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SENSITIZED PHOTO-REDUCTION OF METHYL VIOLOGEN BY METALLOPORPHYR--ETC(U)
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BY

A.B.P. Lever*, B.S. Ramaswamy and S. Licoccia

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by: A.B.P. Lever^{*}, B.S. Ramaswamy^{*} and S. Licoccia

ABSTRACT:-

We report the sensitized photo-reduction of methyl viologen by a series of porphyrins and metalloporphyrins, by visible light, in the presence of triethanolamine. Electrochemical studies and absorption and emission spectra are used to identify the redox potentials of the relevant photo-excited states and to calculate 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)Rh(III)TPP (L = solvent molecule) is shown to be an effective catalyst, photoreducing methyl viologen via an oxidative pathway with a quantum yield as high as 51%. Lifetimes and quenching constants are also reported for these species.



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SENSITIZED PHOTO-REDUCTION OF METHYL VIOLOGEN BY METALLOPORPHYRINS

by: A.B.P. Lever^{*}, B.S. Ramaswamy^{*} and S. Licoccia

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Porphyrins [1-7], phthalocyanines [8-12], 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 achieve solar energy conversion. The tris(bipyridyl)ruthenium(II) cation has been studied in most detail for 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 (TPPS⁴⁻) thereof, zinc tetramethylpyridinium porphyrin (ZnTMPyP⁴⁺) and hematoporphyrin.

Interest has centered on identifying the photoactive excited states and their energies, measuring luminescent quantum yields and excited state lifetimes, and with quenching studies. These last include use of electron donors (reductive quenching) such as mercaptoethanol, 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, with a platinum catalyst, to generate hydrogen gas [36]. In some cases, significant net yields of reduced methyl viologen (ca 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, 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)Rh(III)TPP, 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 rationalised with kinetic and thermodynamic data. Such a study is reported here.

Experimental:- The Zn(II)TPP complex was prepared by published methods [37]. CORuTPP(EtOH) was prepared according to the method of Tsutsui [38]. Rh(III)TPP(OAc) was prepared by refluxing TPP and $\text{Rh}_2(\text{OAc})_4$ in DMF for 12 hours and purified by chromatography over alumina with chloroform as the eluent. Final purity was checked by HPLC with CHCl_3/THF , (1:1), on a 25cm silica analytical column. The rate was 1ml/Min at room temperature.

Analysis: $\text{C}_{46}\text{H}_{37}\text{N}_4\text{O}_5\text{Rh}$ requires C,66.67,H,4.50,N,6.76%

Found: C,66.9,H,4.8,N,7.1%

Hematoporphyrin was purchased from Sigma. Triethanolamine and methyl viologen were purchased from Aldrich and used as such.

Electronic spectra were recorded on a Hitachi-Perkin Elmer model 340 microprocessor controlled spectrophotometer.

Electrochemical Data:- Cyclic voltammetry measurements were performed in spectra grade DMF with a Pt wire working electrode and n-butylammoniumperchlorate as the supporting electrolyte. The measurements were made vs SCE using Princeton Applied Research Models 173, 174A, 175 and 179 equipment, a Houston 9002A XY recorder and a Tektronix 5103N storage

oscilloscope. Full details of the experiments are presented elsewhere [39]. The measured potentials in SCE/DMF were converted to NHE/H₂O by adding 0.24V.

Quenching Studies:- Emission spectra were recorded on a Varian SF330 Spectrofluorimeter. Degassed solutions of the photosensitiser were recorded for their emission by exciting the Soret band. Solutions of the quencher were made at different molar concentrations and degassed with bubbling argon. Solvents were similarly degassed. Photosensitiser (3 ml) and quencher (3 ml) were mixed and the emission intensity measured. This was carried out for various concentrations of the quencher. The measurements were compared with a standard containing photosensitiser (3 ml) and solvent (3 ml).

