

MICELLAR EFFECTS ON THE FORWARD AND THE BACK PHOTOELECTRON TRANSFER FROM A WATER-SOLUBLE PORPHYRIN TO DIALKYL VIOLOGENS

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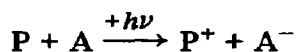
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Summary

Photoelectron transfer from a water-soluble porphyrin to various dialkyl viologens was studied in aqueous solution in the absence and in the presence of micellar assemblies. For dialkyl viologens with less than eight carbon atoms, no micellar effects were observed; the forward and the back reactions occur in the bulk aqueous phase. For viologens with alkyl chains of eight carbon atoms or more, the forward photoelectron transfer occurring in the aqueous phase is followed by the entrance of reduced viologen into the micelle.

1. Introduction

The photochemical investigation of systems which mimic membrane functions is an extremely active area of current research [1]. Micelles, micro-emulsions and vesicles have been explored as membrane mimetic agents [2 - 5]. In the photoredox reactions



light acts as an electron pump, promoting charge transfer from the photosensitizer P to the acceptor A via the high energy intermediates A^- and P^+ . If the chemical potential of A^- and P^+ is to be utilized in subsequent fuel-generating processes, the back reaction must be prevented or retarded [6]. Molecular organizations such as micelles and microemulsions can serve this purpose since they possess a hydrophobic core and charged microscopic interfaces which act as barriers to the charge recombination process.

In this paper we describe the favourable intervention of amphiphilic electron relays in a photoredox reaction. The process studied is the reduction of a series of functionalized viologens, by the excited state of zinc tetra-

p-*N*-methylpyridylporphyrin (ZnTMPyP⁴⁺). The aim of this study is to examine micellar effects on the forward and back electron transfer reactions of substituted alkyl viologens.

2. Experimental section

2.1. Apparatus

The flash photolysis experiments were carried out either with a 20 ns neodymium laser [7] or with a conventional flash photolysis apparatus [7].

2.2. Materials

The cetyltrimethylammonium chloride (CTAC) surfactant, produced by Eastman Kodak, was purified by numerous recrystallizations from methanol and ether. Cyclohexane was used without further purification and butanol was distilled.

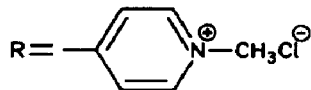
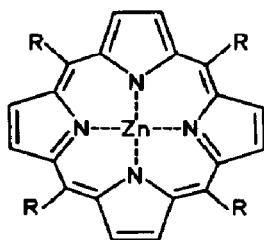
2.3. Composition of micellar aggregates

The concentration of the CTAC micelles used was 2×10^{-2} M; the composition of a litre of CTAC microemulsion was 6.4 g of CTAC surfactant, 36.6 ml of butanol as a cosurfactant and 2.5 ml of cyclohexane oil; the concentration of Triton micelles used was 10^{-2} M.

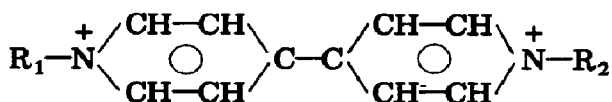
The solutions obtained were transparent isotropic dispersions of oil in water which were kinetically and thermodynamically stable.

2.4. Sensitizer and electron acceptors

The sensitizer was ZnTMPyP⁴⁺:



The electron acceptors were alkyl viologens and propyl viologen sulphonate:



with $R_1 \equiv C_xH_{2x+1}$ and $R_2 \equiv C_yH_{2y+1}$, represented by the alkyl viologens $C_xC_yV^{2+}$, or $R_1 \equiv R_2 \equiv (CH_2)_3-SO_3^-$, represented by propyl viologen sulphonate (PVS).

3. Experimental results

ZnTMPyP⁴⁺ is a water-soluble porphyrin, characterized by its absorption spectrum with maxima centred at 562 and 606 nm and a Soret band centred at 433 nm.

In aqueous solution, laser photolysis of ZnTMPyP⁴⁺ afforded a triplet-triplet absorption spectrum characterized by an absorption band centred at 470 nm [4, 5]. The triplet lifetime was found to be equal to 3 ± 0.5 ms, longer than those lifetimes reported in the literature [8]. Similar absorption spectra and lifetimes for the excited triplet state of ZnTMPyP⁴⁺ were obtained in CTAC and Triton micellar solutions.

