SENSITIZED PHOTOREDUCTION OF METHYL VIOLOGEN BY METALLOPORPHYRINS

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Summary

We report the sensitized photoreduction of methyl viologen by a series of porphyrins and metalloporphyrins using visible light in the presence of triethanolamine. Electrochemical studies and absorption and emission spectra are used to identify the redox potentials of the relevant photoexcited states and to calculate the thermodynamic driving forces for quenching and subsequent thermal reactions. Electron spin resonance data are used to confirm the occurrence of oxidative and/or reductive quenching in these various systems. In general, the quantum yields for methyl viologen reduction parallel the thermodynamic driving force in a regular manner. The complex (L)(OAc)rhodium(III)tetraphenylporphyrin (L ≡ solvent molecule) is shown to be an effective catalyst which photoreduces methyl viologen via an oxidative pathway with a quantum yield as high as 51%. Lifetimes and quenching constants are also reported for these species.

1. Introduction

Porphyrins [1 - 7], phthalocyanines [8 - 12] and polypyridyl complexes of ruthenium and chromium [13 - 35] have been extensively studied as catalysts in the photoreduction of methyl viologen leading thereby to hydrogen production and to the achievement of solar energy conversion. The tris(bipyridyl)ruthenium(II) cation has been studied in most detail because of its photophysical and photochemical properties. Few metalloporphyrins have been studied in such detail. Those for which a significant amount of data have been published include tetraphenylporphyrin (TPP) derivatives of zinc, manganese and ruthenium, some sulphonated derivatives ($TPPS^{4-}$) of these metals, zinc tetramethylpyridinium porphyrin ($ZnTMPyP^{4+}$) and haematoporphyrin.

Interest has centred on identifying the photoactive excited states and their energies, measuring the luminescent quantum yields and excited state lifetimes, and studying the quenching behaviour. The quenching studies have

included the use of electron donors (reductive quenching), such as mercapto-ethanol, ethylenediaminetetraacetic acid (EDTA), triethanolamine (TEOA) etc., and electron acceptors (oxidative quenching), usually methyl viologen and its derivatives or a quinone. In particular, research groups have used these species to photogenerate reduced methyl viologen which can react with water, in the presence of a platinum catalyst, to generate hydrogen gas [36]. In some cases, significant net yields of reduced methyl viologen (about 80%) have been observed in three-component systems in which a sacrificial donor, such as EDTA, provides the electrons for reduction.

Many porphyrins exhibit triplet state lifetimes of the order of a few milliseconds and triplet quantum yields approaching unity and absorb significantly near 450 - 500 nm in the visible solar spectrum.

We report here further three-component data for some of these species, including some new quantum yield measurements, and introduce (L)(OAc)rhodium(III)tetraphenylporphyrin ((L)(OAc)Rh(III)TPP; L ≡ axial solvent molecule), a new and powerful photocatalyst.

Ground state electrochemical data, in association with emission data, can be used to provide a fairly accurate assessment of the excited state redox potentials. The driving force for reductive and oxidative quenching can then be calculated and rationalized with kinetic and thermodynamic data. Such a study is reported here.

2. Experimental details

The Zn(II)TPP complex was prepared by published methods [37]. CORuTPP(EtOH) was prepared according to the method of Tsutsui *et al.* [38]. Rh(III)TPP(OAc) was prepared by refluxing TPP and $Rh_2(OAc)_4$ in dimethylformamide (DMF) for 12 h and was purified by chromatography over alumina with chloroform as the eluent. The final purity was checked by high pressure liquid chromatography with a 1:1 chloroform:tetrahydrofuran eluent on a silica analytical column 25 cm long. The rate was 1 ml min^{-1} at room temperature. The theoretical content of $C_{46}H_{37}N_4O_5Rh$ is 66.67% C, 4.50% H and 6.76% N; the sample prepared contained 66.9% C, 4.8% H and 7.1% N.