A 1:1 DMF/water solvent mixture was used for lifetime studies. The concentration of photosensitiser (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 Incorporated) producing a 500kW pulse of half-line width 5ns, at 337 nm.

ESR Irradiation Studies:- Light from a Photochemical Research Associates 450 watt Xenon Arc Source in a PRA model ALH220 lamp housing and using a PRA 301S and 302 power supply was transmitted through the esr cavity using a concave lens. The heat generated by the infrared radiation was absorbed by a water jacketed Pyrex glass filter and uv light was eliminated using appropriate filters. A degassed solution of the photosensitiser and the quencher was taken in an esr tube and degassed by numerous freeze-thaw processes. The tube was placed in the esr cavity and irradiated for 10 minutes. The esr spectra were recorded before irradiation, during the irradiation and after irradiation. Solutions of methyl viologen and TEOA, recorded separately both in the presence and the absence of light, were used as controls.

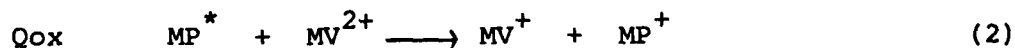
Quantum Yields:- Irradiations were carried out using a 250 watt quartz halogen lamp in conjunction with a 350 nm cutoff filter and narrow band filters centered at 400 and 430 nm. The narrow band filters had a half band width of less than 3 nm. Quantum yields were measured using Ferrioxalate as the actinometer [40]. All solutions were prepared immediately before measurements degassed through several freeze-thaw cycles, and maintained at 25 ° C by a thermostated water bath.

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 nomenclature used).

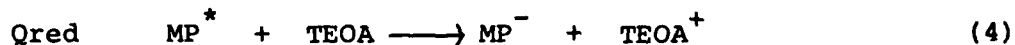
The catalyst MP absorbs a visible light photon:



This may be followed by oxidative quenching:



Or reductive quenching:



The relevant mechanism for each photocatalyst can be deduced from Stern-Volmer quenching studies. Where the lifetime of the emitter τ_0 , in the absence of a quencher is known, the Stern-Volmer equation may 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 multi-line signal of the MV^+ radical is observed within seconds after the light is switched on, due to the photo-stationary quantity of 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 photo-excited states of (L)(OAc)Rh(III)TPP, (L)CORu(II)TPP (L = solvent) and hematoporphyrin, and to a smaller extent, ZnTPP. Neither ZnTPP nor (L)CORu(II)TPP are quenched by TEOA, even at 1M concentration, but (L)(OAc)Rh(III)TPP and hematoporphyrin are quenched inefficiently. Stern-Volmer plots lead to the data shown in Table 1.

In a three component system, with TEOA as electron donor, there is a net build-up of reduced methyl viologen characterised 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 methyl viologen, these yields are also dependent thereon as demonstrated in Table 1. The efficiency of these photocatalysts decreases in the sequence:



Table 2 contains catalyst ground state electrochemical data, many measured for the first time. In all cases, both the first reduction and the first oxidation occur at the porphyrin ring [47-49]. Previous studies [47-49] 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 $E(\text{MP}^+/\text{MP})$ and $E(\text{MP}/\text{MP}^-)$ and spin triplet energy E_T :

$$E(\text{MP}^+/\text{MP}^*) = E(\text{MP}^+/\text{MP}) - E_T \quad (6)$$

$$E(\text{MP}^*/\text{MP}^-) = E(\text{MP}/\text{MP}^-) + E_T \quad (7)$$

A slightly more positive value of E_T should be used, than is experimentally observed, 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 equations (2-5) can be calculated therefrom [8] and are listed in Table 2. Under standard conditions both oxidative quenching, Q_{ox} , and the thermal follow-up reaction, Th_{ox} , are thermodynamically downhill for the four photocatalysts. Reductive quenching, Q_{red} , on the other hand, is uphill, under standard conditions. Therefore, the experimental observations 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 co-workers [3,50] report that ZnTPP is not quenched by methyl viologen in a cationic micelle but 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 [50]. Okura and Thuan quote [7] 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 observe reduced methyl viologen in an esr cavity using visible light irradiated ZnTPP/methyl viologen/water/DMF. The quantum yields, in a three component system are, however, much lower than the other catalysts studied (Table 1).

