

METALLOPORPHYRIN-SENSITIZED PHOTOREDOX REACTIONS: MECHANISTIC STUDIES ON THE ROLE OF AXIAL LIGANDS ON PHOTOREACTIVITY

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Summary

An investigation of the tin(IV) porphyrin-sensitized photoredox reactions between triphenylphosphine (Ph_3P) as an electron donor and methyl viologen (MV^{2+}) as an electron acceptor is reported. The reaction is induced only in the presence of water molecules as axial ligands. A number of different axially ligated porphyrin complexes sensitize this reaction with quantum efficiencies that depend strongly on the ligand, pH and the concentrations of the various reagents involved. The reactivities of the sensitizers are in the order $\text{SnTPP}(\text{OH})_2 > \text{SnTPP}(\text{OPPh}_3)_2 > \text{SnTPP}(\text{H}_2\text{O})_2 > \text{SnTPP}(\text{H}_2\text{O})(\text{Ph}_3\text{P}) \gg \text{SnTPP}(\text{Ph}_3\text{P})_2$ (TPP \equiv tetraphenylporphyrin). The limiting quantum yield of $\text{MV}^{\cdot+}$ production with $\text{SnTPP}(\text{OH})_2$ is 0.3, while that with $\text{SnTPP}(\text{Ph}_3\text{P})_2$ is almost zero. Kinetic and flash photolysis investigations indicate that an oxidative quenching of the triplet tin porphyrin by MV^{2+} initiates the photoredox reactions. The key to obtaining net redox conversion in each case is the dark oxidation of a partially (one-electron) oxidized Ph_3P -water (or Ph_3P -hydroxide adduct to Ph_3PO by MV^{2+} . The photoreactivity is strongly affected by the rates of coordination of potential ligands in the reaction system to an unstable metalloporphyrin with a vacant coordination site which is generated in the course of the reaction. Hydroxide ion can reproduce the reactive $\text{SnTPP}(\text{OH})_2$ by effective coordination to the vacant species which maintains a constant build-up of $\text{MV}^{\cdot+}$.

1. Introduction

Porphyrins and metalloporphyrins have been widely used as sensitizers in photo-induced redox reactions. It has been well established that their excited states can serve as electron donors or acceptors in various processes,

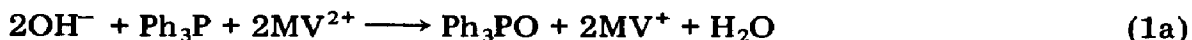
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depending on the specific porphyrin used and the reagents present [1 - 13]. In a number of cases synthetic metalloporphyrins have been proposed as nearly optimal sensitizers in schemes involving "artificial photosynthesis", particularly in reactions coupling the oxidation of a sacrificial donor with water reduction [4, 5, 8 - 13]. Although a number of different metalloporphyrins have been used in these investigations, relatively few systematic studies of the role of the metal, axial ligands coordinated to the metal, or porphyrin ring substituents appear to have been made. While it is reasonable to assume that the redox potentials of the complexes used as excited donors or acceptors will play the major roles in determining overall electron transfer quenching rates, it is less certain what effects these other factors may cause. Certainly the role of ground state complex formation between porphyrin and electron acceptor or donor has been shown in some cases to result in an attenuation of the yield of separated redox products [14, 15].

In the present paper we report an investigation of the tin porphyrin-photosensitized redox reaction between water, triphenylphosphine (Ph_3P) and methyl viologen (MV^{2+}).



This reaction is interesting in that the reagents involved include both electron donors and acceptors as well as potential axial ligands for the metal. The reaction can be driven to moderate conversions using light absorbed only by the metalloporphyrin excited state, and it appears that all the reactivity originates from the porphyrin triplet. In terms of any energy storage or conversion possibilities the reaction is of minimal interest. Since the heats of formation of Ph_3P (+55.5 kcal mol⁻¹ [16]) and Ph_3PO (-14.4 kcal mol⁻¹ [16]) indicate that the oxidation of the former is a highly favorable process, the overall energy stored in the reaction is relatively small under otherwise standard conditions at pH 0 ($\Delta G = 24$ kcal mol⁻¹), and under strongly basic conditions (pH 14) the standard free energy change for reaction (1a) is negative ($\Delta G \approx -3$ kcal mol⁻¹).



Nonetheless the reaction is a prototypical sacrificial system which involves net chemical change coupling one- and two-electron redox reactions.

Our study of this reaction has revealed several aspects of the process including the delineation of at least two different photochemical mechanisms for reaction (1) the importance of which can be controlled by changing parameters such as pH and reagent concentrations. One of the more interesting findings of the study is the pronounced role that axial ligands can play in both the quenching processes that occur and the overall quantum efficiencies obtained.

2. Experimental details

2.1. Materials

Tin(IV) tetraphenylporphyrin dichloride (SnTPPCl_2), tetraphenylporphyrin (TPP) (1.64×10^{-2} mol) and stannous chloride (3.6×10^{-2} mol) in dry pyridine (17 ml) were refluxed for 3 h. Half the pyridine was distilled from the mixture and the precipitated crystals were filtered. The crude SnTPPCl_2 was purified by repeated recrystallization from a chloroform-benzene mixture (2:3 by volume). Its properties were in satisfactory agreement with those previously reported (a procedure analogous to that reported in ref. 14 was followed) (UV spectrum in CHCl_3 (λ_{max} in nanometres with $\log \epsilon$ in parentheses): 427 (5.84), 521 (3.48), 561 (4.30), 600 (4.13); IR spectrum: 306 cm^{-1} for Cl-Sn-Cl stretching). Methyl viologen di(hexafluorophosphate) ($\text{MV}^{2+}(\text{PF}_6)_2$) was prepared as follows: the PF_6 salt was prepared by adding a saturated aqueous solution of NH_4PF_6 to the aqueous solution of MV^{2+}I_2 ; the precipitate was filtered and purified by repeated recrystallization from aqueous acetone. Acetonitrile was refluxed over P_2O_5 , distilled and distilled again over K_2CO_3 . All the refluxing and distillation procedures were done in a dry nitrogen atmosphere. The acetonitrile was stored under nitrogen. Ph_3P and Ph_3PO (Aldrich, reagent grade) were used without further purification. Triply distilled water was used in all studies.

