 0.08 to 1.5 as a function of pH, are very divergent from those of other investigators.

Recently, in an attempt to standardize this important model system, we undertook a systematic examination of $\Phi(MV^{+\cdot})$ as a function of pH and the con-

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centrations of the various species in solution (ref.9). The quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+}, and the efficiency of cage release of the redox products from that reaction (ref.10) are strongly affected by ion-pair (ref.11-13) and aggregation (ref.14) interactions among the ionic species in the solution, especially when relatively high concentrations of solutes are employed in order to effect extensive excited state quenching and redox scavenging.

In this paper, we examine the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+}, and the quantum yield of $MV^{+\cdot}$ formation in alkaline solution at high concentrations of $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA. We also make an attempt to understand the basis of the variations in reported values of $\Phi(MV^{+}\cdot)$.

EXPERIMENTAL SECTION

Materials

Methyl viologen dichloride (B.D.H.) was recrystallized several times from methanol and dried at 70° under vacuum for more than 24hr. $Ru(bpy)_3Cl_2$ (G.F. Smith) was recrystallized three times from water upon addition of methanol and dried. Disodium-EDTA and Na_2SO_4 (Baker Analyzed Reagents) were used without further purification. Distilled water was further treated by passage through a Millipore Purification Train.

Apparatus

Photolyses were performed at 450(±10)nm with a Bausch and Lomb high intensity monochromator and associated 200W super pressure mercury lamp as previously described (ref.9). The quenching of the $Ru(bpy)_3^{2+}$ luminescence by MV^{2+} was examined using a Perkin-Elmer MPF-2A spectrofluorimeter. Absorbance measurements were made using Cary 118 and 210 spectrophotometers.

For the *in situ* monitoring of the generation of $MV^{+\cdot}$, the light source was set up perpendicular to the monitoring beam of a conventional flash photolysis unit which was passed through a 600(±50)nm-band-pass filter into a Hilger-Engis monochromator set at 605nm and an RCA 440 red-sensitive photomultiplier, the signal from which was displayed simultaneously on a chart recorder and an oscilloscope.

The lifetime of the luminescence from $^*Ru(bpy)_3^{2+}$ was determined using a frequency-doubled Quantel Model 580 Nd:YAG laser (8 ns pulse at 532nm) in conjunction with a Camac Crate Kinetic System and a LeCroy transient recorder controlled by a PDP11/23 computer. Data acquisition was at the rate of one point per 10 ns; a minimum of ten points is necessary for the precise evaluation of τ.

Procedures

Photolyses. Solutions were contained in 1-cm cuvettes possessing a greaseless vacuum stopcock, and were rigorously degassed by four freeze-pump-thaw cycles on a vacuum line. Solutions were always stirred, unless otherwise indicated, with a small Teflon-coated magnetic bar in order to ensure homogeneity. The intensity of light incident on the solutions, as determined relative to the ferrioxalate actinometer (ref.15), was ~1 x 10^{-5}ein $L^{-1}min^{-1}$; the intensity of the absorbed light was established for each sample from Beer's Law. Spectrophotometric analyses for $MV^{+\cdot}$ were performed *in situ* or within 10s of the end of the irradiation period. The concentration of the $MV^{+\cdot}$ generated was established from the absorbance of the solution at 605nm, taking $\epsilon_{605} = 1.37 \times 10^{-4}M^{-1}cm^{-1}$ (ref.16).

Luminescence measurements. Air-equilibrated solutions were contained in 1-cm spectrofluorimeter cells.

Lifetime measurements. Solutions were contained in 1-cm cuvettes, and could be deaerated by purging with Ar. Emission from the solutions was monitored at 90° to the excitation pulse.

RESULTS

Quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+}

The quenching of the luminescence from $^*Ru(bpy)_3^{2+}$ by MV^{2+} was examined on air-saturated solutions (pH 11.0) containing 5.0μM and 1.0mM $Ru(bpy)_3^{2+}$ in 0.10 and 0.20M EDTA, respectively; the excitation and emission wavelengths were 450 and 608nm, respectively. Figure 1 shows Stern-Volmer plots of the data; deviation from linear behavior is readily apparent for the solution containing high concentrations of all the components. EDTA itself does not quench the luminescence from 5.0μM-1.0mM $Ru(bpy)_3^{2+}$.

In deaerated solutions at ambient temperature, the measured lifetime of $^*Ru(bpy)_3^{2+}$ was 0.60μs under all combinations of conditions of pH (4.7-11.0), [EDTA] (0-0.20M), and $[Ru(bpy)_3^{2+}]$ (5.0μM-1.0mM); in air-saturated solutions, τ was 0.41μs. Values of τ_0/τ for air-saturated solutions in the presence of up to 10mM MV^{2+} at pH 11.0 in 0.20M EDTA were the same as I_0/I for corresponding values of $[MV^{2+}]$; the limitation of the time resolution of the pulsed laser system prevented the evaluation of τ at higher concentrations of MV^{2+}.

Formation of $MV^{+\cdot}$

Irradiation of the $Ru(bpy)_3^{2+}/MV^{2+}$/EDTA system leads to the photosensitized formation of $MV^{+\cdot}$ which, in the absence of air, is very stable in alkaline, neutral, and mildly acidic solution. As has been shown before (ref.9), the formation of $MV^{+\cdot}$ is linear with photolysis time for stirred solutions containing sufficient EDTA to scavenge the $Ru(bpy)_3^{3+}$ in competition with its back electron transfer with $MV^{+\cdot}$. Values of $\Phi(MV^{+\cdot})$ were determined from the ratio of the rate of $MV^{+\cdot}$ formation to the rate of light absorption and were reproducible to ±10%.