3.1. Photoelectron transfer processes

3.1.1. In aqueous solution

The photoelectron transfer from ZnTMPyP⁴⁺ to various viologens has been studied in aqueous solution. At the end of the laser pulse, the triplet-triplet absorption spectrum of ZnTMPyP⁴⁺ was observed. A few microseconds after the laser pulse, the triplet absorption decreased and new species appeared characterized by absorption bands at 395 and 600 - 800 nm with a maximum at 700 nm (Fig. 1). By comparison with the absorption spectra of reduced viologen ($\lambda_{\max} = 395$ and 610 nm) and the porphyrin cation ($\lambda_{\max} = 700$ nm), the quenching of the triplet is attributed to the following electron transfer:

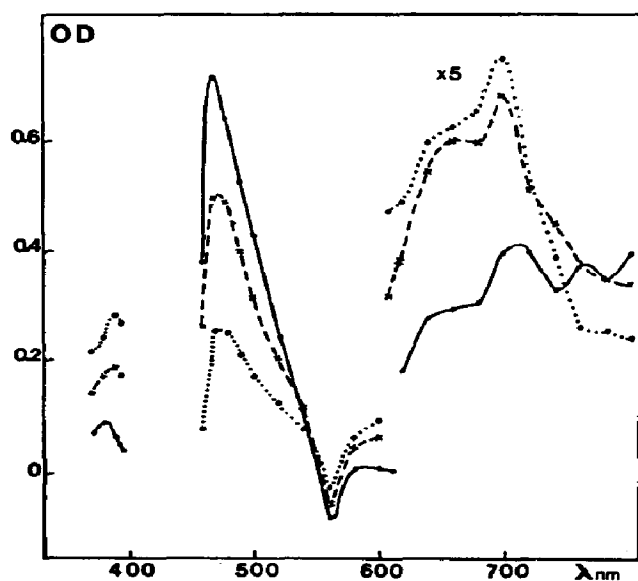
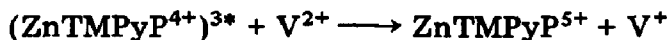


Fig. 1. Transient absorption spectra observed at the end (—) and 0.5 ms (---) and 0.7 ms (.....) after the laser pulse of ZnTMPyP⁴⁺ in aqueous solution in the presence of 10^{-3} M of methyl viologen.

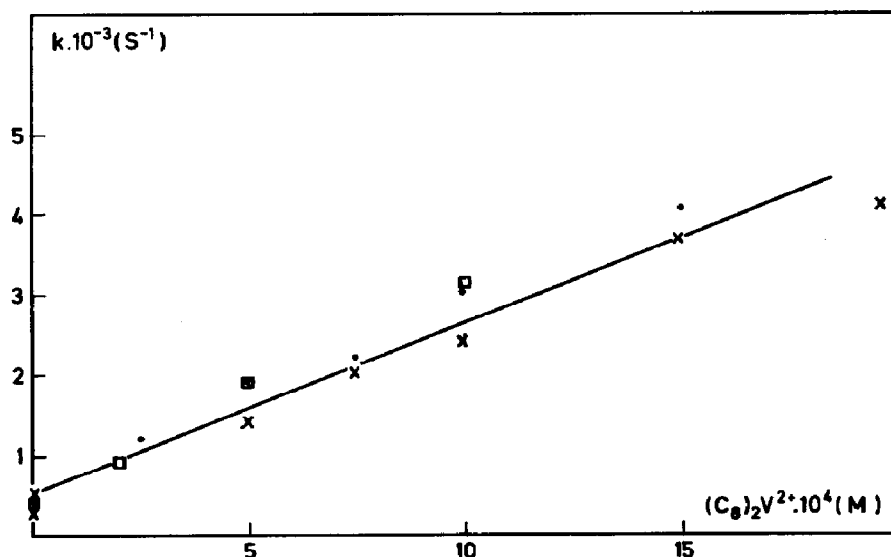


Fig. 2. Plot of the triplet quenching rate constant observed at 460 nm vs. the viologen concentration: x, in aqueous solution; •, in CTAC microemulsion; □, in CTAC micelles.

