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"Zwitterion" Mediator/Quenchers. Coulombic Minimization of the Back-Reaction in Photocatalysis

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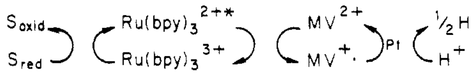
Zwitterionic analogues of methyl viologen, *N,N'*-bis(carboxyethyl)-4,4'-bipyridyl (CEB), and *N,N'*-bis(sulfonatopropyl)-4,4'-bipyridyl (SPB) have been studied as electron-transfer quenchers of excited-state photocatalysts. The molecules are formally neutral when oxidized but become negatively charged when reduced. This charge buildup minimizes undesirable back-recombination of the photogenerated redox products. This Coulombic effect is demonstrated both by direct flash photolysis measurements of back-recombination and by catalytic studies of water reduction. Results are compared for the zwitterion quenchers and methyl viologen, reacting with soluble anionic porphyrins and with micelle-associated reactants. For the anionic porphyrin system zinc tetrakis(sulfonatophenyl)porphyrin(4–) the rates of back-recombination are as follows: $ZnTSPP^{3-} + MV^{+\cdot} \rightarrow ZnTSPP^{4-} + MV^{2+}$ (k), $k = 2 \times 10^9$ M^{-1} s^{-1}; $ZnTSPP^{3-} + CEB^{-\cdot} \rightarrow ZnTSPP^{4-} + CEB^{\pm}$ (k), $k = 6 \times 10^8$ M^{-1} s^{-1}. In a corresponding catalytic system incorporating ZnTPPS as the photoacceptor, CEB or methyl viologen as the quencher, and *N*-phenylglycine as the electron donor, a >2-fold enhancement of catalysis is observed by replacing MV^{2+} with CEB. These events can be greatly accentuated by increasing the charge on the components, via micellar localization. Thus, by using an amphiphilic derivative of $Ru(bpy)_3^{2+}$ as photoactive donor solubilized in anionic micelles and SPB as electron acceptor, one can achieve 200-fold reduction in the rate of the back-reaction.

Introduction

Since the first reports of photocatalytic reduction of water to hydrogen,[1-4] rapid progress has been made in utilizing excited-state electron transfer to catalyze water splitting.[1-10] A basic catalytic system is outlined in reaction I. Here $Ru(bpy)_3^{2+}$ is excited by visible light and



(I)

deexcited by electron transfer to a quencher (e.g., methyl viologen, MV^{2+}). The reduced quencher can be coupled at dispersed Pt to reduce water to hydrogen, while oxidized $Ru(bpy)_3^{3+}$ can oxidize H_2O to dioxygen (in the presence of RuO_2). Alternatively, for model studies, a simple amine can function as an electron donor in lieu of water.

A principal problem with these systems is that the redox products produced in the photoreaction may rapidly recombine, at a diffusion-limited rate, before they can produce H_2 or O_2.

The present manuscript presents a novel approach to minimizing this diffusion-controlled recombination. Previous attempts to mitigate the back-reaction have been based on competitive reactions which scavenge the redox products. For example, in the presence of excess organic amines, the oxidized ruthenium produced in reaction I can be rapidly reduced by the amine, preventing back-recombination. Later, Grätzel[11] showed that sufficiently active platinum could compete with $Ru^{III}(bpy)_3$ for methyl viologen radical, resulting in actual catalytic cleavage of H_2O to O_2 and H_2. Many improvements in this system have since been made.[12] In principle, rather than solely increasing the rate of these competing reactions, it should be possible to slow the rate of the back-reaction itself.

Since effective photocatalysts undergo facile electron transfer, both the redox quenching reaction and the redox back-reaction are generally diffusion controlled. The problem, then, is to devise a scheme for minimizing diffusion of redox products, while the forward reaction remains unaffected.

$$k_q = \frac{-4\pi(D_A + D_B)Z_A Z_B r_0 N_0}{1000(1 - \exp(Z_A Z_B r_0/R))}$$

where D_A, D_B = diffusion coefficients, R = distance of approach, N_0 = Avogadro's number, and $r_0 = e^2/(DKT)$ (D = diffusion constant).