Figures 2 and 3 show the dependences of $\Phi(MV^{+\cdot})$ on [EDTA] and $[MV^{2+}]$, respectively, at high and low $[Ru(bpy)_3^{2+}]$ at pH 11.0 using conventional spectrophoto-

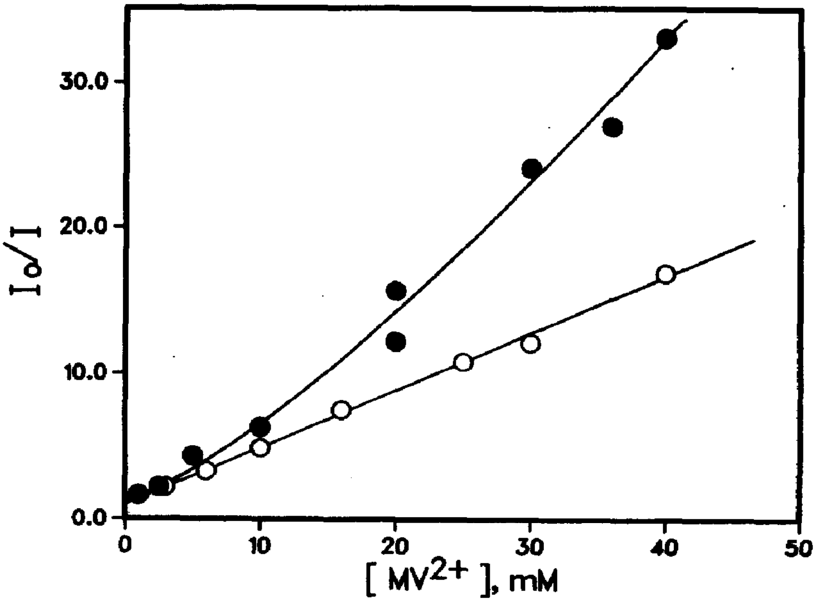

Fig. 1. Stern-Volmer plot of the quenching of the luminescence from $^*Ru(bpy)_3^{2+}$ by MV^{2+} at pH 11.0. Conditions: 5.0μM $Ru(bpy)_3^{2+}$ and 0.10M EDTA (○); 1.0mM $Ru(bpy)_3^{2+}$ and 0.20M EDTA (●).

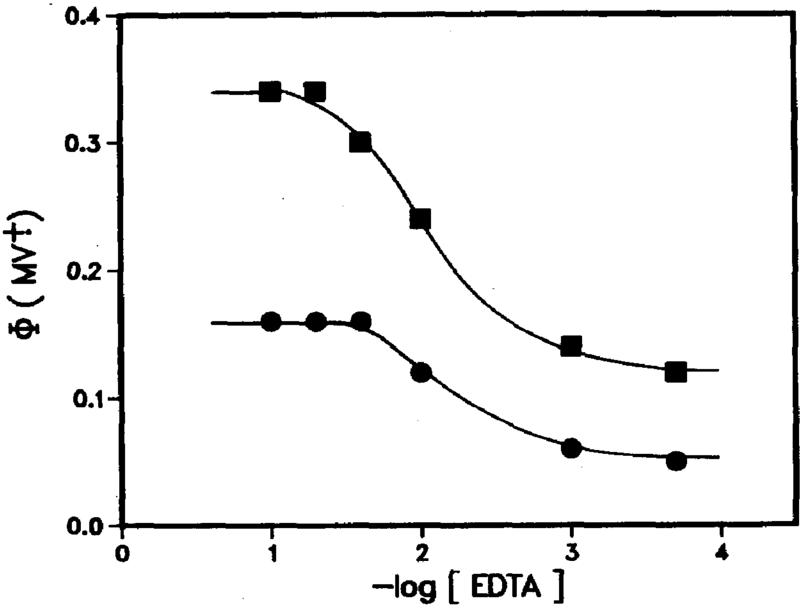

Fig. 2. Dependence of $\Phi(MV^{+}\cdot)$ on [EDTA] at pH 11.0 in 0.020M MV^{2+} and 0.010mM (●) and 0.50mM (■) $Ru(bpy)_3^{2+}$.

metric monitoring of $MV^{+\cdot}$. Some experiments at high concentrations of photosensitizer were performed using excitation wavelengths up to 500nm in order to ascertain whether the total absorption of light close to the front window of the cell had any adverse effect on the photochemistry; the observed values of $\Phi(MV^{+\cdot})$ were independent of wavelength.

Figure 4 shows the absorbance at 605nm as a function of irradiation time (*in situ* monitoring of $MV^{+\cdot}$) for stirred and unstirred solutions. The generation of $MV^{+\cdot}$ in stirred solutions is linear with photolysis time over the entire period of the experiments; ultimately, when the concentration of $MV^{+\cdot}$ becomes sufficiently high, the rate of formation of $MV^{+\cdot}$ decreases and a photolytic steady-state is reached. In the case of unstirred solutions, a high rate is observed initially which gradually falls off to a lower rate that is approximately the same as that observed for stirred solutions. Values of $\Phi(MV^{+\cdot})$ were determined from the slopes of the linear portions of such plots. The effect of stirring was examined for a range of conditions including those used by Nenadovic, *et al.* (ref.8); the results are given in Table 1.

DISCUSSION

Mechanism of the Reaction

The mechanism of the photosensitized formation of $MV^{+\cdot}$ in the $Ru(bpy)_3^{2+}$/MV^{2+}/EDTA system is given by reactions 1-8. The symbols "EDTA", "$EDTA_{ox}^{+}$", and "EDTA'" represent all the forms of those substances present in the solution at the pH of interest.