where V^{2+} and V^+ are the oxidized and the reduced forms of the viologens at concentrations from 10^{-5} to 2×10^{-3} M. By plotting a pseudo-first-order rate constant decay for the triplet state versus the V^{2+} concentration, a linear relationship was obtained (Fig. 2). The triplet quenching rate constant k_q can be calculated from the slope. Table 1 gives the k_q values obtained with the various viologens used; for alkyl viologens $k_q = 2.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Hence k_q is independent of the length of the alkyl chain. In the case of PVS the triplet quenching rate was faster than that observed with alkyl viologens and was diffusion controlled (Table 1). These differences in the k_q values between PVS and the alkyl viologens were probably due to the disappearance of electrostatic repulsions between ZnTMPyP^{4+} and the viologen: PVS is neutral in its oxidized form whereas the alkyl viologens are positively charged.

TABLE 1

Variation in k_q determined from the slope of Fig. 2

	$k_q \times 10^{-6} \text{ (M}^{-1} \text{ s}^{-1}\text{) for the following viologens}$				PVS
	$(C_1)_2V^{2+}$	$(C_3)_2V^{2+}$	$(C_6)_2V^{2+}$	$(C_{12})_2V^{2+}$	
Aqueous solutions	2	3	3	2	200
CTAC micelles	3	—	2.5	2	80
CTAC microemulsions	2	2	2	2	200
Triton micelles	2	3	2	2	200
SDS micelles	—	—	—	—	200

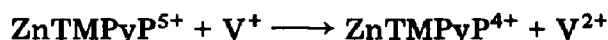
SDS, sodium dodecylsulphate.

3.1.2. In micellar solutions

In micellar solutions the ZnTMPyP^{4+} triplet state was quenched by the viologens used and the formation of reduced viologens was observed. From the same kinetic treatment as that used in aqueous solution, the triplet quenching rate constants for the various viologens were determined. The k_q values (Table 1) obtained in micellar and microemulsion solutions are similar to those determined in aqueous solution. Hence, for the alkyl viologens, k_q is the same in CTAC micelles, CTAC microemulsions and in Triton micelles; for PVS, k_q is unchanged in sodium dodecylsulphate (SDS), CTAC or Triton micelles. The same yields of reduced viologen and the same triplet quenching rate constants were observed in all cases.

3.2. Back electron transfer reaction

The back reaction



was studied by monitoring the disappearance of reduced viologen at 395 nm.

3.2.1. In aqueous solutions

In aqueous solutions the back electron transfer followed a second-order kinetic rate law (Fig. 3(a)). The kinetic rate constants k_b are the same with the various alkyl viologens and are equal to $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Table 2). Table 2 shows that the PVS back electron transfer rate was faster than that observed with alkyl viologens. This is probably due to the attractive electrostatic interactions between the porphyrin cation ZnTMPyP^{5+} and the negatively charged reduced viologen PVS^- .

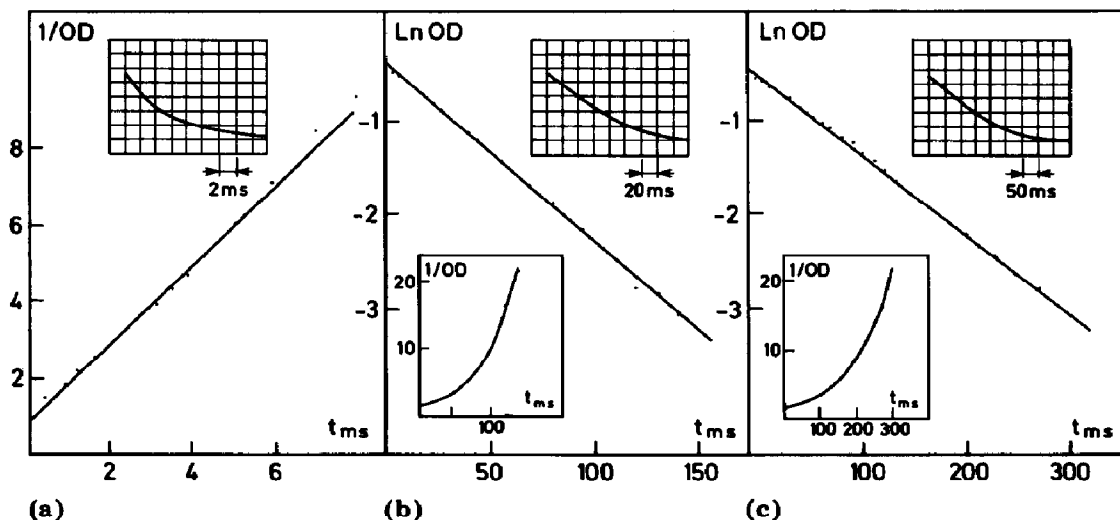


Fig. 3. Kinetic decay of the reduced dioctyl viologen: (a) in aqueous solution (second order); (b) in CTAC microemulsion (first order); (c) in CTAC micelles (first order). The insets show the decay of the reduced viologen with time.

