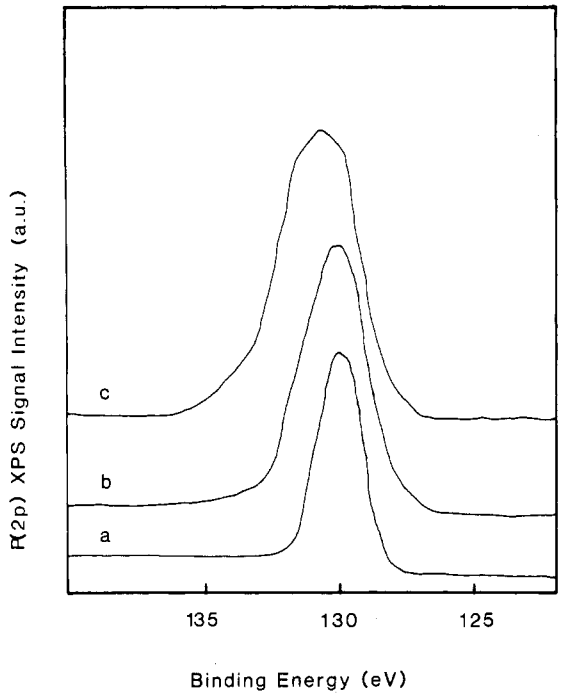

Figure 6. XPS P(2p) spectra for 3 langmuirs of PH_3 (a) with 1 langmuir of D_2O postdosed, (b) with 1 langmuir of D_2O predosed, and (c) on the clean Rh surface. All at 100 K.

does not change the desorption temperature of either PH_3 or D_2O. In either order, there is some displacement of the first adsorbate by the second. Preadsorbing PH_3 reduces both the amount of PH_3 and D_2O detected (see D_2O/PH_3 of Table I). In contrast, preadsorbing D_2O decreases the amount of molecular PH_3 by only 5% compared to PH_3 alone.

After PH_3 exposure, the H_2/PH_3 peak area ratio from the clean surface was compared to the same ratio obtained from the D_2O predosed surface. For a 3-langmuir dose of PH_3 in the presence of preadsorbed D_2O, this ratio decreased 15% indicating a greater percentage of PH_3 desorbing molecularly. However, if PH_3 was predosed, the ratio (compared to the clean surface) remained unchanged even though some PH_3 was displaced during the D_2O exposure.

After coadsorption, H_2, HD, and D_2 were all present in TPD. No deuterated species (i.e., PH_2D, PHD_2, and PD_3) other than those associated with D_2O were detected, indicating that no D for H exchange occurred between D_2O and PH_3.

Summary

The work presented here is summarized as follows:

By comparison with gas-phase data, He II UPS of a multilayer of PH_3 adsorbed on Ni(100) at 25 K shows peaks readily identified with molecular phosphine.

There is evidence for some dissociation when PH_3 gas at 300 K interacts with Ni(100) at 25 K.

On Rh(100) at 100 K, adsorption of PH_3 leads to both dissociated and molecular states.

Molecular PH_3 and atomic P are readily distinguished on the basis of the P(2p) binding energy.

Coadsorbed PH_3 and D_2O on Rh(100) interact very weakly. There is no D-for-H isotope exchange in the molecularly desorbing species and the UPS and XPS are adequately described as superpositions of the spectra of the individual components.

Preadsorbed D_2O on Rh(100) inhibits dissociative adsorption of PH_3.

In coadsorption at 100 K on Rh(100), there is some displacement of the first adsorbate by the second.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. PH_3, 7803-51-2; H_2O, 7732-18-5; Rh, 7440-16-6; Ni, 7440-02-0.

Complex Formation between Anthraquinone-2,6-disulfonate and a Neutral Zinc Porphyrin. Effects of CTAB Micelles on Complex Stability and Photoinduced Electron Transfer

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Zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin, Zn-TPSPyP^0, forms a complex with anthraquinone-2,6-disulfonate, AQS_2^{2-}. The porphyrin is statically quenched by the quinone acceptor in the complex structure. In the presence of CTAB micelles the complex is separated and AQS_2^{2-} is bound to the micelles. The excited sensitizer decays to a long-lived triplet state (0.5 ms) and induces the reduction of AQS_2^{2-}. The micelles also function in the charge separation of the electron-transfer products.