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

$$^*Ru(bpy)_3^{2+} \longrightarrow Ru(bpy)_3^{2+} \quad (2)$$

$$^*Ru(bpy)_3^{2+} + MV^{2+} \longrightarrow Ru(bpy)_3^{3+} + MV^{+\cdot} \quad (3)$$

$$Ru(bpy)_3^{3+} + MV^{+\cdot} \longrightarrow Ru(bpy)_3^{2+} + MV^{2+} \quad (4)$$

$$Ru(bpy)_3^{3+} + EDTA \longrightarrow Ru(bpy)_3^{2+} + EDTA_{ox}^{+} \quad (5)$$

$$MV^{+\cdot} + EDTA_{ox}^{+} \longrightarrow MV^{2+} + EDTA \quad (6)$$

$$EDTA_{ox}^{+} \longrightarrow EDTA' + H^{+} \quad (7)$$

$$EDTA' + MV^{2+} \longrightarrow MV^{+\cdot} + \text{products} \quad (8)$$

The rate constants for some of the steps of the mechanism are very well established. The natural lifetime of $^*Ru(bpy)_3^{2+}$ is 0.60μs in deaerated aqueous solution; $k_2 = 1.6 \times 10^6 s^{-1}$. There appears to be no controversy about the value of k_4 ($2.6 \times 10^9 M^{-1}s^{-1}$; ref.3,17), nor that k_6 is at or near the diffusion-controlled limit.

Because of the ionic nature of the mechanistic steps, the values of the rate constants are a function of the solution medium. The rate constant for quenching

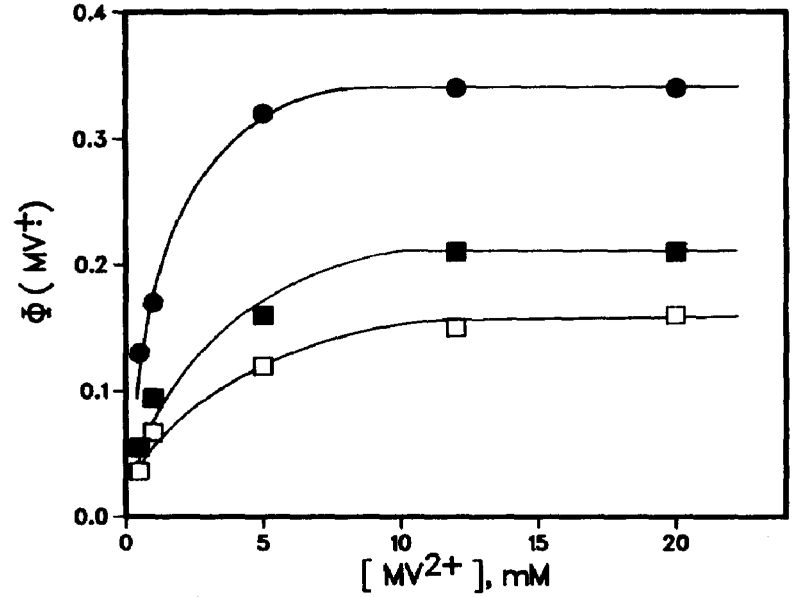

Fig. 3. Dependence of $\Phi(MV^{+}\cdot)$ on $[MV^{2+}]$ at pH 11.0 in 0.10M EDTA and 0.050mM (□), 0.10mM (■), and 0.50mM (●) $Ru(bpy)_3^{2+}$.

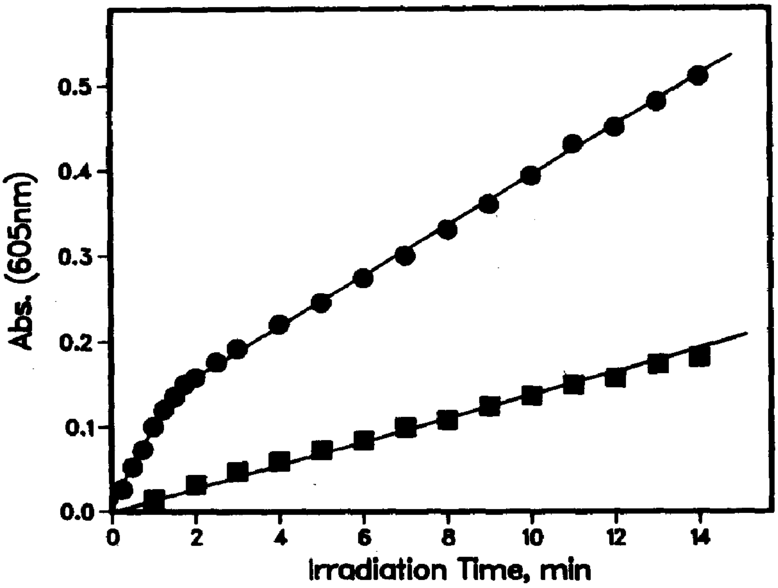

Fig. 4. Absorbance at 605nm as a function of irradiation time for the *in situ* monitoring of $MV^{+}\cdot$ in stirred (■) and unstirred (●) solutions containing 0.10mM $Ru(bpy)_3^{2+}$, 5.0mM MV^{2+}, and 0.10M EDTA at pH 8.7.