One variable that can readily be controlled is the reactant charge (Z_A, Z_B). Examples of charge-limited diffusion abound. For example, although $Fe(CN)_6^{4-}$ quenches $Ru(bpy)_3^{2+*}$ with a rate $k_q = 10^8$ M^{-1} s^{-1} in bulk solution, the rate is reduced 2–3 orders of magnitude when $Ru(bpy)_3^{2+}$ is sequestered in an anionic SDS micelle.[13]

A key concept in the present report is the use of "zwitterionic" mediator/quenchers which become nega-

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tively charged only on reduction. Thus, the forward reaction can proceed rapidly, without Coulombic barrier, while the back-reaction is retarded by Coulombic repulsion. Examples of this Coulombic effect are given both for small-molecule reactions and for micelle-localized systems.

Experimental Section

Materials. Zinc 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin was prepared according to the procedure of Adler.[14] Methyl viologen (Aldrich) was recrystallized from ethanol. All other reagents of the highest purity available were used without further purification.

The *N,N'*-bis(carboxyethyl)-4,4'-bipyridyl (CEB) was prepared as the dihydrochloride salt by a previously published procedure.[15] 4,4'-Bipyridyl dihydrate (2.6 mmol, 0.5 g, Aldrich) was dissolved in 4 mL of $CHCl_3$. Acrylic acid (1 mL) was added and the solution refluxed for 1 h. HCl in ethanol was added and the resulting white precipitate was recrystallized from ethanol. The product was characterized by NMR (δ = 8.5 and 9.2 (aromatic), 5.0 ($N-CH_2$), 3.1 ($CO-CH_2$)) and by IR spectroscopy. Elemental analysis was satisfactory. *N,N'*-Bis(carboxymethyl)-4,4'-bipyridyl (CMB) was provided us by Dr. J. Farrington (ICI, England). The *N,N'*-bis(sulfonatoethyl)-4,4'-bipyridyl (SEB) was prepared according to a published procedure.[16] *N,N'*-Bis(sulfonato-*n*-propyl)-4,4'-bipyridyl (SPB) was synthesized as follows. 4,4'-Bipyridyl (16 mmol, Fluka, purum 99%) was slowly added to 114 mmol of 1,3-propane sultone (Aldrich, 97%) at 40 °C. The white precipitate was washed in acetone. Further purification was carried out by dissolving the product in water and subsequent precipitation with acetone. This procedure was repeated 3 times. Elemental analysis was satisfactory.

$Ru(bpy)_3^{2+}Cl_2$ (Strem) was used as supplied. Bis(2,2'-bipyridyl)(4,4'-dinonadecyl-2,2'-bipyridyl)ruthenium ($Ru(bpy)_3{\cdot}2C_{19}^{2+}$) was synthesized and kindly provided us by Dr. W. Sasse (CSIRO, Australia). Sodium dodecyl sulfate (NaLS) (Merck, p.a.), sodium tetradecyldioxyethylene sulfate ($C_{14}(OEG)_2SO_4^-Na^+$) (Henkel, Düsseldorf) and octaethylene glycol *n*-dodecyl ether ($C_{12}(OEG)_8OH$) (Nikko Chemicals, Tokyo) were used as supplied. Deionized water was refluxed over $KMnO_4$ and subsequently distilled 3 times in a quartz still. The preparation of the Pt colloidal solution paralleled the procedure in the literature.[11]

Apparatus. The flash photolysis system is described elsewhere.[17] By use of appropriate filters, the sample was irradiated with light of $\lambda > 500$ nm, while the change in absorbance was followed at the Soret band. Laser photolysis experiments were carried out with a frequency doubled Nd laser using fast kinetic spectroscopy as a detection technique. Samples were contained in 1-cm quartz cells and were deaerated by flushing with Ar for at least 35 min.