Introduction

Mimicking photosynthesis by artifical photosensitized electron-transfer reactions (eq 1) is extensively studied as a means

$$A + D \xrightarrow{h\nu} A^- + D^+ \qquad (1)$$

of solar energy conversion and storage.[1-3] A basic limitation that accompanies these reactions is the rapid recombination of the electron-transfer products.[4] Various organized media such as charged micelles,[5,6] colloids,[7,8] or polyelectrolytes[9] as well as hy-

(1) (a) Whitten, D. G.; Russel, J. C.; Schmell, R. H. *Tetrahedron* **1982**, *38*, 2455-87; *Acc. Chem. Res.* **1980**, *13*, 83-90. (b) "Energy Resources through Photochemistry and Catalysis"; Gratzel, M., Ed.; Academic Press: New York, 1983.

(2) (a) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376-84. (b) Sutin, N.; Greutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717-38. (c) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159-244.

(3) (a) Bard, A. J. *Science* **1980**, *207*, 139. (b) "photogeneration of Hydrogen"; Harriman, A., West, M. A., Eds.; Academic Press: London, 1983.

(4) Willner, I.; Laane, C.; Otvos, J. W.; Calvin, M. In "Inorganic Reactions in Organized Media"; Holt, S. L., Ed.; American Chemical Society: Washington, DC, 1982; ACS Symp. Ser. No. 177, pp 71-95.

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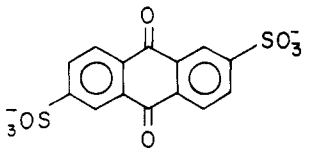
drophilic–hydrophobic environments such as water-in-oil microemulsions[10] have been successfully applied as a means of controlling the photoinduced electron-transfer process and for stabilization of the photoproducts against recombination. Quinones play a major role in the photoinduced electron-transfer chain in the mitochondria and chloroplasts.[11] In photosynthesis, electron-transfer reactions of quinones are important in linking photosystems I and II via a "plastoquinone pool".[12] Thus, the photoreduction of quinones in artificial environments might offer a model for the functions of quinones in natural photosynthesis.

Here we wish to report on the photosensitized reduction of anthraquinone-2,6-disulfonate, AQS_2^{2-} (**1**) in a CTAB micellar



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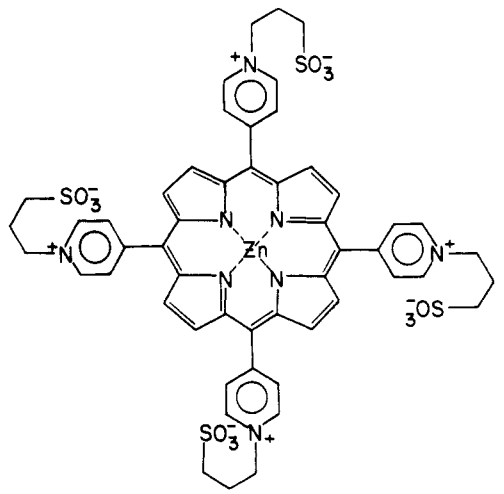
system, using a neutral, water-soluble Zn porphyrin, zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin,[13,14] Zn-TPSPyP^0 (**2**) as sensitizer, and cysteine as electron donor. We



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find that in an aqueous solution a macromolecular complex between Zn-TPSPyP^0 and AQS_2^{2-} is formed. This complex structure prevents the separation of the photosensitized electron-transfer products. CTAB micelles affect the separation of this complex, and subsequently stabilize the photoinduced electron-transfer products against the back electron-transfer reaction. As a result, the reduction of AQS_2^{2-} under steady-state illumination is accomplished.

Experimental Section

Absorption spectra were recorded with a Uvikon-820 (Kontron) spectrophotometer equipped with a ψ-80 computer (Kontron) for spectra accumulation and manipulation. Fluorescence spectra were recorded with a SEM-25 spectrophotometer (Kontron). Flash photolysis experiments were performed with a DL200 (Molectron) dye laser pumped by a UV-IU (Molectron) nitrogen laser. Flashes were recorded on Biomation 8100 and pulse collection was performed with a Nicolet-1170. Steady-state illuminations were performed with a 150-W xenon arc lamp (PTI A-1000). Light was filtered through an interference filter, $\lambda >$ 400 nm, photon flux 3×10^{-3} einsteins L^{-1} min^{-1}.

Zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridinio]-porphyrin, Zn-TPSPyP^0 (**2**) was prepared[13] by the metallation of the zwitterionic ligand *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridinio]porphyrin. The zwitterionic ligand was prepared by reacting *meso*-tetrapyridylporphyrin (200 mg, 0.32 mmol)(Strem) with 1,3-propane sultone[15] (Aldrich), (1 g, 8.2 mmol). The mixture was heated under nitrogen for 2 h. The resulting mixture was washed several times with acetone and the dark green precipitate was filtered. The solid obtained (220 mg) is *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridinio]porphyrin. The zwitterionic ligand, *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridinio]-porphyrin, (150 mg, 0.13 mmol) was dissolved in 20 mL of an aqueous solution of $ZnCl_2$ (20 mg, 0.15 mmol). The solution was boiled under nitrogen, and the absorption spectra of aliquots of the reaction were recorded at time intervals of boiling. After metallation was completed, the hot aqueous solution was passed through an anion exchange resin (Amberlite IRA-410, OH^- form) to remove excess of $ZnCl_2$. Upon cooling of the aqueous black-green solution a precipitate (120 mg) of zinc(II) *meso*-tetrakis-[1-(3-sulfonatopropyl)-4-pyridinio]porphyrin, Zn-TPSPyP^0 (**2**) was obtained. The product gave satisfactory elementary analysis.

For steady-state illuminations the system was composed of an aqueous 0.02 M phosphate buffer, pH 6.0, that included the sensitizer, Zn-TPSPyP^0, (5×10^{-6} M), the electron acceptor, AQS_2^{2-}, (3×10^{-4} M), and L-cysteine (2×10^{-3} M) as electron donor. Different concentrations of CTAB micelles were applied in these systems. Samples (3 mL) of these aqueous solutions were transferred into 1 × 1 cm Pyrex glass cuvettes equipped with a valve and serum stopper. Samples were deaerated by repeated evacuation followed by flushing with oxygen-free argon. The samples were illuminated with a 150-W xenon arc lamp ($\lambda >$ 400 nm) and formation of the reduced product, the protonated semiquinone radical, $AQHS_2^{2-\cdot}$, was followed at λ = 385 nm (ϵ = 12000 M^{-1} cm^{-1}). Fluorescence measurements were performed in aqueous 0.02 M phosphate buffer samples (3 mL) that included the sensitizer Zn-TPSPyP^0 (3×10^{-6} M). Fluorescence decay upon addition of AQS_2^{2-} was followed at λ = 622 nm. Quenching of the triplet *Zn-TPSPyP by AQS_2^{2-} was recorded by following the decay of the triplet *Zn-TPSPyP at λ = 790 nm. In these systems a deaerated aqueous 0.02 M buffer solution that included the sensitizer Zn-TPSPyP^0 (3×10^{-6} M) was employed, excitation at λ = 448 nm.

Results and Discussion

Complex Formation between Zn-TPSPyP^0 and AQS_2^{2-}. Metalloporphyrins form complexes with various electron acceptors.[16-18] For example, the formation of macromolecular complexes of *N,N'*-dimethyl-4,4'-bipyridinium with various metal porphyrins such as Zn-TPPS^{4-} and Pd-TPPS^{4-} has been established in recent years.[16,17] In these complexes, that might be attributed primarily to electrostatic attractions of the two components, the electronic spectrum of the metalloporphyrin is altered. We find that a complex structure is also formed between the

(5) (a) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675–96. (b) Brugger, P. A.; Infelta, P. P.; Braun, A. M.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320–6.
(6) Matsuo, T.; Takuma, K.; Tsusui, Y.; Nishigima, T. *Coord. Chem. Rev.* **1980**, *10*, 195–216.
(7) (a) Willner, I.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1981**, *103*, 3203–5. (b) Willner, I.; Yang, J. M.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1981**, *85*, 3277–82.
(8) Degani, Y.; Willner, I. *J. Am. Chem. Soc.* **1983**, *105*, 6228–6233.
(9) (a) Meisel, D.; Matheson, M. *J. Am. Chem. Soc.* **1977**, *99*, 6577. (b) Meisel, D.; Matheson, M.; Rabani, J. *Ibid.* **1978**, *100*, 117.
(10) Mandler, D.; Degani, Y.; Willner, I. *J. Phys. Chem.* **1984**, *88*, 4366–70.
(11) (a) Brodie, A. F. In "Biochemistry of Quinones"; Morton, R A., Ed.; Academic Press: New York, 1965; p 384. (b) Avron, M. In "Current Topics in Bioenergetics"; Sanadi, D. R., Ed.; Academic Press: New York, 1967; p 1.
(12) Amesz, J. *Biochim. Biophys. Acta* **1973**, *301*, 35.
(13) Willner, I.; Degani, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1249–51.
(14) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1955–70.
(15) Willner, I.; Ford, W. E. *J. Heterocycl. Chem.* **1983**, *20*, 1113–14.
(16) (a) Shelnutt, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4275. (b) Okura, I.; Aono, S., Takeuchi, M.; Kusunoki, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3637.
(17) Okura, I.; Kusunoki, S.; Aono, S. *Inorg. Chim. Acta* **1983**, *77*, 99–100.
(18) Rougee, M.; Ebbesen, T.; Ghetti, F.; Bensasson, R. V. *J. Phys. Chem.* **1982**, *86*, 4404.