TABLE 1

$\Phi(MV^{+\cdot})$ as a function of pH, $[MV^{2+}]$, and [EDTA] in the *in situ* monitoring of $MV^{+\cdot}$ formation.[a]

$[MV^{2+}]$, mM	[EDTA], M	pH	μ, M[b]	conditions	$\Phi(MV^{+\cdot})$[c]
0.020	0.10	4.7	0.6	unstirred; s.t.	0.43
				unstirred; l.t.	0.20
				stirred	0.13
		8.7	0.6	unstirred; s.t.	0.70
				unstirred; l.t.	0.27
				stirred	0.21
		11.0	1.0	unstirred; s.t.	0.70
				unstirred; l.t.	0.25
				stirred	0.24
0.0050	0.010	3.0	0.02	unstirred[d]	0.004
				stirred	0.004
		4.7	0.05	unstirred; s.t.	0.56
				unstirred; l.t.	0.12
				stirred	0.13
		8.7	0.08	unstirred; s.t.	0.87
				unstirred; l.t.	0.32
				stirred	0.15
0.0050	0.10	4.7	0.3	unstirred; s.t.	0.68
				unstirred; l.t.	0.16
				stirred	0.12
		8.7	0.6	unstirred; s.t.	0.85
				unstirred; l.t.	0.15
				stirred	0.13

[a] $[Ru(bpy)_3{}^{2+}]$ = 0.10mM. s.t. = determined at short irradiation times; l.t. = determined at long irradiation times.

[b] Ionic strength controlled with EDTA and Na_2SO_4.

[c] Corrected (stirred solutions only) for the generation of $MV^{+\cdot}$ caused by the monitoring light.

[d] The same behavior is exhibited at short and long irradiation times.

reaction 3, obtained from linear Stern-Volmer plots, increases with increasing ionic strength (ref.3,18) and is a function of pH in the presence of EDTA (Table 2); deviations from the Debye-Bronsted law are attributed (ref.19) to the existence of specific ionic interactions at high ionic strength. At pH 4.7 and 11.0 in solutions containing EDTA (pK_a 0.0, 1.5, 2.0, 2.8, 6.1, 10.2; ref.20), the ion pairing of $^*Ru(bpy)_3{}^{2+}$ and MV^{2+} is primarily with EDTA in its -2 and -4 forms, respectively; the value of k_3 (= k_q) shows the increased electrostatic repulsion of similarly charged species. It should be noted that k_q exhibits no dependence on $[Ru(bpy)_3{}^{2+}]$ (5.0μM-1.0mM) in the presence of 0.10M EDTA at pH 4.7 and 11.0.

The exact value of k_5 is not clear. Values as high as $1.1 \times 10^8 M^{-1}s^{-1}$ at pH 5 have been estimated (ref.21) from laser flash photolysis; values ranging from $8 \times 10^3 M^{-1}s^{-1}$ at pH 4 (ref.22) to $2 \times 10^6 M^{-1}s^{-1}$ at pH 8.2 (ref.23) from stopped-

TABLE 2

Rate constants for the quenching of $^*Ru(bpy)_3^{2+}$ by MV^{2+} as a function of solution medium.[a]

pH	[EDTA], M	k_q, $M^{-1}s^{-1}$
natural [b]		4.0×10^8
natural [c]		1.4×10^9
4.7 [d]	0.0010	1.2×10^9
	0.010	1.4×10^9
	0.10	1.5×10^9
11.0 [e]		1.6×10^9
	5.0×10^{-5}	1.3×10^9
	0.0010	1.2×10^9
	0.10	9.5×10^8

[a] From K_{SV} in ref. 9 using $\tau_o = 0.41\mu s$ in air-saturated solution; $[Ru(bpy)_3^{2+}] = 5.0 \times 10^{-6}M$.
[b] in the absence of EDTA; no ionic strength control.
[c] in the absence of EDTA; $\mu = 0.5M$.
[d] $\mu = 0.5\text{-}0.6M$.
[e] $\mu = 1.0M$.

flow experiments have been reported. From our observation of the linear initial generation of $MV^{+}\cdot$, even at low [EDTA], we estimated k_5 to be $\sim10^8M^{-1}s^{-1}$ at pH 4.7 and $\sim5 \times 10^9M^{-1}s^{-1}$ at pH 11.0 (ref.9). We attribute these variations to the differences in the concentrations of EDTA employed, and, hence, to the extent of ion pairing of the reactive species.

The oxidized form of EDTA, $EDTA_{ox}^+$, produced in reaction 5, can be represented as $R_2\dot{N}^+CH_2$--; it appears that deprotonation of the carbon atom adjacent to the nitrogen radical site to form the reducing EDTA' radical ($R_2N\dot{C}H$--) in reaction 7 is fast and quantitative in alkaline and neutral solution (ref.5). Alternatively, it has been proposed (ref.24) that $EDTA_{ox}^+$ can undergo decarboxylation to yield a carbon-based radical similar to EDTA'. In any event, the reaction of reducing EDTA-radicals with MV^{2+} will generate a second equivalent of $MV^{+}\cdot$; values of k_8 of 2.8×10^9, 7.6×10^8, and $8.5 \times 10^6M^{-1}s^{-1}$ at pH 12.5, 8.2, and 4.7, repectively, have been determined (ref.25).

We have shown (ref.9) that the application of a steady-state treatment to reactions 1-8 predicts that the formation of $MV^{+}\cdot$ will be linear with photolysis time as long as $rate_5 >> rate_4$ and $rate_7 >> rate_6$. The first condition is satisfied if [EDTA] is sufficiently high and $[MV^{+}\cdot]$ does not build up to a high level; the second condition is satisfied without difficulty under the conditions of continuous photolysis. Thus, if each step in the mechanism were quantitative, $\Phi(MV^{+}\cdot) = 2k_3[MV^{2+}]/(k_2 + k_3[MV^{2+}])$ during the initial linear generation of

$MV^{+}\cdot$. Under conditions of high $[MV^{2+}]$ where $k_3[MV^{2+}] >> k_2$, a maximum value of $\Phi(MV^{+}\cdot)$ of two is predicted.