2.2. Measurements

The absorption spectra were recorded using a Perkin-Elmer spectrophotometer (model 576 ST) and Cary 17 spectrophotometer. The fluorescence spectra were recorded on a Hitachi-Perkin-Elmer MPF-2A spectrofluorometer. A conventional flash photolysis apparatus was used for the flash photolysis experiment.

2.3. Irradiations

A 1000 W Hg-Xe lamp equipped with a monochromator (Bausch & Lomb 33-86-79) was used. Solutions were irradiated with monochromatic light ($\lambda = 420 \text{ nm}$). The number of photons of the incident light at $\lambda = 420 \text{ nm}$ was counted by a Reinecke's salt actinometer as 1.5×10^{-9} einstein s^{-1} .

2.4. General procedures

3 ml of the sample were placed in a 30 ml round-bottomed flask equipped with a ground-glass joint on the top and a Pyrex cell (1 cm \times 1 cm \times 4 cm) on a side arm. The sample was degassed by repeated freeze-pump-thaw cycles (six times) and was sealed at pressures below 10^{-6} Torr. All the procedures were carried out in the dark. The degassed sample was irradiated and absorption spectra were recorded periodically. The amount of $\text{MV}^{\cdot+}$ produced was calculated from the increase in the absorbance at $\lambda = 605 \text{ nm}$ assuming the extinction coefficient to be $10\,000 \text{ M}^{-1} \text{ cm}^{-1}$.

The apparent quantum yields for the production of MV^{\ddagger} from the photoreaction in neutral solutions (without hydroxide added to the system) were determined by an initial 1 min irradiation of the samples. In the cases of the photoreactions with hydroxide added to the system, the quantum yields were determined from the slopes in a time-conversion plot and these exhibited good linearity. The number of photons absorbed by the tin porphyrin was calculated by removing the internal filtering effect due to charge transfer (CT) complexation between MV^{2+} and hydroxide ion from the total number of photons absorbed by the reaction mixture. The irradiation ($\lambda = 420$ nm) of the CT complex between MV^{2+} (5 mM) and hydroxide ion (0.5 mM) in acetonitrile-water (95:5 by volume) without added SnTPP did not produce any appreciable amount of MV^{\ddagger} as compared with that observed in the photoreaction sensitized by SnTPP. In the dark, the CT complex produced MV^{\ddagger} very slowly on prolonged standing for more than two days, but the rate of production was negligible as compared with that of the photoreaction sensitized by SnTPP. All the photoreactions were done within two days of preparing the samples.

3. Results

3.1. Coordination chemistry of tin(IV) tetraphenylporphyrin

The finding (see below) that addition of potential ligands to samples of SnTPP under the conditions necessary for photoreaction (1) produces significant changes in both the quantum efficiency of the reaction and its rate suggested that an investigation of the coordination chemistry of the tin porphyrin in the presence of these ligands was a necessary prerequisite to any mechanistic determination. It was found, as shown in Fig. 1, that addition of water to dry acetonitrile solutions of $SnTPPCl_2$ leads to small but significant changes in both the absorption and fluorescence spectrum of the porphyrin. The blue shift in the major absorption (Soret band) of the porphyrin occurs on addition of water and the isosbestic points observed suggest that a single species, most probably the dihydrate $SnTPP(H_2O)_2^{2+}$ is formed. A concomitant increase of the fluorescence intensity occurs on the addition of water to $SnTPPCl_2$ as shown in Fig. 2, indicating the coordination of water to the metal center. A corresponding spectral change occurs when Ph_3P is added to dry acetonitrile solutions of $SnTPPCl_2$; however in this case the spectral change occurs much more slowly, requiring up to several days for complete conversion at room temperature with $[Ph_3P] = 1 - 80$ mM. In contrast, addition of Ph_3P to solutions of the tin porphyrin in acetonitrile-water (95:5 by volume) leads to small blue shifts in the spectrum over the same range of Ph_3P concentrations. The spectral shifts are rather small and there is no isosbestic point. This suggests that at least two species are formed on addition of Ph_3P ; a quantitative analysis (a procedure analogous to that reported in ref. 14 was followed) of the spectrum