Haematoporphyrin was purchased from Sigma. TEOA and methyl viologen were purchased from Aldrich and used as received.

The electronic spectra were recorded on a Hitachi–Perkin–Elmer model 340 microprocessor-controlled spectrophotometer.

2.1. Electrochemical data

Cyclic voltammetry measurements were performed in spectral grade DMF with a platinum wire working electrode and *n*-butyl ammonium perchlorate as the supporting electrolyte. The measurements were made against a saturated calomel electrode (SCE) using Princeton Applied Research models 173, 174A, 175 and 179 equipment, a Houston 9002A *x–y* recorder

and a Tektronix 5103N storage oscilloscope. Full details of the experiments have been presented elsewhere [39]. The measured potentials in SCE/DMF were converted to normal hydrogen electrode (NHE)/H_2O by adding 0.24 V.

2.2. Quenching studies

The emission spectra were recorded on a Varian SF330 spectrofluorometer. Degassed solutions of the photosensitizer were recorded for their emission by exciting the Soret band. Solutions of the quencher were made at different molar concentrations and degassed by bubbling argon through them. The solvents were similarly degassed. The photosensitizer (3 ml) and quencher (3 ml) were mixed and the emission intensity was measured. This was carried out for various concentrations of the quencher. The measurements were compared with a standard containing 3 ml of photosensitizer and 3 ml of solvent.

A 1:1 DMF:water solvent mixture was used for the lifetime studies. The concentration of the photosensitizer (porphyrin) was similar to the concentration used in the quantum yield measurements. Solutions were excited with a nitrogen laser model NRB 0.5-5-150/B (National Research Group Inc.) which produced a 500 kW pulse of halfwidth 5 ns at 337 nm.

2.3. Electron spin resonance irradiation studies

Light from a Photochemical Research Associates 450 W xenon arc source in a PRA model ALH220 lamp housing and using a PRA 301S and 302 power supply was transmitted through the electron spin resonance (ESR) cavity using a concave lens. The heat generated by the IR radiation was absorbed by a water-jacketed Pyrex glass filter and UV light was eliminated by using appropriate filters. A solution of the photosensitizer and the quencher was placed in an ESR tube and degassed by numerous freeze–pump–thaw processes. The tube was placed in the ESR cavity and irradiated for 10 min. The ESR spectra were recorded before, during and after irradiation. Solutions of methyl viologen and TEOA, the ESR spectra of which were recorded separately in both the presence and the absence of light, were used as controls.

2.4. Quantum yields

Irradiations were carried out using a 250 W quartz halogen lamp in conjunction with a 350 nm cut-off filter and narrow-band filters centred at 400 and 430 nm. The narrow-band filters had a half-bandwidth of less than 3 nm. The quantum yields were measured using ferrioxalate as the actinometer [40]. All the solutions were prepared immediately before measurements, degassed by several freeze–pump–thaw cycles and maintained at 25 °C by a thermostatted water bath.
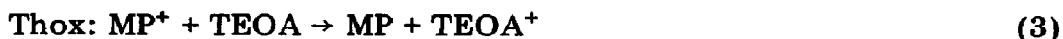
3. Results and discussion

The mechanistic aspects whereby methyl viologen can be reduced in a three-component system via an oxidative or reductive pathway have been

very adequately discussed in the past [41 - 45]. For convenience of discussion, we indicate here the relevant equations without further comment (see ref. 8 for the nomenclature used).
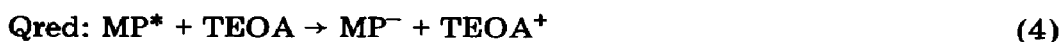
The catalyst MP absorbs a visible light photon:

$$MP + h\nu \rightarrow MP^* \tag{1}$$

This may be followed by oxidative quenching

$$Qox: MP^* + MV^{2+} \rightarrow MV^+ + MP^+ \tag{2}$$

$$Thox: MP^+ + TEOA \rightarrow MP + TEOA^+ \tag{3}$$

or reductive quenching

$$Qred: MP^* + TEOA \rightarrow MP^- + TEOA^+ \tag{4}$$

$$Thred: MP^- + MV^{2+} \rightarrow MP + MV^+ \tag{5}$$

MP and MV represent metalloporphyrin and methyl viologen respectively, Qox and Thox denote oxidative quenching and its thermal follow-up reaction, and Qred and Thred denote reductive quenching and its thermal follow-up reaction.