Cage Release of Redox Products

The fact that observed values of $\Phi(MV^{+}\cdot)$ are substantially less than two indicates that some of the steps in the mechanism are not quantitative. The sources of inefficiencies in this system are the geminate cage recombination of the redox pairs from the excited-state electron-transfer quenching reaction, and competitive degradative processes involving the EDTA-derived radicals. The cage release yield of the products of reaction 3, albeit in the absence of EDTA, has been determined to be ~0.25 from flash photolysis experiments (ref.26); similar direct measurements in the presence of EDTA have not been reported. It seems certain that reactions 7 and 8 are quantitative in alkaline and neutral solution; in mildly acidic solution, however, the degradation of $EDTA_{ox}^{+}$ and EDTA' may be competitive.

The expression for $\Phi(MV^{+}\cdot)$ based on the initial linear formation of $MV^{+}\cdot$ can be rewritten in terms of the efficiencies of the various steps: $\Phi(MV^{+}\cdot) = \eta_{*}\eta_{q}\eta_{cr}(1 + \eta_{r})$, where η_{*} is the efficiency of formation of the luminescent lowest excited state of $^{*}Ru(bpy)_3^{2+}$; η_q is the efficiency of quenching of $^{*}Ru(bpy)_3^{2+}$ by MV^{2+} $(= k_3[MV^{2+}]/(k_2 + k_3[MV^{2+}]))$; η_{cr} is the efficiency of production of $Ru(bpy)_3^{3+}$ and $MV^{+}\cdot$ in reaction 3; and η_r is the efficiency of formation of the second equivalent of $MV^{+}\cdot$ via the intermediacy of $EDTA_{ox}^{+}$ and EDTA'. Now, η_{*} is well known to be ~1 (ref.27), and η_q can be easily calculated. Quenching reaction 3 can be written in more detail showing the generation of the redox products within the solvent cage (reaction 9), release of the redox products from the solvent cage (reaction 10), and geminate pair back electron transfer (reaction 11). Thus, $\eta_{cr} = k_{10}/(k_{10} + k_{11})$. The value of η_r reflects the extent to which degradative reactions of $EDTA_{ox}^{+}$ and EDTA' occur in competition with reactions 7 and 8. Under conditions of high $[MV^{2+}]$, η_q ~ 1 so that η_{cr} ~ $\Phi(MV^{+}\cdot)/(1 + \eta_r)$.

$$^{*}Ru(bpy)_3^{2+} + MV^{2+} \longrightarrow [Ru(bpy)_3^{3+}...MV^{+}\cdot] \quad (9)$$

$$[Ru(bpy)_3^{3+}...MV^{+}\cdot] \longrightarrow Ru(bpy)_3^{3+} + MV^{+}\cdot \quad (10)$$

$$[Ru(bpy)_3^{3+}...MV^{+}\cdot] \longrightarrow Ru(bpy)_3^{2+} + MV^{2} \quad (11)$$

In alkaline and neutral solution, η_r ~ 1; in mildly acidic solution, $\eta_r < 1$, and depends on pH and, very likely, $[MV^{2+}]$ (ref.25); as a result of this inequality, a quantitative treatment of the system at pH 4.7 is not possible. Nevertheless, the maximum value of $\Phi(MV^{+}\cdot)$ at pH 4.7 of 0.14 in 0.10M EDTA and 20mM MV^{2+} (ref.9) implies that $\eta_{cr} < 0.25$ under those conditions. The existence of ion pairs between EDTA and the reactive cations will reduce the mutual repulsion of the geminate pairs within the solvent cage, thereby increasing the rate of back electron transfer relative to separation of the redox products, and decreasing the value of η_{cr}.

The equilibrium constant for the formation of 1:1 ion pairs between MV^{2+} and EDTA has been measured as a function of pH (ref.12); K_{eq} values are 1.3, 13, 13, and 18 at pH 4.7, 8.0, 10.0, and 11.0, respectively. The value of K_{eq} for $Ru(bpy)_3^{2+}$/EDTA has been estimated (ref.13) as $>78M^{-1}$, presumably at the ambient pH of EDTA solutions (4.7); it is very likely that K_{eq} has an even higher value in alkaline solution. Reactions 12-14 describe the equilibria formation and the excitation of the ion paired photosensitizer.

$$Ru(bpy)_3^{2+} + EDTA \rightleftharpoons Ru(bpy)_3^{2+},EDTA \tag{12}$$

$$MV^{2+} + EDTA \rightleftharpoons MV^{2+},EDTA \tag{13}$$

$$Ru(bpy)_3^{2+},EDTA \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+},EDTA \tag{14}$$

The "titration" of $\Phi(MV^{+\cdot})$ as a function of [EDTA] in acidic (ref.9) and alkaline (ref.10; Figure 2 in this paper) solution indicates that the quenching reactions involve non-ion paired (reaction 9) and ion paired species (reaction 16; the cross reactions are not shown for the sake of simplicity), and the resulting changes in η_{cr} can be controlled through variation of the solution medium. The association of EDTA with $Ru(bpy)_3^{3+}$ and $MV^{+\cdot}$ in the solvent cage, designated as $[Ru(bpy)_3^{3+}...MV^{+\cdot},EDTA]$, can result in some static quenching of the oxidized photosensitizer (reactions 17-19; the ion pairing of the solvent-separated products is not shown). Therefore, in the presence of high [EDTA], $\eta_{cr} = (k_{16} + k_{17})/(k_{16} + k_{17} + k_{18})$.