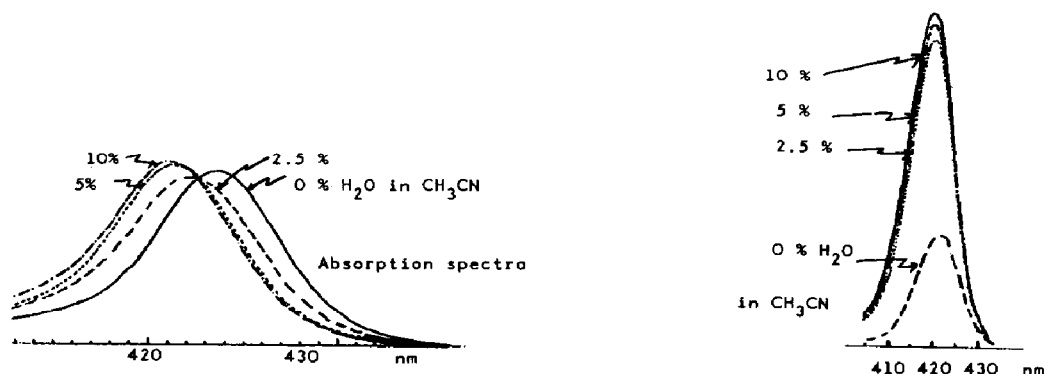
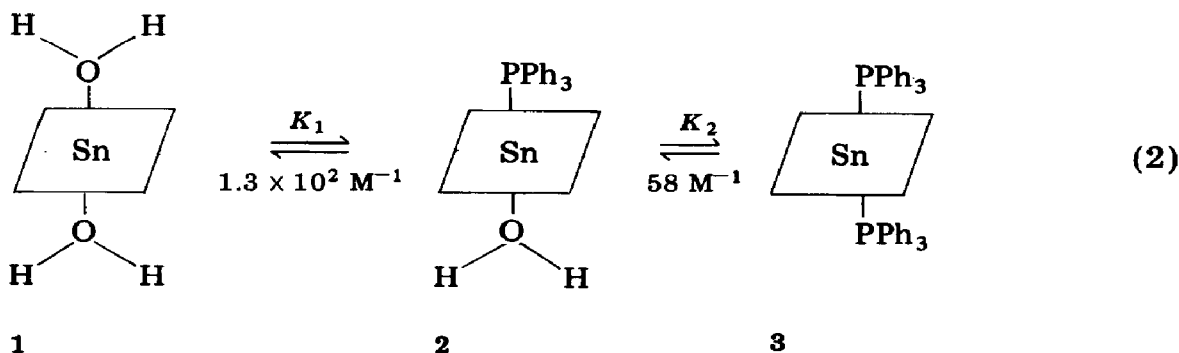


Fig. 1. Changes in the Soret band of SnTPP in a dry acetonitrile solution: (—), no water; (---), 2.5 vol.% water added; (- · -), 5 vol.% water added; (- - -), 10 vol.% water added.

Fig. 2. Changes in the excitation spectra of fluorescence of SnTPP monitored at $\lambda = 602$ nm upon addition of water to a dry acetonitrile solution: (---), no water; (- · -), 2.5 vol.% water added; (- · -), 5 vol.% water added; (—), 10 vol.% water added.

assuming the presence of the above mentioned dihydrate, a monohydrate-monophosphine complex and a diphosphine complex leads to an estimation of the equilibrium constants for these species as shown in reaction (2)



Although addition of the neutral ligands produces a blue shift in the absorption spectrum of SnTPP as noted above, addition of anionic ligands such as hydroxide or Ph₃PO produces a red shift (see Table 1). On addition of hydroxide (5×10^{-4} M) to a solution of the Ph₃P complex 3, the Soret band (420 nm) exhibits a red shift to 422 nm. Addition of hydroxide even in a trace amount of 5×10^{-5} M to the water-tin porphyrin complex 1 in acetonitrile-water (95:5 by volume) also induces a red shift of the Soret band from 421 nm to 422 nm and no further spectral shift is observed on further addition of hydroxide up to 1.25×10^{-3} M. The absorption bands of the longer wavelength region (558 nm and 597 nm) undergo similar red shifts to 560 nm and 599 nm respectively. The addition of hydroxide

TABLE 1

Axial coordination to SnTPP: spectra in acetonitrile solution

	Ligand	Complex	Soret band (nm)
Anionic ligands	Cl ⁻	SnTPPCl ₂	423.5
	OH ⁻	SnTPP(OH) ₂	422
	-O-PPh ₃	SnTPP(OPPh ₃) ²⁺	422
Neutral ligands	H ₂ O	SnTPP(OH ₂) ₂ Cl ₂	421
	PPh ₃	SnTPP(PPh ₃) ₂ Cl ₂	420

(5×10^{-4} M) to the aquo complex 1 also induces a modest increase in the fluorescence intensity (about 15%). These results strongly indicate a complete replacement of the axial neutral ligands by hydroxide ion. The increase of fluorescence intensity accompanied by coordination of water and hydroxide with SnTPPCl₂ could be rationalized by a decrease of spin-orbit interaction [17], which results in the expulsion of the heavy chloride atoms from the metal center. The chloride atoms bound directly to the metal in SnTPPCl₂ are liberated in the diaquo complex as counter-ions and are completely expelled from the metal center in the dihydroxy complex.

Thus under various reaction conditions there exist several possible coordination species whose relative concentrations depend on the pH, the concentration of reactant Ph₃P and even the concentration of the product Ph₃PO.

3.2. Porphyrin-sensitized photoredox reactions between viologen and phosphine in neutral and basic acetonitrile-water solutions

When a mixture containing the tin porphyrin (2×10^{-6} M), Ph₃P (1.25×10^{-3} M) and MV²⁺(PF₆)₂ (5×10^{-3} M) in acetonitrile-water (95:5 by volume) is irradiated at 420 nm, there is a rapid initial build-up of the reduced viologen radical cation MV^{•+} that is clearly shown by an increase in absorption at 396 nm and 605 nm. Ph₃PO can also be detected as a product by gas chromatography analysis. There is no detectable depletion of the porphyrin, even upon prolonged irradiation; thus it is clear that under the irradiation conditions where light is absorbed only by the porphyrin, the net reaction is that described by reaction (1) in which the porphyrin functions as a non-consumed photosensitizer or photocatalyst. Water is also a necessary reagent for the process since it is found that irradiation of the same reagents in anhydrous acetonitrile does not lead to any accumulation of reduced viologen (Table 2).