TABLE 2
 Values of the back reaction rate constant k_b for various viologens

k_b for the following viologens							
	$(C_1)_2V^{2+}$	$(C_3)_2V^{2+}$	$(C_6)_2V^{2+}$	$(C_8)_2V^{2+}$	$(C_{12})_2V^{2+}$	$C_{12}V^{2+}$	PVS
Aqueous solutions	$4 \times 10^8 M^{-1} s^{-1}$	$3 \times 10^8 M^{-1} s^{-1}$	$4 \times 10^8 M^{-1} s^{-1}$	$6 \times 10^8 M^{-1} s^{-1}$	$3 \times 10^8 M^{-1} s^{-1}$	$6 \times 10^8 M^{-1} s^{-1}$	$2 \times 10^9 M^{-1} s^{-1}$
CTAC micelles	$4 \times 10^8 M^{-1} s^{-1}$	$4 \times 10^8 M^{-1} s^{-1}$	$1 \times 10^8 M^{-1} s^{-1}$	$9 s^{-1}$	$9 s^{-1}$	$23 s^{-1}$	$3 \times 10^8 M^{-1} s^{-1}$
CTAC micro-emulsions	$4 \times 10^8 M^{-1} s^{-1}$	$4 \times 10^8 M^{-1} s^{-1}$	$2 \times 10^8 M^{-1} s^{-1}$	$19 s^{-1}$	$15 s^{-1}$	$105 s^{-1}$	$6 \times 10^8 M^{-1} s^{-1}$
Triton micelles	$3 \times 10^8 M^{-1} s^{-1}$	$3 \times 10^8 M^{-1} s^{-1}$	$1 \times 10^8 M^{-1} s^{-1}$	$41 s^{-1}$	$41 s^{-1}$	$26 s^{-1}$	$2 \times 10^9 M^{-1} s^{-1}$
SDS micelles	—	—	—	—	—	—	$2 \times 10^8 M^{-1} s^{-1}$

3.2.2. In Triton and cetyltrimethylammonium chloride micellar or cetyltrimethylammonium chloride microemulsion solutions

In Triton and CTAC micellar or CTAC microemulsion solutions the results obtained with alkyl viologens can be divided into two categories.

(i) For dialkyl viologens with chain lengths of less than eight carbon atoms, the results were similar to those obtained in aqueous solution; the kinetic decay was second order and the back electron transfer rate constant was equal to $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The same results were obtained in CTAC or Triton micelles and in CTAC microemulsions. Micelles and microemulsions did not perturb the back electron transfer reaction (Fig. 3(a)).

(ii) For dialkyl viologens with chain lengths greater than or equal to eight carbon atoms, the back electron transfer was strongly retarded in comparison with those observed in the previous cases. The kinetic decay was first order (Figs. 3(b) and 3(c)) and the back reaction rate constant was between 100 and 9 s^{-1} (Table 2).

3.2.3. In neutral, anionic and cationic micelles

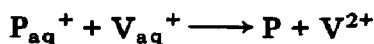
In neutral, anionic and cationic micelles the back reaction between ZnTMPyP^{5+} and PVS^- differs with the surfactant used. In Triton micellar solution, the results were similar to those obtained in aqueous solution and k_b was equal to $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For SDS micelles and CTAC micelles, the back reaction was slowed down and the rate constant still followed a second-order rate law. Table 2 gives the back reaction rate constants obtained in the various cases. With addition of $5 \times 10^{-2} \text{ M NaCl}$, the delay in the back reaction observed with SDS and CTAC micelles disappeared.