$${}^*Ru(bpy)_3^{2+},EDTA + MV^{2+},EDTA \longrightarrow [Ru(bpy)_3^{3+}...MV^{+\cdot},EDTA] \tag{15}$$

$$[Ru(bpy)_3^{3+}...MV^{+\cdot},EDTA] \longrightarrow Ru(bpy)_3^{2+} + MV^{+\cdot} + EDTA_{ox}^{+} \tag{16}$$

$$[Ru(bpy)_3^{3+}...MV^{+\cdot},EDTA] \longrightarrow Ru(bpy)_3^{3+} + MV^{+\cdot} \tag{17}$$

$$[Ru(bpy)_3^{3+}...MV^{+\cdot},EDTA] \longrightarrow Ru(bpy)_3^{2+} + MV^{2+} \tag{18}$$

Effect of $[Ru(bpy)_3^{2+}]$

Figures 2 and 3 demonstrate the surprising observation that $\Phi(MV^{+\cdot})$ and, by extension, η_{cr} are strikingly dependent on $[Ru(bpy)_3^{2+}]$ in alkaline solution. In fact, as Figure 5 illustrates, the dependence of $\Phi(MV^{+\cdot})$ on $[Ru(bpy)_3^{2+}]$ at 20mM MV^{2+}, 0.10M EDTA, and pH 11.0 describes a "titration curve" between two plateaus. This behavior is not predicted by the conventional mechanism, nor can it be attributed to variations in values of k_q. It is apparent that the nature of the photosensitizer in this highly ionic medium undergoes a transformation between at least two forms as its concentration is changed.

At the same time, the chemical system remains well behaved. Reactions 1-8 predict that the data from Figure 3, if $1/\Phi(MV^{+}\cdot)$ is plotted vs. $1/[MV^{2+}]$, should yield a straight line with an intercept of $1/\Phi_o(MV^{+}\cdot)$, where $\Phi_o(MV^{+}\cdot)$ is the quantum yield under conditions of the complete dynamic quenching of $^{*}Ru(bpy)_3^{2+}$ at infinite $[MV^{2+}]$, and an intercept/slope ratio of k_3/k_2. Figure 6 shows the treatment of the data; the values of $\Phi_o(MV^{+}\cdot)$ and k_3/k_2 thus derived are given in Table 3. Several features are evident from this treatment. Firstly, the dependence of the behavior of the system on $[Ru(bpy)_3^{2+}]$ is not coupled to $[MV^{2+}]$. Secondly, the apparent values of k_3/k_2 correlate reasonably well with the experimentally determined value of the ratio ($5.7 \times 10^{2} M^{-1}$); at 0.5mM complex, the apparent value of k_3/k_2 is high; the reason for this deviation is not clear. Thirdly, the limiting values of η_{cr} ($= \Phi_o(MV^{+}\cdot)/2$) remain <0.25, but increase by a factor of two as the concentration of $Ru(bpy)_3^{2+}$ is increased.

At a low concentration in the presence of a large excess of EDTA, $Ru(bpy)_3^{2+}$ is undoubtedly highly ion paired as a 1:1 complex according to reaction 12. As the concentration of $Ru(bpy)_3^{2+}$ is increased, the probability of the formation of larger ion paired aggregates increases. We suggest that at high concentrations, $Ru(bpy)_3^{2+}$ is associated with EDTA as 2:1 aggregates formed via reaction 19; our previous suggestion (ref.9,10) that $Ru(bpy)_3^{2+}/MV^{2+}/EDTA$ triple aggregates are formed is not supported by the lack of a dependence of $[MV^{2+}]$ on the behavior of the system at high $Ru(bpy)_3^{2+}$. At low or high concentration, the ion pairing of $Ru(bpy)_3^{2+}$ with EDTA does not result in any change in its absorption or emission spectra, or the lifetime of the luminescent state. Excitation of the aggregates (reaction 20) and their subsequent quenching (reaction 21) can be visualized as yielding the oxidized photosensitizer, reduced electron relay, and sacrificial electron donor within the same solvent-caged unit; the resulting scavenging of $Ru(bpy)_3^{3+}$ by caged EDTA can contribute to higher overall cage release yields. It is not possible, at this time, to evaluate the equilibrium constant of reaction 19 from existing data because of the great uncertainty in the value of K_{eq} of reaction 12, and the possibility that η_{cr} may not be a simple function of the composition of the bulk solution.

$$Ru(bpy)_3^{2+},EDTA \; + \; Ru(bpy)_3^{2+} \rightleftharpoons (Ru(bpy)_3^{2+})_2,EDTA \qquad (19)$$

$$(Ru(bpy)_3^{2+})_2,EDTA \xrightarrow{h\nu} {}^{*}(Ru(bpy)_3^{2+})_2,EDTA \qquad (20)$$

$$^{*}(Ru(bpy)_3^{2+})_2,EDTA \; + \; MV^{2+},EDTA \longrightarrow [Ru(bpy)_3^{3+}...EDTA...MV^{+}\cdot] \qquad (21)$$

The Stern-Volmer quenching plots in Figure 1 show the difference in the behavior of the system at high and low $[Ru(bpy)_3^{2+}]$ at pH 11.0. At 5.0μM in the presence of 0.10M EDTA, the plot shows no significant nonlinearity to the highest concentration of MV^{2+} used (40mM); at 1.0mM in the presence of 0.20M EDTA,