Initial quantum yields for reaction (1) in acetonitrile-water (95:5 by volume) were determined as a function of Ph₃P concentration. Although Ph₃P is a necessary reagent for reaction, it was found that its addition over the range $(2.5 - 10.6) \times 10^{-3}$ M causes a decrease in the quantum yield from

TABLE 2

Effect of water, hydroxide and Ph_3PO on the quantum yield $\Phi_{\text{MV}^\ddagger}$

$[\text{H}_2\text{O}]$ (%)	$[\text{OH}^-]$ (M)	$[\text{Ph}_3\text{PO}]$ (M)	Soret band (nm)	$\Phi_{\text{MV}^\ddagger}$
0	0	0	423.5	0
2.5	0	0	422	0.01
5.0	0	0	421.3	0.02
5.0	5×10^{-4}	0	422.3	0.15
5.0	0	1.0×10^{-2}	422	0.07
5.0	5×10^{-4}	1.0×10^{-2}	422.3	0.15

 $[\text{SnTPP}] = 1 \times 10^{-6} \text{ M}$; $[\text{MV}^{2+}] = 1 \times 10^{-2} \text{ M}$ in acetonitrile.

0.032 to 0.017 and that at concentrations of Ph_3P higher than $3 \times 10^{-2} \text{ M}$ the quantum yield for reaction (1) is negligible (Table 3). Because the quantum yields vary widely over the range when the coordination of the tin(IV) is changing according to reaction (2) it is possible to determine approximately the quantum yields for reaction (1) initiated by the various species 1 - 3. Since the quantum efficiency is practically zero under conditions where conversion to 3 is complete, a graphic treatment assuming $\phi_3 = 0.0$ gives $\phi_2 = 0.024$ and $\phi_1 = 0.037$. Thus it appears that at least one coordinated water molecule is necessary for reaction in neutral aqueous acetonitrile solutions. Although the initial quantum yield for reaction is appreciable under the concentrations described above, there is a noticeable decrease in the rate of reaction under prolonged irradiation that is evident even in the

TABLE 3

Effect of $[\text{PPh}_3]$ on the photochemical generation of MV^\ddagger in 95:5 (by volume) acetonitrile-water

$[\text{PPh}_3]$ (mM)	Estimated coordinated species (%)			$\Phi_{\text{MV}^\ddagger}$
	$[\text{SnTPP}(\text{H}_2\text{O})_2]\text{Cl}_2^{\text{a}}$	$[\text{SnTPP}(\text{PPh}_3)(\text{H}_2\text{O})]\text{Cl}_2^{\text{b}}$	$[\text{SnTPP}(\text{PPh}_3)_2]\text{Cl}_2^{\text{c}}$	
2.6	72.0	24.3	3.7	0.032
4.4	58.2	33.3	8.5	0.029
7.8	40.5	41.0	18.5	0.026
10.6	31.0	42.7	26.3	0.017
13.2	24.8	42.6	32.6	0.005
17.7	17.7	40.6	41.7	0.002
33.0	7.4	31.8	60.8	0.001
48.3	4.0	25.3	70.7	0.001

 $[\text{SnTPP}] = 1 \times 10^{-6} \text{ M}$; $[\text{MV}^{2+}] = 1 \times 10^{-2} \text{ M}$.^a $\Phi_{\text{MV}^\ddagger}^0 = 0.037$.^b $\Phi_{\text{MV}^\ddagger}^0 = 0.024$.^c $\Phi_{\text{MV}^\ddagger}^0 = 0$.

early stages of the reaction (Fig. 3). However, on addition of hydroxide a constant build-up of $MV^{\dot{+}}$ without such a decrease in the rate of reaction is observed and the quantum yield obtained after correcting for the internal filtering effect (see Section 2.4) is 0.15 (Table 2). This suggests that the nature of the reactive species in the photoreaction without hydroxide present varies during the irradiation, but the corresponding reactive species in the photoreaction with hydroxide present remains constant during the irradiation. As indicated in Table 1, addition of hydroxide to solutions of the tin(IV) porphyrins results in spectral changes consistent with formation of a hydroxide-ligated species $SnTPP(OH)_2$ (4). It has been reported that the addition of hydroxide to solutions of dimethyl viologen can result in the formation of the radical cation $MV^{\dot{+}}$ in a dark process [18, 19]. As anticipated, a small amount of $MV^{\dot{+}}$ can be detected when potassium hydroxide is added to aqueous acetonitrile solutions of the porphyrin, MV^{2+} and Ph_3P at the concentration levels described above. However, the rate and extent of the dark reaction are negligible compared with the rate of photoproduction of $MV^{\dot{+}}$ under the reaction conditions employed. Thus it was found that irradiation of solutions containing potassium hydroxide (5×10^{-4} M), Ph_3P ($(0.12 - 1) \times 10^{-3}$ M) and MV^{2+} (5×10^{-3} M) in acetonitrile-water (95:5 by volume) leads to reaction (1) with quantum yields in the range 0.07 - 0.15 which increase with increasing concentration of Ph_3P . Under these conditions all of the tin porphyrin is in the form of the dihydroxy complex and a plot of $1/\phi$ versus $1/[Ph_3P]$ is linear with an intercept to slope ratio of 3.8×10^3 M $^{-1}$ (Fig. 4). At a high concentration of Ph_3P (2×10^{-2} M), the plot shows a positive deviation indicative of an