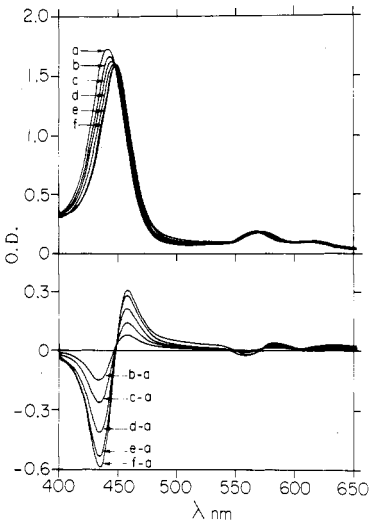

Figure 1. Absorption spectra (top) and differential absorption spectra (bottom) of Zn-TPSPyP^0 (8×10^{-6} M) obtained after addition of AQS_2^{2-}: (a) no added AQS_2^{2-}; (b) $[AQS_2^{2-}] = 3.3 \times 10^{-6}$ M; (c) $[AQS_2^{2-}] = 6.7 \times 10^{-6}$ M; (d) $[AQS_2^{2-}] = 13.3 \times 10^{-6}$ M; (e) $[AQS_2^{2-}] = 26.7 \times 10^{-6}$ M; (f) $[AQS_2^{2-}] = 60.0 \times 10^{-6}$ M.

zwitterionic Zn porphyrin, Zn-TPSPyP^0, and anthraquinone-2,6-disulfonate, AQS_2^{2-}. The visible absorption spectrum of *Zn-TPSPyP^0 exhibits the Soret absorption band at $\lambda = 439$ nm ($\epsilon = 2.15 \times 10^5$ M^{-1} cm^{-1}). Upon addition of AQS_2^{2-} a considerable shift in the Soret band is observed (Figure 1). From the spectral changes observed upon addition of successive amounts of AQS_2^{2-}, and application of the Benesi–Hildebrand[19] equation the association constant of the complex (eq 2) has been estimated

$$\text{Zn-TPSPyP}^0 + AQS_2^{2-} \overset{K_1}{\rightleftharpoons} [\text{Zn-TPSPyP-}AQS_2^{2-}] \quad (2)$$

to be $K_1 = (4 \pm 1) \times 10^5$ M^{-1}. This complex has a maximum Soret absorption band at $\lambda = 452$ nm, ($\epsilon = 2.02 \times 10^5$ M^{-1} cm^{-1}).

Since quinones are effective as quenchers of metalloporphyrins, we have examined the effect of the Zn-TPSPyS^0···AQS_2^{2-} complex formation on the photophysical properties of the porphyrin (Figure 2). Under air, Zn-TPSPyP^0 exhibits a fluorescence emission at $\lambda_{max} = 622$ nm. Addition of minor amounts of AQS_2^{2-} results in quenching of the fluorescence emission of Zn-TPSPyP and at a concentration of AQS_2^{2-} of 5×10^{-5} M the fluorescence of the sensitizer is totally quenched. The decay of the fluorescence is attributed to a static quenching of the singlet excited porphyrin as a result of the complex structure formation [Zn-TPSPyP^0··· AQS_2^{2-}], (eq 2). Several observations support the assumption that indeed the fluorescence decay is due to a static quenching process of the excited singlet state: The Stern–Volmer plot of the fluorescence intensity is nonlinear, consistent with a static quenching process. Furthermore, the singlet excited state of Zn-TPSPyP^0 has a very short lifetime[14,20] of ca. 10×10^{-9} s. It decays effectively to the triplet state ($\phi = 0.9$)[14,20] that is long lived $\tau = 0.50$ ms. Addition of a small amount of AQS_2^{2-} (in the range of 5×10^{-6} M) to an aqueous solution of Zn-TPSPyP^0 (5×10^{-6} M) decreases the fluorescence intensity of the sensitizer (Figure 2). Simultaneously, flash experiments on the same systems reveal that the triplet lifetime is unaffected by the addition of AQS_2^{2-} and only the quantum yield of the triplet formation is decreased as the AQS_2^{2-} concentration is increased. These results imply that the excited singlet state of Zn-TPSPyP^0 is statically quenched in the complex structure, and that only the fraction of uncomplexed sensitizer decays to the triplet state. The fluorescence intensity at different concentrations of AQS_2^{2-} allows us to estimate the amount of free sensitizer in equilibrium with the complex structure. Using this method, the association constant of the