The relevant mechanism for each photocatalyst can be deduced from Stern−Volmer quenching studies. Where the lifetime τ_0 of the emitter in the absence of a quencher is known, the Stern−Volmer equation can be used to derive the quenching rate constant k_q [46].

Mechanistic information can also be obtained by observing radicals which may be formed when the catalyst, in the presence of a donor or acceptor, is irradiated with visible light in an ESR cavity. Oxidative quenching by methyl viologen can be detected in this fashion with some of the photocatalysts discussed here. At room temperature in fluid solution the characteristic multiline signal of the MV^+ radical is observed within seconds after the light is switched on owing to the photostationary quantity of the reduced methyl viologen so produced. It decays to zero "instantly" the light is switched off, reflecting the rapidity of the back reaction in the cage. Reductive quenching with TEOA leads to a free-radical signal [2] which does not decay rapidly when the light is switched off because of the decomposition of this radical to other radicals which do not react readily with the photocatalyst. Using these methods, we were able to demonstrate oxidative quenching by methyl viologen of the photoexcited states of (L)(OAc)Rh(III)TPP, (L)(CO)Ru(II)TPP (L ≡ solvent), haematoporphyrin and to a lesser extent ZnTPP. Neither ZnTPP nor (L)(CO)Ru(II)TPP are quenched by TEOA, even at 1 M concentration, but (L)(OAc)Rh(III)TPP and haematoporphyrin are quenched inefficiently. Stern−Volmer plots lead to the data shown in Table 1.

In a three-component system, with TEOA as the electron donor, there is a net build-up of reduced methyl viologen characterized by its electronic spectrum (λ_{max}, 395 and 605 nm). Quantum yields are also shown in Table 1. Since the degree of quenching is dependent upon the concentration of

TABLE 1

Lifetimes τ_P of the triplet excited state, quantum yields ϕ and quenching constants k_q for the photoreduction of methyl viologen as a function of concentration

Compound	τ_P	k_q $(10^{-6}$ M^{-1} $s^{-1})$	$[MV^{2+}]$ $(10^2$ M)	ϕ
(L)(OAc)Rh(III)TPP	144 μs[a]	1.3[b], 8.8[c]	0.453	0.18
			2.360	0.38
			5.320	0.51
(L)(CO)Ru(II)TPP	36 μs[d] [47]	664[d] [47]	0.353	0.06
			2.66	0.30
Zn(II)TPP	2.5 ms[e] [48]	0.37[e] [48]	0.359	0.014
			2.82	0.08
			5.63	0.09
Hm[f]	227 μs[a]	4.6[a]	0.243	0.06
			2.69	0.22

[a]Measured in 1:1 DMF:H_2O at 293 K.
[b]Lifetime quenching.
[c]Intensity quenching.
[d]Measured in dimethyl sulphoxide.
[e]Measured in water–Triton X.
[f]Hm, haematoporphyrin.

methyl viologen, these yields are also dependent thereon as demonstrated in Table 1. The efficiency of these photocatalysts decreases in the sequence: Rh > Ru $\gg$ Zn $\approx$ Hm.