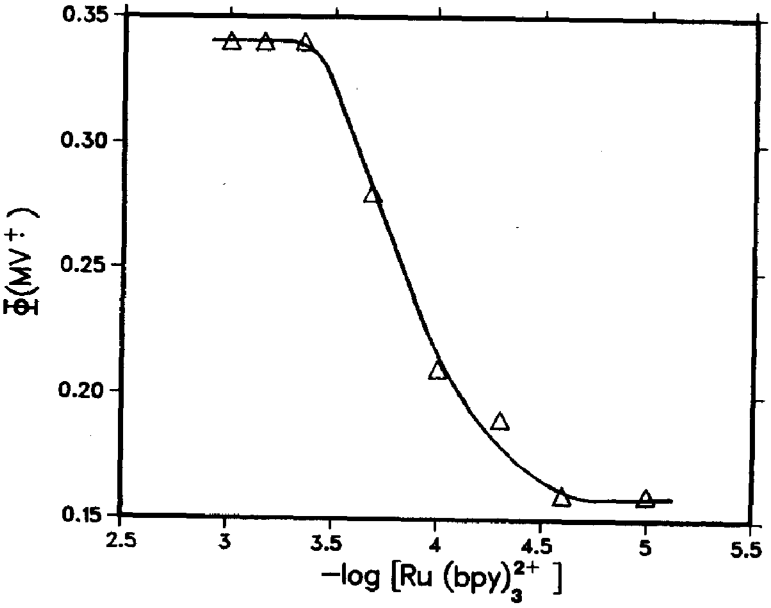

Fig. 5. Dependence of $\Phi(MV^{+}\cdot)$ on $[Ru(bpy)_3^{2+}]$ at pH 11.0 in 0.10M EDTA and 20mM MV^{2+}. (Reprinted with permission from ref.10; copyright (1984) American Chemical Society.)

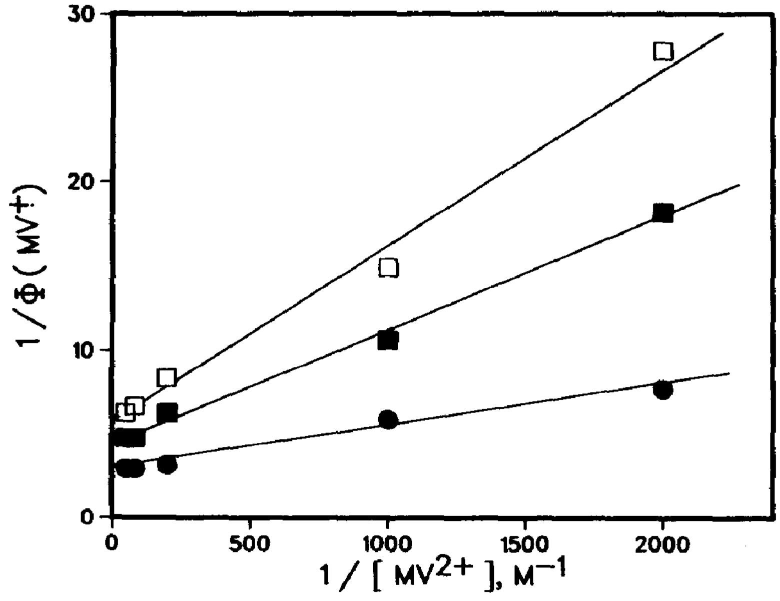

Fig. 6. Reciprocal plot of data from Figure 3.

TABLE 3

Values of $\Phi_o(MV^{+}\cdot)$ and k_3/k_2 from Figure 6.[a]

$[Ru(bpy)_3^{2+}]$, M	$\Phi_o(MV^{+}\cdot)$	k_3/k_2, M^{-1}
5.0×10^{-4}	0.36	1.1×10^{3}
1.0×10^{-4}	0.23	6.6×10^{2}
5.0×10^{-6}	0.18	5.3×10^{2}

[a]0.10M [EDTA], pH 11.0, μ = 1.0M

the deviation from linear behavior over the same range of $[MV^{2+}]$ is striking. For the concentrations of the components used in the quantum yield measurements, nonlinear Stern-Volmer behavior also is not significant. Now, deviations from linear Stern-Volmer lumnescence quenching behavior are characteristic of systems in which "static" quenching of the fluorophore occurs at high quencher concentrations due to molecular association of fluorophore and quencher. If the lifetime of the excited fluorophore-quencher pair is very short due to rapid non-radiative deactivation or chemical reaction, the lifetime of the unassociated fluorophore will be controlled exclusively by dynamic quenching; $\tau_o/\tau = (1 + k_q\tau_o[Q])$. Our results show that τ_o/τ parallels I_o/I at high $[Ru(bpy)_3^{2+}]$ up to 10mM MV^{2+}; within that concentration regime, there is no evidence of static quenching. Lifetime measurements at higher quencher concentrations will require a shorter time resolution than is currently available with our instrumentation; until those measurements can be made, static quenching at high $[MV^{2+}]$ cannot be excluded.

On the other hand, Keizer has pointed out (ref.28) that positive curvature of Stern-Volmer luminescence plots for diffusion-controlled quenching is expected for quencher concentrations greater than ~0.01M with the extent of positive curvature dependent on the nonequilibrium statistical distribution of quencher molecules around the fluorophore. The difference in the Stern-Volmer plots at low and high $[Ru(bpy)_3^{2+}]$ can be attributed to differences in the diffusional behavior and electrostatic properties of the various $Ru(bpy)_3^{2+}$/EDTA aggregates.

