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Zinc Porphyrin Sensitized Reduction of Simple and Functional Quinones in Micellar Systems

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The photoinduced reduction of duroquinone (DQ) and a long-chain substituted duroquinone ($C_{11}DQ$) by zinc porphyrin was studied by means of laser photolysis techniques in micellar solution. The mean time required for intramicellar electron transfer is 0.2 μs for DQ and $C_{11}DQ$. Quenching through intermicellar migration of the acceptor occurs only in the case of DQ for which the rates of entry and exit into and from the micelle are 5×10^{10} M^{-1} s^{-1} and 6×10^5 s^{-1}. $C_{11}DQ$ is immobilized by the long chain in the micelle and migration does not occur on a millisecond time scale. Partial charge separation is achieved in the case of $C_{11}DQ$ through ejection of the cation from the micelle.

Introduction

Photoinduced redox reactions are presently appealing to an increasing number of researchers as attractive processes for the conversion of light into chemical energy.[1] In these systems light acts as an electron pump promoting electron transfer from a donor to an acceptor molecule

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

The back conversion of D^+ and A^- into D and A can be coupled to hydrogen[2] and oxygen[3] production from water via redox catalysis. The absorption and redox properties of zinc porphyrin make it an attractive candidate to serve as the photoactive donor in such a system. This compound is, however, sparsely soluble in water, making the use of solubilizing agents such as micelles mandatory. The photoreduction of anthraquinone sensitized by ZnTPP has

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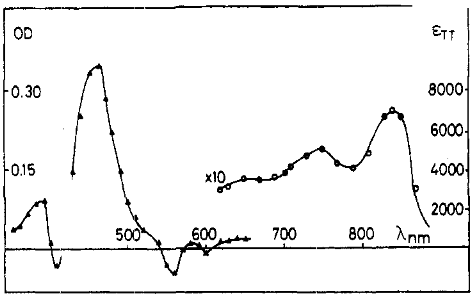


Figure 1. Left: Triplet–triplet absorption spectrum of ZnP immediately after the laser pulse; right: differential absorption spectra of ZnP (ground state depopulation and triplet–triplet absorption spectra). At 460 nm the triplet–triplet extinction coefficient is about 100.000 M^{-1} cm^{-1}: [ZnP] = 5×10^{-5} M; [CTAC] = 5×10^{-2} M. Absorption spectrum obtained 50 ns (—) and 100 ns (- - -) after the laser pulse: [ZnP] = 5×10^{-5} M; [DQ] = 4×10^{-4} M; [CTAC] = 5×10^{-2} M.

been investigated before.[4] We have been interested previously[5] in exploring the characteristics of light-initiated redox reactions in simple and functional micellar systems. In the present paper the photoinduced reduction of quinones by ZnP and its tetraphenyl derivative ZnTPP is scrutinized. By comparing the data obtained with simple duroquinone and a long-chain substituted duroquinone, a fast intramicellar and slower intermicellar component in the electron-transfer reaction can be identified.

Experimental Section

Materials. Zinc porphyn and zinc tetraphenylporphyrin were produced by Ferak Berlin and by K & K, respectively. These two porphyrins were used without further purification. Duroquinone, DQ, was an Aldrich-Europe product.

$C_{11}DQ$ was synthesized by Dr. Fischer, Hahn-Meitner Institute, Berlin. In this compound one of the four methyl groups of duroquinone was exchanged by a long hydrocarbon tail ($C_{11}H_{23}$).

The CTAC (cetyltrimethylammonium chloride) surfactant, Eastman Kodak, was purified by numerous recrystallizations from methanol and ether. Deionized water was distilled from alkaline permangate and subsequently twice from a quartz still.

Apparatus. Flash photolysis experiments were carried out by using a JK-2000 frequency-doubled Nd laser with a pulse of 15 ns duration and an energy of 50–100 mJ as measured by a bolometer. A small fraction of the laser beam was directed through beam-splitting into an ITT-F-4044 S4 photodiode to monitor its intensity. Conventional kinetic spectroscopy consisting of a pulsed xenon lamp, a Bausch & Lomb monochromator, and a photomultiplier and diode was employed to detect transients produced by the flash in the sample cell. This system allows for a time resolution of approximately 3 ns. All experiments were carried out at room temperature.