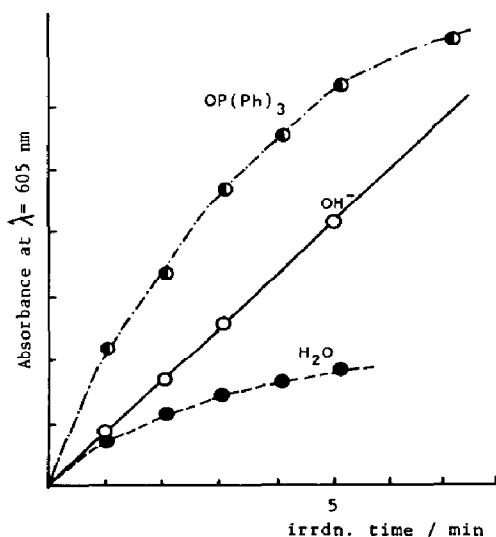
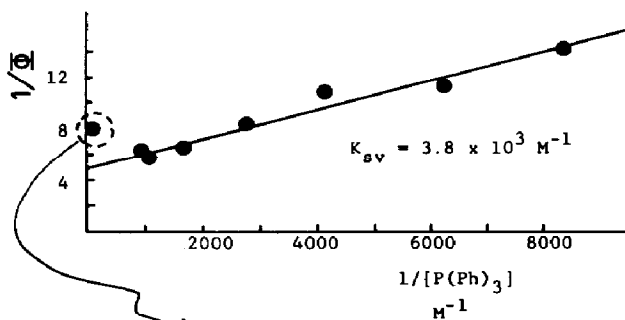


Fig. 3. Effect of axial ligands of $SnTPPX_2$ on the photo-production of $MV^{\dot{+}}$ under the conditions where $[SnTPPX_2] = 2 \times 10^{-6}$ M, $[Ph_3P] = 1 \times 10^{-3}$ M and $[MV^{2+}] = 5 \times 10^{-3}$ M in 95:5 acetonitrile-water with irradiation at $\lambda = 420$ nm; (—●—), X = H_2O ; (—○—), X = OH upon addition of potassium hydroxide (5×10^{-4} M); (---●---), X = $OPPh_3$ upon addition of $OPPh_3$ (1×10^{-2} M).



Soret band	
422 nm	before irrdsn.
420 nm	during irrdsn.
422 nm	24 hrs after irrdsn.

Fig. 4. Effect of $[PPh_3]$ on the photo-production of MV^{2+} under the conditions where $[SnTPP] = 2 \times 10^{-6} M$, $[MV^{2+}] = 5 \times 10^{-3} M$ and $[potassium\ hydroxide] = 5 \times 10^{-4} M$ in 95:5 acetonitrile–water with irradiation at $\lambda = 420\text{ nm}$.

apparent fall-off in the quantum yield; under these conditions a decrease in the reaction rate is observed which is similar to that in the photoreaction without hydroxide present. Concurrent with this decrease in reaction rate there is a slight blue shift in the Soret band of the porphyrin from 422 to 420 nm. From data listed in Table 1 it is apparent that the Soret shift could be attributed to an increase in the relative extent of Ph_3P -coordinated porphyrin. Interestingly, it was found that for solutions allowed to stand for 24 h in the dark after irradiation, the original Soret band at 422 nm was regenerated. The intercept of the linear portion of the double reciprocal plot described above gives a limiting quantum yield for the reaction in the presence of $5 \times 10^{-4} M$ hydroxide of $\phi = 0.22$. To verify that the light-induced reaction involves tin porphyrin sensitization, irradiations were carried out on solutions containing all the reagents described above except the porphyrin; under these conditions the detected yield of reduced viologen is negligible.

Since Ph_3PO , a product of the photoreaction, can also serve as a ligand for the tin porphyrin, irradiations were carried out in acetonitrile–water solutions containing 0.01 M Ph_3P with and without added potassium hydroxide. In the presence of potassium hydroxide ($5 \times 10^{-4} M$) the Soret band position suggested the presence of the dihydroxy complex (4) and the quantum yield measured was the same within experimental error as that measured with no Ph_3PO present (0.15). In the absence of potassium hydroxide the Soret band position suggested the presence of a bis(triphenylphosphine oxide) complex (5) and the quantum yield measured (0.073) was higher by a factor of 3 than that obtained for the irradiation of 1. Taken together, the experiments described above indicate that the effectiveness of the complexes with a range of different axial ligands in promoting the photoreaction is $4 > 5 > 1 > 2 \gg 3$.

The effect of $[MV^{2+}]$ on the reaction quantum yield was investigated in aqueous acetonitrile containing 5×10^{-4} M potassium hydroxide at two different Ph_3P concentrations, 8×10^{-4} M and 1×10^{-2} M. In each case, the quantum yields were found to increase as $[MV^{2+}]$ increased from 0.002 to 0.02 M; relative quantum yields for the two Ph_3P concentrations plotted as ϕ_{lim}/ϕ versus $1/[MV^{2+}]$ gave identical slopes, indicating a Stern–Volmer constant $K_{sv} = 5.7 \times 10^2 \text{ M}^{-1}$ for quenching of a reactive intermediate by MV^{2+} ; in contrast similar experiments with Ph_3P indicate that it does not quench the same intermediate at an appreciable rate. When solutions containing tin porphyrin, Ph_3P and hydroxide without MV^{2+} were irradiated, some permanent products were found to be produced in very low yield. The permanent products appear to be ring-reduced chlorin or substituted chlorins [7, 20, 21]. They are not formed in the presence of the moderate concentration of MV^{2+} used under the conditions where reaction (1) or (1a) is the net process. The effect of Ph_3P concentration on the *photo-reduction* of the tin porphyrin (without MV^{2+} present) was investigated by following the loss of the porphyrin absorption. Although the relative quantum yield of the photoreduction increased with Ph_3P concentration, the linearity of the double reciprocal plot was rather poor, probably owing to the very low efficiency of the photoreduction. Thus an exact Stern–Volmer constant could not be obtained but can be estimated to be smaller than 600 M^{-1} .