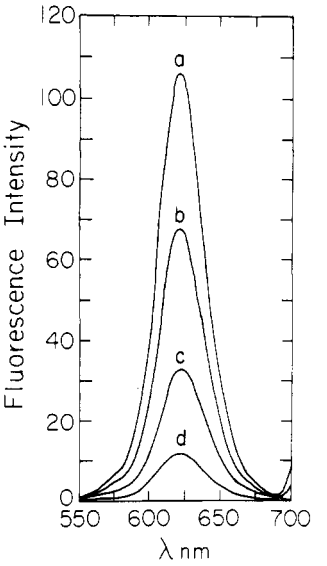

Figure 2. Fluorescence spectra of Zn-TPSPyP^0 (2.2×10^{-6} M) upon addition of AQS_2^{2-}: (a) no added AQS_2^{2-}; (b) 2×10^{-6} M; (c) 6×10^{-6} M; (d) 12×10^{-6} M.

complex (eq 2) was derived to be $K_1 = 3.7 \pm 0.1 \times 10^5$ M^{-1}. This value is in total agreement with that obtained earlier by spectroscopic means. We thus conclude that the addition of AQS_2^{2-} to Zn-TPSPyP^0 forms a complex structure that quenches statically the excited singlet state of the sensitizer and prevents the formation of the triplet long-lived species.

Positively charged micelles might affect the separation of the [Zn-TPSPyP^0–AQS_2^{2-}] complex by binding the negatively charged component of the structure to the micelles. Indeed addition of the surfactant CTAB (5×10^{-3} M) to an aqueous solution that contains a Zn-TPSPyP^0 (8×10^{-6} M) and AQS_2^{2-} (2×10^{-4} M), under conditions where the porphyrin is completely bound [Zn-TPSPyP^0···AQS_2^{2-}], results in the original absorption spectrum and fluorescence intensity of the free porphyrin, Zn-TPSPyP^0. These results suggest that the positively charged CTAB micelles destroy the complex structure by binding of AQS_2^{2-} to the micellar interface. Consequently, the emission properties of the Zn porphyrin are restored. The restoration of the emission properties of the Zn-TPSPyP^0 by the addition of CTAB micelles allow us to determine the concentrations of AQS_2^{2-} bound to the Zn porphyrin, the amount free in solution (eq 3) and the amount

$$[AQS_2^{2-}]_{free} = K_1[\text{Zn-TPSPyP}^0]/[\text{Zn-TPSPyP}^0\cdots AQS_2^{2-}] \quad (3)$$

bound to the micellar interface.

Photosensitized Reduction of AQS_2^{2-}. The complex formation between Zn-TPSPyP^0 and AQS_2^{2-} and subsequent quenchings of the excited singlet state is anticipated to prevent any net separation of electron-transfer products due to rapid back reaction in the complex structure. The separation of the complex by CTAB micelles suggests that in the micellar medium the T state of Zn-TPSPyP^0 might be formed and subsequent charge separation by the charged micelles might be assisted.

Indeed, illumination ($\lambda > 400$ nm) of an aqueous solution that includes the sensitizer Zn-TPSPyP^0 (5×10^{-6} M), anthraquinone-2,6-disulfonate, AQS_2^{2-} (3×10^{-4} M) and cysteine (2×10^{-3} M) does not yield any reduction of the electron acceptor. Addition of CTAB micelles at a concentration of 5×10^{-3} M, where all the sensitizer is practically in its free form, results in the photoreduction of AQS_2^{2-}. The reduced photoproduct at the pH conditions of the aqueous medium is the protonated semiquinone,[21] $AQHS_2^{2-}\cdot$. The rate of $AQHS_2^{2-}\cdot$ formation was followed spectroscopically[21] ($\lambda = 385$ nm, $\epsilon = 12\,000$ M^{-1} cm^{-1}) and the quantum yield of $AQHS_2^{2-}\cdot$ formation corresponds to $\phi = 2.35 \times 10^{-2}$. To account for the ability to photoreduce AQS_2^{2-} in the presence of CTAB micelles, we have followed the photo-

(19) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
(20) Houlding, V. H.; Kalyanasundaram, K.; Gratzel, M.; Milgrom, L. R. *J. Phys. Chem.* **1983**, *87*, 3175–3179.
(21) Rao, P. S.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 2274–2276.