Table 2 contains catalyst ground state electrochemical data, many of which have been measured for the first time. In all cases both the first reduction and the first oxidation occur at the porphyrin ring [47, 49, 50]. Previous studies [47, 49, 50] leave little doubt that the photoemitting and photoactive state is a spin triplet $\pi\pi^*$ transition. A moderately accurate evaluation of the excited state redox couples is obtained from the ground state potentials $E(MP^+|MP)$ and $E(MP|MP^-)$ and the spin triplet energy E_T:

$$E(MP^+|MP^*) = E(MP^+|MP) - E_T \qquad (6)$$

$$E(MP^*|MP^-) = E(MP|MP^-) + E_T \qquad (7)$$

A slightly more positive value of E_T than is experimentally observed should be used to account for vibrational contributions and the difference in electronic entropy between the ground state singlet and excited state triplet [47].

A summary of these data is also shown in Table 2. The driving forces for eqns. (2) - (5) can be calculated from these data [8] and they are also listed in Table 2. Under standard conditions both the oxidative quenching Qox and the thermal follow-up reaction Thox are thermodynamically downhill for the four photocatalysts. In contrast, the reductive quenching

TABLE 2

Calculated and excited state redox energies, ground state and excited state driving energies and back-reaction driving energies together with the triplet state energies for some porphyrins and metalloporphyrins

Compound[a]	$P^+|P$ (V(NHE))	$P|P^-$ (V(NHE))	T_{0-0} (eV)	$P^+|P^*$ (V(NHE))	$P^*|P^-$ (V(NHE))	Qox (eV)	Thox (eV)	Qred (eV)	Thred (eV)	Bacox (eV)	Bacred (eV)
Zn(II)TPP	1.03	−1.13	1.60	−0.57	0.47	0.13	0.21	−0.35	0.69	1.47	1.95
Hm	1.01	−1.09	1.8	−0.79	0.71	0.35	0.19	−0.11	0.65	1.45	1.91
(L)(CO)Ru(II)TPP	1.15	−1.20	1.8	−0.65	0.60	0.21	0.33	−0.22	0.76	1.59	2.02
(L)(OAc)Rh(III)TPP	1.06	−1.07	1.8	−0.74	0.73	0.30	0.24	−0.09	0.63	1.50	1.89

[a]The electrochemical data remeasured in the common solvent DMF agreed well with previous literature values in various solvents. The data for (L)(OAc)Rh(III)TPP (L = DMF) are reported here for the first time.

Qred is uphill under standard conditions. Therefore the experimental obser-vations of facile oxidative quenching and the difficulty or absence of reductive quenching are consistent with the thermodynamic data. Clearly kinetic factors are at work and thermodynamic arguments can only be used as a guide [8].

Pileni and coworkers [3, 48] have reported that ZnTPP is not quenched by methyl viologen in a cationic micelle but that the C_{14} analog of methyl viologen can effectively quench this photocatalyst. Methyl viologen itself will quench excited ZnTPP in the neutral micelle composed of Triton X [48]. Okura and Kim-Thuan [7] report hydrogen production from a mercaptoethanol–ZnTPP–hydrogenase system, also using Triton X. The thermodynamic data in Table 2 suggest that oxidative quenching might indeed occur where kinetic constraints do not impede. We directly observed reduced methyl viologen in an ESR cavity using ZnTPP–methyl viologen–water–DMF irradiated with visible light. The quantum yields in three-component systems, however, are much lower than those for the other catalysts studied (Table 1).

Our data for (L)(CO)Ru(II)TPP are consistent with a previous detailed study by Meyer and coworkers [41, 47] and work by Okura and Kim-Thuan [4] who generated hydrogen via hydrogenase. The electrochemical potentials in DMF solution shown in Table 2 are similar to those reported by Meyer and coworkers who, however, used different solvents for reduction and oxidation [47]. Quantum yields for methyl viologen reduction are reported here for the first time. The K_{sv} values are similar to those reported by Meyer and coworkers [47].

A previous study of haematoporphyrin [2] using mercaptoethanol as a donor demonstrated reductive quenching with the formation of the Hm⁻ anion. Our study reveals quenching by both TEOA and methyl viologen. The thermodynamic data (Table 2) favour oxidative quenching. Lifetime and quenching data are shown in Table 1. Methyl viologen quenching (k_q = 4.6 × 10^6 M^{-1} s^{-1}) was much more efficient than TEOA (reductive) quenching.