The emission spectra were measured with a Perkin-Elmer MPF-44 fluorimeter. The excitation wavelengths corresponded to Soret peaks of the particular sample. The emission decay was monitored at the maxima of the respective emission bands.

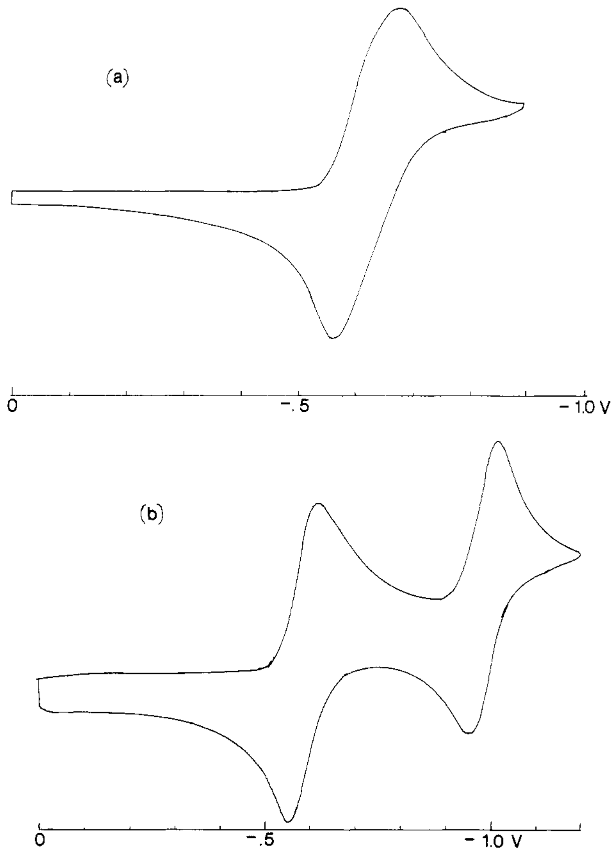

Figure 1. CEB, 20 mV s^{-1}, HMDE, 0.1 M KCl; voltage scale is vs. SCE. (b) SEB, 100 mV s^{-1}, HMDE, 0.1 M KCl; voltage scale is vs. SCE.

TABLE I

quencher	$10^{-3}K_{sv}{}^{a,b}$, M^{-1}	$10^{-3}K_{sv}{}^{a,c}$, M^{-1}	$10^{-8}k_{back}$, $M^{-1}\ s^{-1}$
MV^{2+}	15	1.6	21
CEB	6	1.4	6
SEB	3	0.7	

[a] For quenching of $ZnTPPS^{4-}$ at 25 °C. [b] $\mu \approx 0$. No added salt. [c] $\mu = 0.1$.

The cyclic voltammograms were measured with a PAR Model 175 universal programmer in conjunction with a PAR Model 173 potentiostat.

In all runs, the working electrode was a HMDE, and the concentration of the electrolyte (KCl) was constant at 0.1 M.

Results and Discussion

The cyclic voltammograms (Figure 1) for the zwitterionic mediator/quenchers were very similar to the CV for methyl viologen ($E_{1/2}$ = -0.44 V vs. NHE). The CEB showed a reversible couple centered at -0.39 V (vs. NHE), while, for SEB and SPB, the CV again showed reversibility, with $E_{1/2}$ = -0.35 V (vs. NHE) and -0.37 V, respectively. CMB and CEB have the same $E_{1/2}$.

Both of the zwitterionic species were found to quench the luminescence of $ZnTPPS^{4-}$ quite effectively, though not as effectively as MV^{2+} itself. The values of the relevant kinetic parameters are given in Table I. All three quenchers seemed to show a dependence on ionic strength. This was unexpected for the two formally neutral zwitterions.