3.3. Flash spectroscopic investigations

Microsecond flash spectroscopic investigations of transients formed from the irradiation of the tin porphyrin were carried out for several different coordination species including $SnTPPCl_2$ in acetonitrile, $SnTPP-(H_2O)_2Cl_2$ in acetonitrile–water (95:5 by volume) and $SnTPP(OH)_2$. All three of these porphyrins gave typical triplet–triplet spectra showing the usual bimolecular decay observed in flash spectroscopic investigations of other porphyrins and metalloporphyrins. The $T_n \leftarrow T_1$ absorption spectrum of $SnTPP(OH)_2$ is shown in Fig. 5. The extracted k_d values [22] were all similar and were approximately $5 \times 10^2 \text{ s}^{-1}$ when monitored at $\lambda = 400$, 450 and 460 nm. In the presence of MV^{2+} (5×10^{-3} M) a transient additional to the triplet tin porphyrin is observed (Fig. 5). The large depletion around 420 nm and the disappearance of the peak at $\lambda = 450$ nm strongly suggest a substantial quenching of the triplet porphyrin. In contrast with the bimolecular decay of the $T_n \leftarrow T_1$ absorption observed in the absence of MV^{2+} , the transient produced by addition of MV^{2+} suffers a quasi-unimolecular decay with $k_d = 2 \times 10^3 \text{ s}^{-1}$ over the entire wavelength region monitored. This also suggests that the transient is not the triplet porphyrin, but must be an intermediate formed during or subsequent to the triplet quenching by MV^{2+} . The relative increase in absorption around 390 nm and 605 nm is consistent with absorption due to MV^+ superimposed on the absorption (around 450–500 nm) of another transient. Although one must be cautious in assigning these transients, the unimolecular decay of the

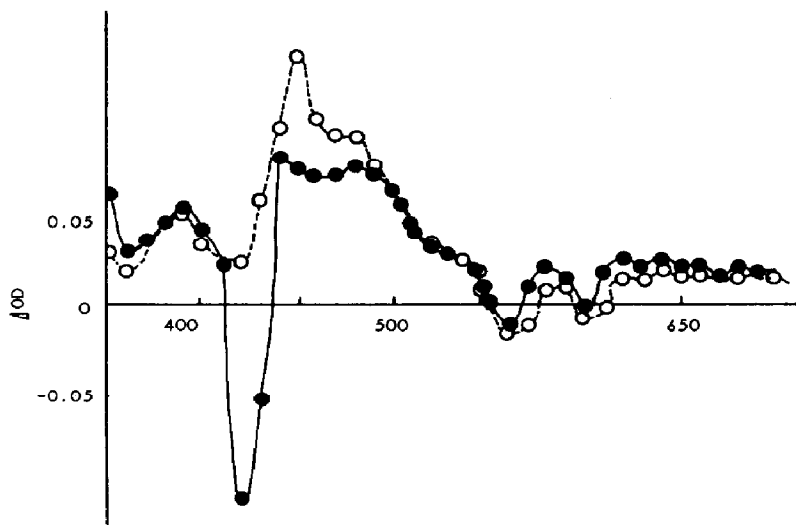


Fig. 5. Transient spectra in the flash photolysis of SnTPP in 95:5 acetonitrile-water; (—○—), SnTPP(OH)₂ 400 μs after the flash; (—●—), SnTPP(H₂O)₂Cl₂ with MV²⁺ (5×10^{-3} M) added 400 μs after the flash.

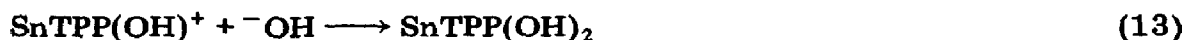
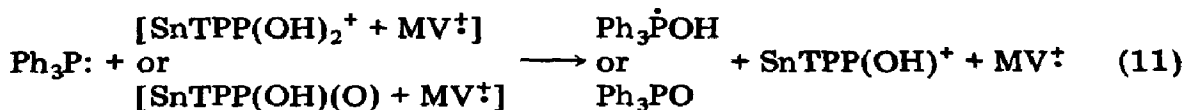
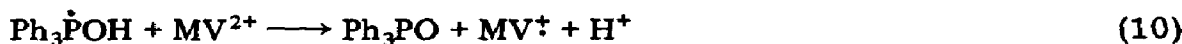
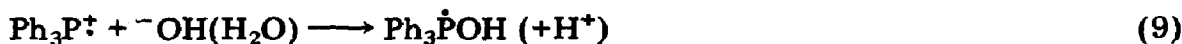
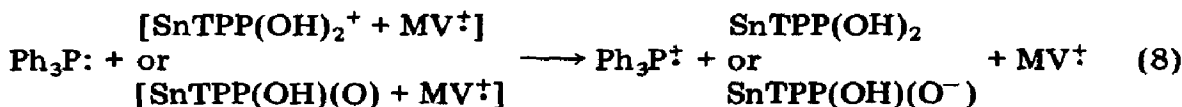
transients which presumably involve MV⁺ suggest the possibility that the transient could be a radical pair consisting of oxidized tin porphyrin and MV⁺ which would be produced by an electron transfer quenching of triplet porphyrin by MV⁺. The yield of MV⁺ calculated from ΔOD (Fig. 5) is about 10^{-6} M; this compares well with the yield of MV⁺ in a system such as Ru(bpy)₃²⁺-MV²⁺ where the quantum efficiency is moderate (0.4) using the same low-powered (about 10 J) flash apparatus.

Flash spectroscopic investigation of SnTPP(OH)₂ in the presence of Ph₃P (2.8×10^{-4} M) led to the presence of at least two transients as well as to some permanent products in low yield which appear to be ring-reduced chlorin or substituted chlorins [7, 20, 21] but their identity could not be established with certainty.