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

A previous study of hematoporphyrin [2] using mercaptoethanol as a donor demonstrated reductive quenching with formation of the Hm^- anion. Our study reveals quenching by both TEOA and methyl viologen. The thermodynamic data (Table 2) would favour oxidative quenching. Lifetime and quenching data are shown in Table 1. Methyl viologen quenching ($k_q = 4.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) 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 [51]. The excited state is reasonably long lived (144 μs). Stern-Volmer plots for oxidative quenching (with methyl viologen) monitoring both relative intensity and lifetime yielded quenching rates $k_q = 1.3 - 8.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Thus significant quenching occurs at methyl viologen concentrations of $10^{-3} - 10^{-4} \text{ M}$. In contrast quenching with TEOA was very inefficient. Certainly under the conditions of the three-component reaction, oxidative quenching will prevail, and leads to quantum yields for net reduced methyl viologen production of as much as 50%. This is a very efficient photosensitizer reported for methyl viologen reduction operating under oxidative quenching conditions. Under similar conditions, $\text{Ru}(\text{Bipy})_3^{2+}$ is oxidatively quenched to yield reduced methyl viologen in about 20% yield.

The $(\text{TPP}^+) \text{Rh(III)}/\text{TPPRh(III)}$ couple is observed at 1.06V (vs NHE)

and should be capable of oxidising water at $\text{pH} = 7$ in the presence of a suitable catalyst such as RuO_2 [22,52,53]. $(\text{L})(\text{OAc})\text{Rh}(\text{III})\text{TPP}$ 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.

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Table 1

Lifetimes of triplet excited state τ_p , 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
Rh(III)TPP(OAc)L	$\tau_p^a = 144 \mu \text{ sec.}$	0.453	0.18
	$k_q = 1.3^b, 8.8^c$	2.360	0.38
		5.320	0.51
Ru(II)TPP(CO)L	$\tau_p^d = 36 \mu \text{ sec. [47]}$	0.353	0.06
	$k_q^d = 664$ [47]	2.66	0.30
Zn(II)TPP	$\tau_p^e = 2.5 \text{ ms [50]}$	0.359	0.014
	$k_q^e = 0.37$ [50]	2.82	0.08
		5.63	0.09
Hm	$\tau_p^a = 227 \mu \text{ sec.}$	0.243	0.06
	$k_q^a = 4.6$	2.69	0.22