4. Discussion

The forward photoelectron transfer rate constants are similar in aqueous solution and in micellar solutions (Table 1). This indicates that the photoelectron transfer from the ZnTMPyP^{4+} triplet state to the viologens takes place in the bulk water even when surfactant assemblies are present. These data suggest that all the alkyl viologens ($C_x, C_y \leq 12$) and PVS are mainly solubilized in the bulk water phase and only sparingly in the micellar core. This is in agreement with the determination of the partition coefficient of viologens in aqueous and dichloromethane solution [8]: only 1% of oxidized dioctyl viologens is solubilized in dichloromethane, whereas 99% remains in the aqueous phase. Similar results were obtained with $\text{C}_1\text{C}_{14}\text{V}^{2+}$ [3, 5].

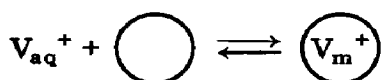
The back reaction process changes with the viologen used.

(i) For alkyl viologens with alkyl chains of less than eight carbon atoms, the reduced viologen kinetic decay is second order and its rate constant is equal to $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous and micellar solutions. This indicates that the back electron transfer occurs in the bulk water of micellar solutions by the following process:



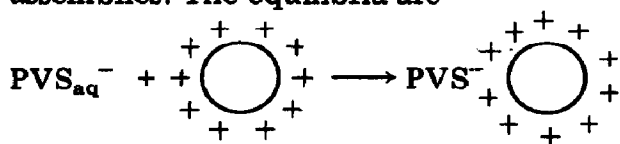
where P^+ and V_{aq}^+ are respectively the porphyrin cation ZnTMPyP^{5+} and the reduced viologen in the aqueous phase.

(ii) For alkyl viologens with chains longer than or equal to eight carbon atoms, the decay is strongly retarded and follows a first-order rate law. The very long lifetime (above 100 ms) of the reduced viologen can be explained by its entry into the micellar core. The partitioning of reduced dioctyl viologen favours hydrophobic solvent [8]; 1% of oxidized dioctyl viologen and 95% of the reduced form are solubilized in dichloromethane. Hence, after reduction, dioctyl viologen is more hydrophobic than before and its affinity for the micellar core increases. The change in the kinetic decay is directly related to the increase in the reduced viologen lifetime and could be explained in terms of (1) kinetic processes

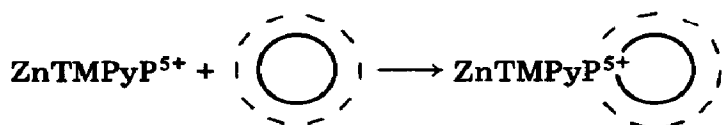


where the circle represents a micelle, V_{m}^+ is the reduced viologen in the micellar core and the rate of exit of the reduced viologen from the micellar assemblies is presumably the rate-determining step and (2) electron transfer back to the oxidized sensitizer which in view of the relative low actual concentration of reduced viologen in the bulk aqueous phase could be pseudo first order. Similar delay in the back reaction has been observed [3, 5]. However, the lifetime of the reduced viologen $\text{C}_1\text{C}_{14}\text{V}^+$ is shorter than those obtained in the present paper and the apparent reduced viologen kinetic decays differ. With $(\text{C}_{12})_2\text{V}^+$ the lifetime reaches 100 ms.

(iii) With PVS, the back electron transfer reaction in aqueous and Triton micellar solutions is faster ($k_{\text{b}} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) than that observed with short-chain dialkyl viologens. This is attributed to electrostatic micellar solutions; the back electron transfer is retarded as a result of electrostatic interaction between one of the species formed and the charged surfactant assemblies. The equilibria are



in CTAC micelles and



in SDS micelles. In these cases, the reduced viologen or the porphyrin cation is adsorbed at the micellar interface. Such phenomena are able to cause a partial delay in the back electron transfer, but the main process is still the bimolecular deactivation.

5. Conclusions

In this paper it has been shown that the forward photoelectron transfer from ZnTMPyP⁴⁺ to dialkyl viologens occurs in the bulk water phase both in the absence and in the presence of micellar assemblies. These results are in agreement with those obtained with C₁C₁₄V²⁺ [3, 5]. The entry of reduced viologen into the micellar core is observed for dialkyl viologens with chain lengths of more than six carbon atoms.

With PVS, the forward and the back reactions occur in the bulk phase, but the presence of SDS micelles or CTAC micelles retards the back reaction because of electrostatic interactions between the charged species and the organized assemblies.

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