4. Discussion

The results described above suggest a mechanism that involves a quenching of the triplet porphyrin by MV²⁺ for the driving of reaction (1) by photoexcited tin(IV) porphyrins. Since the porphyrin fluorescence is unquenched by either Ph₃P or MV²⁺ while the triplet is quenched by both, it is safe to conclude that the excited state precursor for reaction in each case is the metalloporphyrin triplet. The finding that the Stern-Volmer constant for MV²⁺ quenching of a reactive intermediate is not affected by the concentration of Ph₃P indicates that Ph₃P does not interact in appreciable rates with the intermediate quenched by MV²⁺ on the reaction pathway in which MV⁺ is produced. The much larger K_{sv} (3.8×10^3 M⁻¹) obtained from the double reciprocal plot of $1/\phi$ versus $1/[\text{Ph}_3\text{P}]$ (Fig. 3) as compared

with $K_{sv} < 600 \text{ M}^{-1}$ from the similar plot for the *photoreduction* of tin porphyrin without MV^{2+} present suggests that Ph_3P intercepts a species formed during, or subsequent to, the triplet quenching step. If we first consider the reaction in the presence of a base where low concentrations of Ph_3P (below 0.001 M) and moderate concentrations (about 0.005 M) of MV^{2+} are employed and the highest quantum efficiencies for the reaction are obtained, a mechanism (reactions (3) - (14)) can be developed.



Under these conditions the predominant initial porphyrin species is SnTPP(OH)_2 . The excited triplet SnTPP(OH)_2 is quenched by MV^{2+} to form

an ion pair (reaction (4)). The ion pair is further intercepted by Ph_3P (reaction (8) and/or reaction (11)) resulting in a net electron transfer that competes with a back electron transfer within the ion pair (reaction (5)) and a deprotonation to give an oxo-type tin complex- $\text{MV}^{\dot{+}}$ pair (reaction (6)). The resulting oxo-type complex is also easily intercepted by Ph_3P (reaction (8) and/or reaction (11)), and this competes with an electron transfer within the pair (reaction (7)). Possible sequences of reaction include reaction (4) followed by reactions (8) - (10) or by (11) - (14), and (10). The former is certainly a reasonable mechanism in view of the fact that the oxidation potential for Ph_3P is about 0.95 V [23, 24] and that for dihydroxytin(IV) porphyrin is about 1.4 V *versus* SCE [25]. Several studies have indicated that the cation $\text{Ph}_3\text{P}^{\dot{+}}$ is highly reactive towards nucleophiles [24, 26] so its reaction with water or hydroxide ion to generate the neutral radical $\text{Ph}_3\dot{\text{P}}\text{OH}$ should be a rapid and favorable process. Oxidation of this radical to yield a second reduced viologen and Ph_3PO should also be favorable for the completion of the reaction [27].

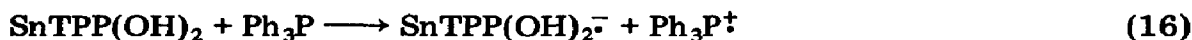
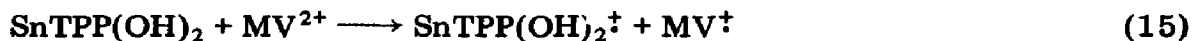
The second sequence, which involves direct generation of $\text{Ph}_3\dot{\text{P}}\text{OH}$ or $\text{Ph}_3\dot{\text{P}}\text{O}$ effectively by a combination of electron and ligand transfer between oxidized porphyrin and Ph_3P , and has some precedence in previous reports of the specific involvement by oxidized or oxo derivatives of metalloporphyrin, is the $\text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{PO}$ conversion [28]. In the present case there is perhaps some support for such a reaction in the finding that irradiation of $\text{SnTPP}(\text{OH})_2$ in the presence of a high concentration of Ph_3P results in a decrease in the reaction efficiency with irradiation time, together with a change in the Soret band of the porphyrins which suggests a Ph_3P complexation which is reversible on standing in the dark. This suggests that reaction may result in the generation of an unstable metalloporphyrin with a vacant coordination site which is captured kinetically by Ph_3P to form a less reactive complex. Thus, while the Ph_3P complex formation may be kinetically favored, its conversion to the starting complex should be thermodynamically favored. The finding that the (bis)triphenylphosphine complex $\text{SnTPP}(\text{Ph}_3\text{P})_2^{2+}$ is apparently totally incapable of inducing reaction (1) tends to support the possibility that the oxidized porphyrin does not simply oxidize Ph_3P by electron transfer (reaction (8)) but that a more complex reaction such as reaction (11) plays an important role [27, 28]. The transient observed in the flash photolysis with MV^{2+} present (Fig. 5) appears to be a key intermediate on the reaction pathway, and this has oxidized porphyrin as a component. The extremely long lifetime (0.5 ms) of the transient strongly suggests that this is not simply the ion pair of the cation radical of tin porphyrin and reduced viologen (reaction (4)), since a back electron transfer within a geminate ion pair should be far faster than the observed decay even when it is a triplet ion pair. The pair consisting of an oxo-type complex and $\text{MV}^{\dot{+}}$ (reaction (6)) might be a more plausible candidate for the transient since proton loss could lead to a less easily reduced radical. The good linear Stern-Volmer plot of $1/\phi$ against $1/[\text{Ph}_3\text{P}]$ in Fig. 4 indicates that Ph_3P intercepts only one intermediate on the reaction