Literature Values of $\Phi(MV^{+}\cdot)$

The values of $\Phi(MV^{+}\cdot)$ reported by Nenadovic, *et al.* (ref.8) (0.08-0.60, 0.8, and 1.4-1.5 at pH 2-4.2, 4.7, and 5.3-8.7, respectively) were obtained by *in situ* monitoring of $MV^{+}\cdot$ formation upon the photolysis of solutions containing 0.1mM $Ru(bpy)_3^{2+}$, 5mM MV^{2+}, and 0.1M EDTA. A number of aspects of this report are of particular concern. Firstly, a value of $\epsilon_{605} = 8.6 \times 10^3 M^{-1}cm^{-1}$ for $MV^{+}\cdot$ (ref.29) was used in the spectrophotometric analysis of that product which renders their values of $\Phi(MV^{+}\cdot)$ more than 50% higher than if the more recent ϵ-value (ref.16) were to be used. Secondly, the solutions were not stirred during photolysis (ref.30); the resulting inhomogeneity of the solutions could be the cause of the wide variations in the values of $\Phi(MV^{+}\cdot)$, especially the observation that the formation of $MV^{+}\cdot$ is linear on the sub-second time scale but is not linear over the course of minutes.

We have seen (Figure 4) this same phenomenon for unstirred solutions wherein the initial generation of $MV^{+}\cdot$ is localized in the region traversed by the analyzing light beam resulting in a high apparent yield; the diffusion of the absorbing material throughout the photolysis cell results in a yield that is approximately the same as obtained for continuously stirred solutions (Table 1). The problem of the inhomogeneity of unstirred solutions is especially severe for short photolysis times and rapid formation of $MV^{+}\cdot$ (*i.e.,* high light intensities, high $[Ru(bpy)_3{}^{2+}]$, high $[MV^{2+}]$). We must conclude that the $\Phi(MV^{+}\cdot)$ values reported by Nenadovic, *et al.* (ref.8) are not representative of the true behavior of the $Ru(bpy)_3{}^{2+}/MV^{2+}/EDTA$ system.

In order to reconcile the other reported values of $\Phi(MV^{+}\cdot)$ with those of our standard system (ref.9), it is necessary to compare them on the basis of the same experimental and analytical parameters ($\epsilon(MV^{+}\cdot)$, η_q, [EDTA], pH). Table 4 presents the experimental conditions used to obtain the observed values of $\Phi(MV^{+}\cdot)$. Normalized values of $\Phi(MV^{+}\cdot)$ were calculated by correcting $\epsilon(MV^{+}\cdot)$ used in the analysis of $MV^{+}\cdot$ to $1.37 \times 10^4 M^{-1} cm^{-1}$ (ref.16), and normalizing η_q for $[MV^{2+}] = 0.02M$; because the effect of [EDTA] on $\Phi(MV^{+}\cdot)$ is not known for the conditions used by other workers, correction for that parameter was not made. It is important to note that in acidic solution, the concentration of $Ru(bpy)_3{}^{2+}$ is not an important factor affecting $\Phi(MV^{+}\cdot)$ (ref.9).

Comparison of the normalized values of $\Phi(MV^{+}\cdot)$ at pH 4.7-5.0 reveals that three of the four citations are in more-or-less reasonable agreement; the value reported by Kiwi and Gratzel (ref.4) must be regarded as suspect. The two values in alkaline solution do not agree at all, suggesting that there are additional facile pathways to $MV^{+}\cdot$ operating at pH 13.5. It is possible that complexation of the cations with OH^{-} causes η_{cr} to increase significantly; our work on the thermal reduction of MV^{2+} in highly alkaline solution (ref.31) shows that MV^{2+}-OH^{-} ion pairs are intermediates in the formation of $MV^{+}\cdot$. The $Ru(bpy)_3{}^{2+}$-photosensitized and direct photoreduction of MV^{2+}, in the presence and absence of EDTA, in alkaline media (ref.7,32,33) have a rich chemistry, and deserve further detailed examination.

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TABLE 4

Observed and normalized values of $\Phi(MV^{+}\cdot)$.

$[Ru(bpy)_3{}^{2+}]$, mM	$[MV^{2+}]$, mM	[EDTA], mM	pH	$\Phi(MV^{+}\cdot)$ (obs)	$\Phi(MV^{+}\cdot)^a$ (norm)	Ref.
0.04	2.0	30	5.0	0.30^b	0.48^c	4
0.06	0.5	100	5.0	0.080^d	0.21	5
0.04	2.0	10	5.0	0.11^e	0.15	6
0.05	1.3	1	13.5	0.42^b	0.82^c	7
0.1	20	100	4.7	0.14^f	0.14	9
0.1	20	100	11.0	0.22^f	0.22	9

[a] $\Phi(MV^{+}\cdot)$ normalized to η_q at $[MV^{2+}]$ = 20mM, and for $\epsilon(MV^{+}\cdot) = 1.37 \times 10^4 M^{-1}cm^{-1}$ (ref.16); no correction made for [EDTA].

[b] no value of $\epsilon(MV^{+}\cdot)$ cited; no stirring reported.

[c] no correction made for $\epsilon(MV^{+}\cdot)$.

[d] $\epsilon(MV^{+}\cdot) = 1.1 \times 10^4 M^{-1}cm^{-1}$ (ref.30); stirred solutions.

[e] $\epsilon(MV^{+}\cdot) = 1.19 \times 10^4 M^{-1}cm^{-1}$; no stirring reported.

[f] $\epsilon(MV^{+}\cdot) = 1.37 \times 10^4 M^{-1}cm^{-1}$ (ref.16); stirred solutions.

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