(L)(OAc)Rh(III)TPP (L ≡ axial solvent molecule) has been examined for the first time and found to be a most promising photocatalyst. The electronic absorption and emission spectra (Fig. 1) are similar to those of Rh(III)(OEP)Cl (OEP ≡ octaethylporphyrin) [51]. The excited state is reasonably long lived (144 μs). Stern–Volmer plots for oxidative quenching (with methyl viologen) monitoring both the relative intensity and the lifetime yielded quenching rates k_q of (1.3 - 8.8) × 10^6 M^{-1} s^{-1}. Thus significant quenching occurs at methyl viologen concentrations of 10^{-3} - 10^{-4} M. In contrast, quenching with TEOA was very inefficient. Certainly, under the conditions of the three-component reaction, oxidative quenching will prevail and will lead to quantum yields for net reduced methyl viologen production of as much as 50%. This is a very efficient photosensitizer for methyl viologen reduction operating under oxidative quenching conditions. Under similar conditions, Ru(bpy)$_3^{2+}$ is oxidatively quenched to yield reduced methyl viologen with about 20% yield.
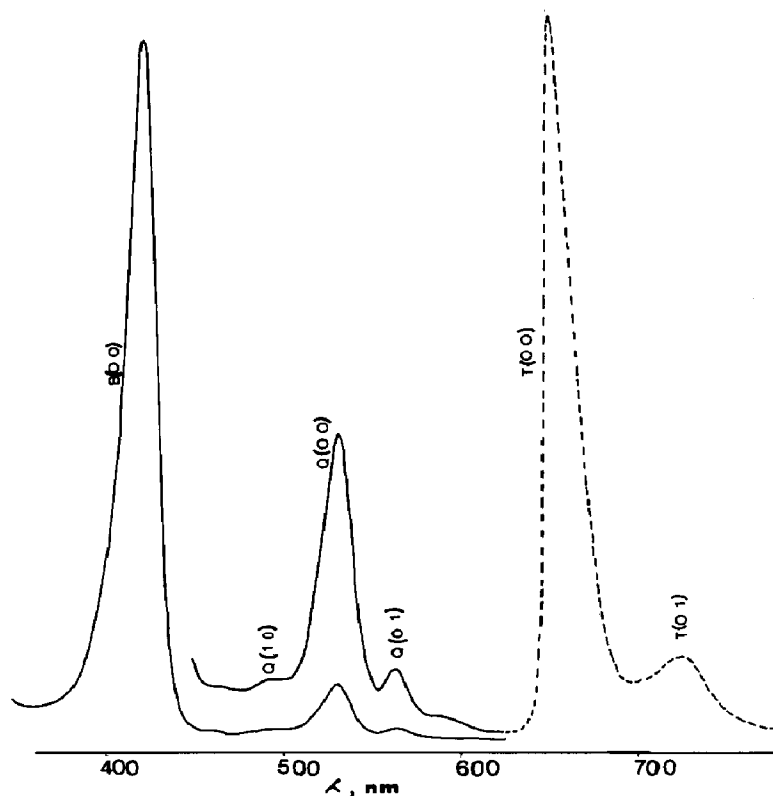
Fig. 1. Absorption and emission spectrum of (L)(OAc)Rh(III)TPP in DMF solution.

The (TPP$^+$)Rh(III)|TPPRh(III) couple is observed at 1.06 V(NHE) and should be capable of oxidizing water at pH 7 in the presence of a suitable catalyst such as RuO$_2$ [22, 52, 53]. (L)(OAc)Rh(III)TPP joins the expanding group of TPP derivatives being studied for solar energy conversion catalysis [54 - 58]. The production of hydrogen and oxygen directly using this catalyst is currently being studied.

Acknowledgments

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