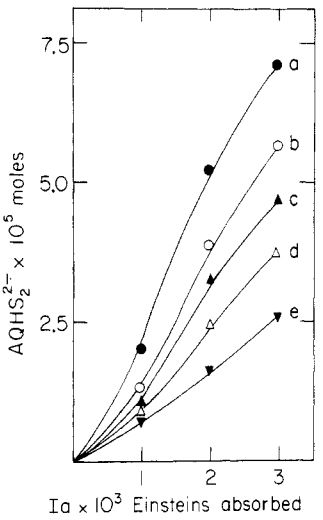

Figure 3. Quantum yield of AQS_2^{2-} reduction at different CTAB micelles concentration. In all systems [Zn-TPSPyP] = 5×10^{-6} M; $[AQS_2^{2-}] = 3 \times 10^{-4}$ M; [cysteine] = 2×10^{-3} M; pH 6. The [CTAB] is (a) 5×10^{-3} M; (b) 1.5×10^{-3} M; (c) 1.20×10^{-3} M; (d) 1.05×10^{-3} M; (e) 1.00×10^{-3} M.

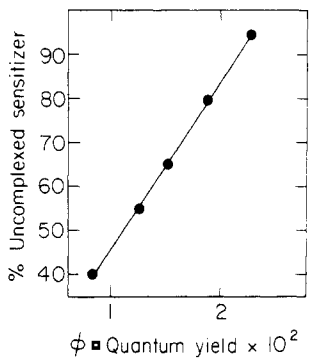

Figure 4. Correlation between the quantum yield of $AQHS_2^{2-}\cdot$ formation and the fraction of free sensitizer.

sensitized electron-transfer process by means of flash photolysis. Upon excitation of an aqueous solution of Zn-TPSPyP^0, the short-lived singlet is transferred to the long-lived T state, $\tau = 0.5$ ms, (eq 4). AQS_2^{2-} eliminates this transformation due to internal

$$*\text{Zn-TPSPyP}^0\ (S) \xrightarrow{\phi = 0.9} *\text{Zn-TPSPyP}^0\ (T) \qquad (4)$$

quenching in the complex structure. In the presence of 5×10^{-3} M CTAB micelles, that decompose the complex, the triplet long-lived species is again formed. Further addition of AQS_2^{2-} results in the oxidative quenching of the triplet $k_q = (7.5 \pm 0.7) \times 10^7$ M^{-1} s^{-1} and formation of the electron-transfer products (eq 5). These observations imply that only the free sensitizer might

$$*\text{Zn-TPSPyP}^0\ (T) + AQS_2^{2-} + H^+ \xrightarrow{k_q} \text{Zn-TPSPyP}^{+}\cdot + AQHS_2^{2-}\cdot \qquad (5)$$

lead to separated electron-transfer products via quenching of the triplet state. This conclusion has been further supported by steady-state illumination experiments. In these systems different concentrations of CTAB micelles have been introduced into an aqueous solution of Zn-TPSPyP^0 (5×10^{-6} M), AQS_2^{2-} (3×10^{-4} M), and cysteine (2×10^{-3} M) and the quantum yields of $AQHS_2^{2-}\cdot$ formation have been determined (Figure 3). From the association constant K_1 of AQS_2^{2-} to ZnTPSPyP^0 and the absorption or fluorescence changes of the sensitizer the amount of free sensitizer at each CTAB concentration can be estimated. The overall quantum yield of $AQHS_2^{2-}\cdot$ formation at different CTAB concentrations shows a linear correlation (Figure 4). This fact confirms that the electron-transfer product $AQHS_2^{2-}\cdot$ originates from the free sensitizer produced in the presence of micelles.

TABLE I: Effects of Ionic Strength of CTAB Micellar Media on the Charge Separation Quantum Yield and Recombination Rate

[NaCl]	<0.025	0.125	0.225
ϕ^a	4.8×10^{-2}	4.7×10^{-2}	3.8×10^{-2}
K_b^b, M^{-1} s^{-1}	2.5×10^8	1.1×10^9	2.5×10^9

[a] Light intensity of laser pulse was determined by actinometry of the system $Ru(bpy)_3^{2+}$, Fe^{3+}, $HClO_4$ 1 M; $\phi = 1.0$. [b] Determined by following the absorption decay of ZnTPSPyP$^+$ at $\lambda = 680$ nm.