a) 1:1 DMF/H₂O, 293K

b) Lifetime quenching

c) Intensity quenching

d) DMSO

e) Water/Triton-X

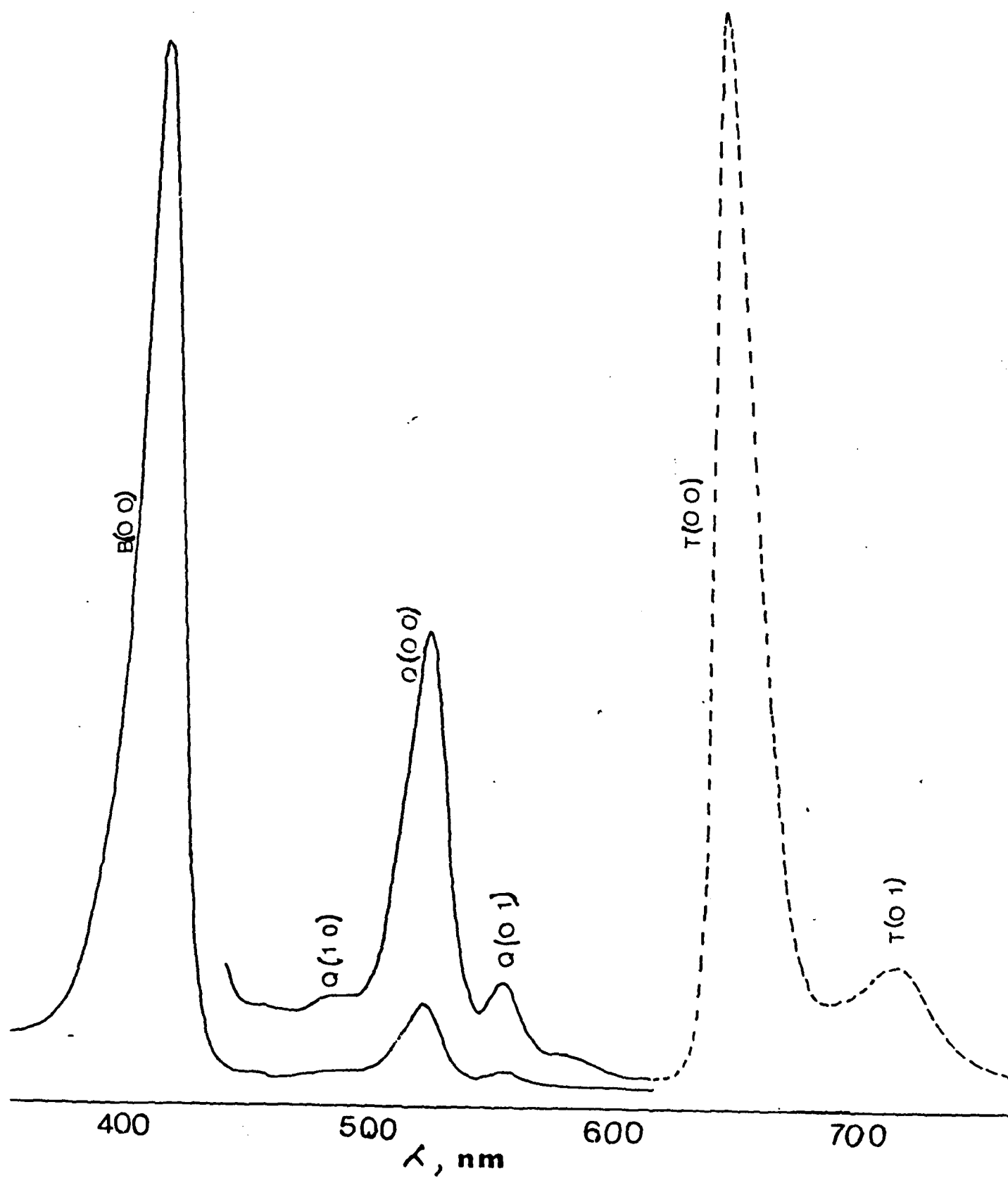
Calculated and excited state redox energies, ground state and excited state driving energies and back reaction driving energies together with the triplet state energies for some porphyrins and metalloporphyrins.

Compound ^a	P ⁺ /P	P/P ⁻	T ₀₋₀	P ⁺ /P [*]	P [*] /P ⁻	Q _{ox}	Th _{ox}	Q _{red}	Th _{red}	Bac _{ox}	Bac _{red}
	vs NHE		T ₀₋₀			Q _{ox}		Q _{red}		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
(CO)LRu(II) TPP	1.15	-1.20	1.8	-0.65	0.60	0.21	0.33	-0.22	0.76	1.59	2.02
(OAc)LRh(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) Electrochemical data remeasured in the common solvent DMF agreed well with previous literature values in various solvents. Data for L(OAc)RhTPP reported here for the first time. L is DMF.

Figure Legend

Fig. 1 Absorption and Emission Spectrum of Rh(III)TPP(OAc)L
in DMF solution.



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