The rates of the back-reaction were measured directly by using the flash photolysis apparatus. The back-recombination of $CEB^{-\cdot}$ with $ZnTPPS^{3-}$ proceeded with a rate constant of $6 \times 10^8\ M^{-1}\ s^{-1}$ while the corresponding rate constant for $MV^{+\cdot}$ is $\sim(2.1 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$.

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TABLE II

surfactant[g]	sensitizer[h]	acceptor[i]	$10^6 C_0^{\text{redox}}$,[a,e] M	$10^{-9}k_b$, M^{-1} s^{-1}
no surfactant	$Ru(bpy)_3^{2+}$	SPB	2.8	7.8 ± 0.8[b]
		CMB	2.8	6.5 ± 0.6[b]
NaLS	$Ru(bpy)_3^{2+}$	SPB	1.2	0.9 ± 0.05[c]
		CMB	1.2	0.95 ± 0.1[c]
	$Ru(bpy)_3 \cdot 2C_{19}^{2+}$	SPB	1.6	0.8 ± 0.2[c]
$C_{14}(OEG)_2SO_4^-Na^+$	$Ru(bpy)_3^{2+}$	SPB	1.3	0.17 ± 0.03[d]
		SPB + 0.1 M NaCl	0.9	2.2 ± 0.2
	$Ru(bpy)_3 \cdot 2C_{19}^{2+}$	SPB	4.3	0.04 ± 0.004[d]
$C_{12}(OEG)_8OH$	$Ru(bpy)_3 \cdot 2C_{19}^{2+}$	SPB	0.15	~60[f]

[a] Taken 5 μs after the laser pulse. [b] Evaluated from second-order plot; refers to ionic strength ≃ 3×10^{-4} M. [c] Ionic strength, 8.3×10^{-3} M. [d] Ionic strength, 1.3×10^{-3} M. [e] Absorbance of $Ru(bpy)_3^{2+}$ at 530 nm = 0.075; that of $Ru(bpy)_3 \cdot 2C_{19}^{2+}$ = 0.12. [f] Only approximate value due to very small yield. [g] 2×10^{-2} M. [h] 10^{-4} M. [i] 10^{-3} M.

The effectiveness of the rate reduction was also measured indirectly in a photocatalytic system. The test system consisted of ~1.1×10^{-5} M $ZnTPPS^{4-}$, 1×10^{-3} M N-phenylglycine, 3×10^{-3} M quencher, and varying amounts of colloidal platinum in a pH 5 buffer ($\mu = 0.1$).

At platinum concentrations of >10 μM, the rate of hydrogen production in the CEB system exceeds that in the MV^{2+} system by 2–3-fold. This shows that the charge-dependent reduction in back-reaction rate can be translated into an increase in catalytic efficiency.

This effect can, of course, be accentuated by increasing Z_A or Z_B. One such approach is to localize the photoactive system in a charged matrix (e.g., a micelle).

Kinetic data obtained with the micellar system are summarized in Table II. Three different surfactants were examined of which two are anionic and one is neutral. The sensitizer employed is $Ru(bpy)_3^{2+}$ or the surfactant derivative $Ru(bpy)_3 \cdot 2C_{19}^{2+}$. The viologens CMB and SPB were tested as quenchers and the parameters C_0^{redox} and k_b determined by laser flash photolysis technique. The former designates the concentration of reduced viologen present 5 μs after the laser pulse and hence is a measure for the efficiency of the forward electron-transfer reaction. (In comparing C_0^{redox} values obtained from $Ru(bpy)_3^{2+}$ and its surfactant derivative, one has to take into account that the absorption of $Ru(bpy)_3 \cdot 2C_{19}^{2+}$ is higher at the excitation wavelength of 530 nm (cf. Table II, footnote e).)