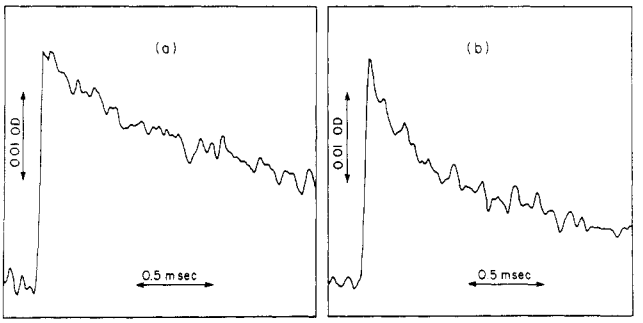

Figure 5. Transient decay of Zn-TPSPyP$^{+}\cdot$ to Zn-TPSPyP^0 followed at $\lambda = 680$ nm. Excitation of [Zn-TPSPyP^0] = 4×10^{-6} M at $\lambda = 448$ nm with $[AQS_2^{2-}] = 4 \times 10^{-4}$ M and [CTAB] = 5×10^{-3} M: (a) without added salt; (b) with NaCl = 0.1 M.

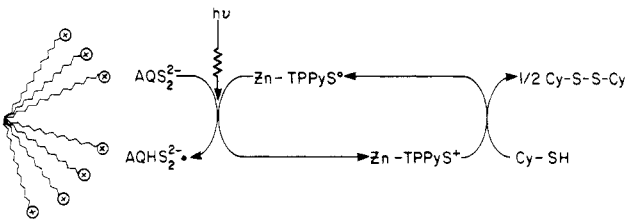

Figure 6. Schematic function of CTAB micelles in binding AQS_2^{2-} and charge separation of photoproducts.

In addition to the function of the CTAB micelles in the separation of the complex [Zn-TPSPyP^0···AQS_2^{2-}], the positively charged interface might also participate in the charge separation process.[5,6] Since the electron-transfer products (eq 6) are oppo-

$$\text{Zn-TPSPyP}^{+}\cdot + AQHS_2^{2-}\cdot \xrightarrow{k_b} \text{Zn-TPSPyP}^0 + AQS_2^{2-} + H^+ \qquad (6)$$

sitely charged, the oxidized product is anticipated to be repelled by the micellar interface with which the reduced product $AQHS_2^{2-}\cdot$ is associated. Consequently, the micellar interface might contribute to the stabilization of the photoproducts against back electron-transfer reactions (eq 6). To account for this function of the CTAB micelles, the effect of added salt on the recombination rate constant (k_b, eq 6) has been examined by means of laser flash photolysis. At high ionic strength of the aqueous media the micellar surface potential should decrease according to the Gouy-Chapman theory,[22] and the recombination rate is expected to be enhanced if electrostatic interactions affect the recombination process. The effect of added salt on the charge separation yield of the photoproducts and recombination rate constants are summarized in Table I. It can be seen that at a salt concentration of [NaCl] = 1.25×10^{-1} M the recombination rate (Figure 5) is increased 4-fold as compared to the system without added salt, while the charge separation yield is not affected. Simultaneous fluorescence and absorption spectra of the salt included system reveal that at [NaCl] = 1.25×10^{-1} M the sensitizer is present in its free form and AQS_2^{2-} is bound to the micelles. At higher ionic strength, [NaCl] = 2.0×10^{-1} M, in addition to acceleration of the recombination rate, the initial quantum yield of separated

(22) (a) Rosen, M. J. "Surfactants and Interfacial Phenomena"; Wiley-Interscience; New York, 1978; pp 28–55. (b) Jones, M. N. "Biological Interfaces"; Elsevier: New York, 1975; Chapter 6, pp 135–162.

photoproducts is decreased. Fluorescence and absorption spectra measurements on this system reveal that at this ionic strength a significant portion of the sensitizer is already in the complex structure, Zn-TPSPyP^0···AQS_2^{2-}. The release of AQS_2^{2-} from the micelles at high salt concentration is attributed to the decrease in the micellar surface potential. The escape of AQS_2^{2-} from the micellar interface regenerates the complex between the sensitizer and the electron acceptor and eliminates the T-state formation. Thus we conclude that the CTAB micellar system, in addition to the separation of the complex structure, functions in the stabilization of the photoproducts against the back electron-transfer reaction. The retardation of the back electron-transfer reaction allows the effective subsequent sacrificial oxidation of cysteine (eq 7, Figure 6).

$$\text{Zn-TPSPyP}^{+\cdot} + \text{CySH} \rightarrow \text{Zn-TPSPyP} + {}^1/_2\text{CyS-SCy} \quad (7)$$