pathway leading to the end products. Thus, these considerations suggest the conclusion that the oxo-type tin complex is the actual intermediate intercepted by Ph_3P on the reaction pathway. Both direct measurement of the triplet lifetime for $\text{SnTPP}(\text{OH})_2^{3*}$ in the absence of MV^{2+} ($k_3 = 5 \times 10^2 \text{ s}^{-1}$) and the Stern–Volmer constant for the MV^{2+} quenching ($K_{sv} = 5.7 \times 10^2 \text{ M}^{-1}$) lead to a quenching constant $k_4 = 2.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. If it is supposed that the transient in the flash photolysis with MV^{2+} present (Fig. 5) is the key intermediate (such as that obtained in reaction (6)), the first-order decay constant ($k_d = 2 \times 10^3 \text{ s}^{-1}$) and the Stern–Volmer constant ($K_{sv} = 3.8 \times 10^3 \text{ M}^{-1}$) in Fig. 4 give the rate constant of interception of the intermediate by Ph_3P as $k = 7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

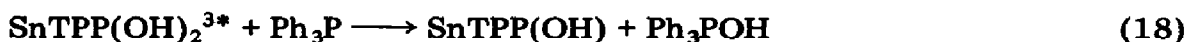
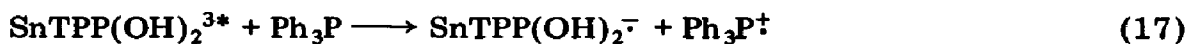
The overall reaction initiated by oxidative quenching of the tin porphyrin by MV^{2+} has an extrapolated limiting quantum yield of 0.22 under conditions where quenching of the porphyrin by MV^{2+} is 74% efficient. Thus the absolute limiting quantum yield must be about 0.3; since two molecules of viologen should be produced, this suggests the overall efficiency of the net electron transfer is 0.15. Sources for inefficiency in the process are probably less than unit intersystem crossing efficiency (minor) and quenching by MV^{2+} that is unproductive in terms of forming ion pairs (major). Although the other complexes that are "reactive" towards MV^{2+} could conceivably react in the same way, it appears that quenching constants with MV^{2+} should be substantially lower for cationic species such as $\text{SnTPP}(\text{OH})_2^{2+}$ and $\text{SnTPP}(\text{OH})_2(\text{Ph}_3\text{P})^{2+}$, but perhaps comparable for $\text{SnTPP}(\text{OPPh}_3)_2^{2+}$.

The apparent reactivity of the various tin complexes under a moderate concentration of Ph_3P could also be explained in terms of a delicate balance between the kinetic coordinations of potential ligands in the reaction system to the unstable metalloporphyrin with a vacant coordination site (vacant species) generated in the course of reaction (reaction (11)). In the absence of hydroxide the expected vacant species could be kinetically captured by Ph_3P rather than water to form a less reactive complex $\text{SnTPP}(\text{H}_2\text{O})(\text{Ph}_3\text{P})^{2+}$ and further irradiation of the resultant complex induces final conversion to the inert complex $\text{SnTPP}(\text{Ph}_3\text{P})_2^{2+}$. Thus a substantial decrease in the reaction rate with irradiation time is observed (Fig. 3). However, addition of hydroxide can reproduce the reactive species $\text{SnTPP}(\text{OH})_2$ by coordination to the vacant species $\text{SnTPP}(\text{OH})^+$ (reaction (13)) to maintain a constant build-up of MV^{\ddagger} without decreasing the reaction efficiency (Fig. 3).

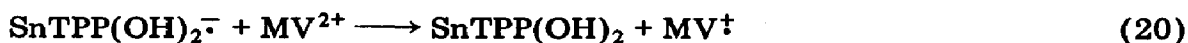
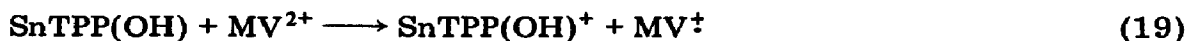
As noted above, irradiation of a solution containing tin porphyrin and Ph_3P without MV^{2+} induces *photoreduction* of the porphyrin ring, although in very low yield ($\phi < 10^{-4}$). Estimates of the net redox potentials for the two processes (reactions (15) and (16)) give very similar values ($\Delta E \approx 1.9 \text{ V}$).



Thus, under conditions where $[\text{Ph}_3\text{P}] \gg [\text{MV}^{2+}]$ it is reasonable to expect that some net redox quenching by Ph_3P occurs. This could be either a simple one-electron transfer process (reaction (17)) or a more complex reaction analogous to reaction (11) (reaction (18)).



In either case in the absence of MV^{2+} the initial product could ultimately yield reduced metalloporphyrin (chlorin) products and Ph_3PO , so that in its presence there could be a net reduction of the viologen to MV^\dagger by reactions similar to and including those described above (reactions (9), (10), (19) and (20)).



However, the finding that the Stern-Volmer constant for triplet quenching by MV^{2+} is not affected by the concentration of Ph_3P (even at the relatively high value of 1×10^{-2} M) clearly indicates that Ph_3P does not quench the triplet state at an appreciable rate, although a minor quenching should be present in the absence of MV^{2+} leading to the photoreduction of the porphyrin ring. The extremely low reactivity at high concentrations of Ph_3P also indicates that the mechanism for reductive quenching by Ph_3P (reactions (17) - (20)) does not operate in the photoproduction of MV^\dagger .

In summary, the results obtained in this study show that various tin porphyrin complexes can mediate net redox reactions such as reaction (1) by an oxidative quenching mechanism. The rather pronounced effects induced by the axial coordination of the metal in the complex, including the total lack of reactivity of the (bis)triphenylphosphine complex, underline the possibilities and pitfalls for using reactions of substitution-labile complexes in solution or organized assemblies, including biomembrane systems.

Acknowledgments

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