In pure water the forward electron transfer between excited $Ru(bpy)_3^{2+}$ and SPB occurs with a rate constant of 1.3×10^9 M^{-1} s^{-1} while the backward reaction has a specific rate of 6.5×10^9 M^{-1} s^{-1}. The latter is about 3 times faster than that obtained with methyl viologen. The yield of redox products is comparable to that obtained with simple methyl viologen and the same sensitizer. Addition of NaLS micelles produces an 8-fold decrease in k_b and diminishes the yield of redox products by a factor of 2–2.5 for both $Ru(bpy)_3^{2+}$ and its surfactant derivative. In contrast, in the presence of $C_{14}(OEG)_2SO_4^-$ micelles, the behavior displayed by these two sensitizers is drastically different. $Ru(bpy)_3^{2+}$ gives a similar yield of reduced viologen as in NaLS. The retardation of the back-reaction is more pronounced and amounts here to a factor of 40 with respect to pure aqueous solution. $Ru(bpy)_3 \cdot 2C_{19}^{3+}$ on the other hand gives a 2.5-times higher yield of redox products as compared to NaLS micelles. The retardation of the back-reaction is here very pronounced and corresponds to a factor of 200 with respect to aqueous solution. Apparently, the effect of light-induced charge separation is optimal with this amphiphilic redox chromophore in the tetradecyloxyethylene sulfate micellar assemblies. Addition of 10^{-1} M NaCl to the $C_{14}(OEG)_2SO_4^-$ micelles enhances the back electron transfer by a factor of 13, while from the kinetic salt effect an increase of k_b by a factor of 2 is expected. The last row in Table II shows that both the yield of redox products and the rate of back-reaction are very unfavorably influenced by nonionic micelles.

These observations may be rationalized in terms of local electrostatic fields present at the micelle–water interface and the site of solubilization of the redox chromophore. Both viologens, CMB and SPB, while neutral in the oxidized state acquire a negative charge upon reduction and hence should be repelled from the micellar surface once electron transfer has occurred. As the oxidized ruthenium complex is retained by the anionic micelle, this provides a mechanism for light-induced charge separation. The yield of redox products C_0^{redox} will depend on the relative rates of intramicellar back electron transfer and escape of the reduced viologen from the micellar surface. (C_0^{redox} is determined 5 μs after the laser pulse and hence measures only the part of radical ions that escapes intramicellar back-reaction.) For the surfactant ruthenium complex, Table II shows a much higher yield for $C_{14}(OEG)_2SO_4^-$ as compared to NaLS micelles. Apparently the site of solubilization of the chromophore as well as high local electric field typical for the former micelles favors light-induced charge separation.

A further advantage of $C_{14}(OEG)_2SO_4^-$ with respect to NaLS micelles is that a more drastic retardation of the back-reaction can be achieved. This apparently is a consequence of the higher surface potential of the former aggregates arising from their low cmc value. With respect to the back-reaction, the behavior of simple $Ru(bpy)_3^{2+}$ is again significantly different from that of its surfactant derivative. The smaller rate constant for the back electron transfer observed may be a consequence of different solubilization sites of the two redox chromophores. Apparently in the case of $Ru(bpy)_3 \cdot 2C_{19}^{2+}$, the two alkyl chains pull the ruthenium complex farther into the micelle, making the access of reduced viologen and hence back electron transfer more difficult. The access of SPB^- to the anionic micelle is controlled by the encounter probability $\exp(-\psi(r)e/kT)$. As the radial potential function $\psi(r)$ is particularly steep in the micellar Stern layer, the ease of encounter between reduced relay and oxidized sensitizer should be particular sensitive to the solubilization site of the latter in the micelle–water interface.

In conclusion, the present study shows that the simple electrostatic model of micellar inhibition of photoredox reactions needs considerable refinement. Drastic differences were observed between the performance of two surfactants of similar chemical structure and identical charge. Also, the solubilization site of the redox chromophore appears to influence greatly the kinetics and yields of the electron-transfer reactions. These data should be of great value for the design of molecular assemblies achieving efficient light-induced charge separation.[17]