Conclusions

We have shown that Zn-TPSPyP^0 forms a complex with anthraquinone-2,6-disulfonate. The formation of this complex eliminates the production of photoinduced electron-transfer products. Positively charged CTAB micelles assist the separation of this macromolecular complex and allow the utilization of the triplet-state Zn-TPSPyP^0 in photosensitized electron-transfer processes. The micellar interface also stabilizes the oppositely charged photoproducts against the degradative recombination reactions. Since quinones and porphyrins play a major role in the photoinduced electron-transfer chain of photosynthesis, we believe that similar interactions with charged membranes might contribute to the effectiveness of these processes. One might also envisage the application of other binding interfaces that could substitute the functions of the micelles, i.e., charged colloids or hydrophobic cyclodextrin receptors.

Finally, in this study we applied the fluorescence and absorption properties of the Zn porphyrin to probe the binding properties of AQS_2^{2-} to the CTAB micelles. Since other electron acceptors, i.e., methylviologen, form complexes with metalloporphyrins, this method could be generalized to probe the binding properties to various interfaces. These different aspects are now being examined in our laboratory.

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Photoformation and Structure of O_2^- and Nitrogen-Containing Anion Radicals Adsorbed on Highly Dispersed Titanium Oxide Anchored onto Porous Vycor Glass

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Photoformation of O_2^- and nitrogen-containing radicals on titanium oxide anchored onto porous Vycor glass has been studied by using ESR and isotopically labeled compounds. UV irradiation of the anchored catalyst at 77 K in the presence of N_2O or O_2 leads to the formation of an unstable nitrogen-containing radical (N_2O^- or $N_2O_2^-$) and O_2^- anion radical, respectively. Hyperfine splittings due to ^{17}O nuclei show that the photoformed O_2^- species are adsorbed on Ti^{4+} ions with slightly nonequivalent oxygen nuclei. The addition of oxygen onto the catalyst at 77 K in the presence of the nitrogen-containing radical leads to the disappearance of the latter species and to the formation of O_2^-, indicating that the electron transfer occurs easily between species adsorbed on the anchored titanium oxide.

Introduction

Although it is well established that coordinative unsaturation at the surface plays a significant role in heterogeneous catalysis, the role of surface ions in low coordination in photocatalysis is still unclear.[1] To investigate this, oxide catalysts prepared by anchoring methods can be used, because they are expected to have more homogeneous surface sites than those of catalysts prepared by usual impregnation methods and also because it is easier to control the degree of coordinative unsaturation at the surface.[2]

In a preceding paper, we have investigated the photoluminescence and photocatalytic reactivity of titanium oxide anchored onto porous Vycor glass and showed that the titanium ions are present in a high dispersion state which results in a less efficient radiationless transfer of photon energy absorbed by the catalyst.[3] Such anchored catalysts would be expected to exhibit characteristics appropriate for various types of surface reactions including photoreactions to occur. For instance, Lyashenko et al.[4] have reported that titanium oxide anchored onto silica possesses a much higher selectivity than bulk TiO_2 catalysts for the formation of acetone in the i-C_4H_8 photooxidation.

Recently, we have reported that the N_2O^- anion radicals are formed by UV irradiation of anchored titanium oxide in the

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(1) (a) Anpo, M.; Aikawa, N.; Kubokawa, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 644. (b) Anpo, M.; Suzuki, T.; Kubokawa, Y.; Tanaka, F.; Yamashita, S. *J. Phys. Chem.* **1984**, *88*, 5778. (c) Kubokawa, Y.; Anpo, M. "Adsorption and Catalysis on Oxide Surfaces"; Che, M., Bond, G. C., Eds.; Elsevier: Amsterdam, 1985; p 127.

(2) (a) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, v. A. "Catalysis by Supported Complexes"; Elsevier: Amsterdam, 1981. (b) Boehm, H.; Knözinger, H. "Catalysis"; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: West Berlin, 1983; Vol. 4, p 39. (c) Iwasawa, Y.; Yamagishi, M. *J. Catal.* **1983**, *82*, 373 and their earlier papers. (d) Kozlowwski, R.; Pettifer, R. F.; Thomas, J. M. *J. Phys. Chem.* **1983**, *87*, 5176.

(3) Anpo, M. Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. *J. Phys. Chem.*, in press.

(4) Lyashenko, L. V.; Belousov, V. M.; Yampol'skaya, F. A. *Kinet. Katal.* **1982**, *23*, 662.

0022-3654/85/2089-5689$01.50/0