Results and Discussion

Zinc porphyrin possesses spectroscopic properties which are related to those of the tetraphenylporphyrin (ZnTPP).[6] Thus the absorption spectrum in micellar solution of CTAC (5×10^{-2} M) is characterized by two bands centered at 610 and 560 nm as well as the Soret band at 420 nm.

Figure 1 shows the absorption spectrum of the ZnP triplet which exhibits maxima at 460 and 840 nm. From a study of the transient optical densities produced at various laser intensities[7] one obtains the extinction coefficients which are also indicated in the figure. The triplet is relatively stable in the absence of oxygen. Its decay follows first-order kinetics with a specific rate of 5×10^3 s^{-1}.

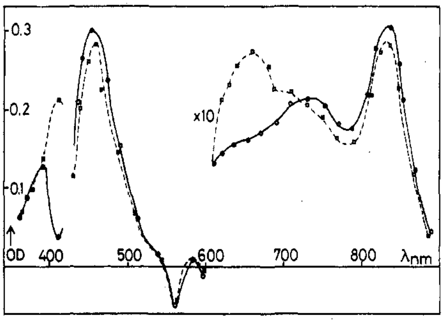
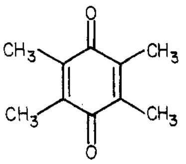
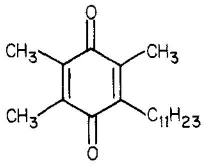


Figure 2. Absorption spectrum obtained 50 ns (—) and 100 ns (- - -) after the laser pulse: [ZnP] = 5×10^{-5} M; [DQ] = 4×10^{-4} M; [CTAC] = 5×10^{-2} M.

We shall now examine the triplet behavior in the presence of two electron acceptors, i.e., duroquinone and a long-chain substituted duroquinone.



DQ



$C_{11}DQ$

Figure 2 shows transient spectra obtained with CTAC solution containing both ZnP and DQ. The absorption curve at the end of the laser pulse resembles closely the ZnP triplet spectrum. After 100 ns one notices a decrease in these triplet peaks and simultaneous formation of new bands centered around 410 and 650 nm. By analogy with the spectral data known for $ZnTPP^+$ these peaks can be assigned to the ZnP^+ cation, produced via oxidative quenching of the triplet states

$$ZnP(T_1) + DQ \rightarrow DQ^- + ZnP^+ \quad (2)$$

Reaction 2 will now be analyzed kinetically for both DQ and $C_{11}DQ$.

(*1*) *Acceptor $C_{11}DQ$.* Through the presence of the hydrocarbon tail this acceptor is expected to be anchored to the micelle. Hence, during the ZnP triplet lifetime practically no intermicellar exchange of $C_{11}DQ$ will occur. Thus, only those micelles that are occupied simultaneously by $C_{11}DQ$ and ZnP shall contribute to the electron-transfer quenching. If the distribution of $C_{11}DQ$ over the aggregates is governed by Poisson's law, then the time dependence of the ZnP triplet concentration is given by[8,9]

$$[^3ZnP] = [^3ZnP]_0 \exp(-kt) \exp\{\bar{n}[\exp(-k_qt) - 1]\} \quad (3)$$

where $[^3ZnP]$ and $[^3ZnP]_0$ are the concentrations of triplets at time t and immediately after the laser pulse, respectively; $\bar{n}$ is the average number of $C_{11}DQ$ per micelle $\bar{n} = [C_{11}DQ]/[M]$ where [M], the concentration of micelles, was about 5×10^{-4} M in our experiments, k is the specific deactivation rate of ^3ZnP in the absence of acceptor, and k_q is the specific electron-transfer rate for micelles containing only one acceptor molecule.

Equation 3 predicts a two-component decay of the triplet for the case where k and k_q differ significantly. In fact it is noted in Figure 3 that the triplet absorption at 840 nm decreases rapidly at shorter times to a plateau. The decay in the plateau region is much slower and corresponds to the kinetics observed in the absence of acceptor. Equation 3 was used to analyze the absorption time curves obtained for a series of $C_{11}DQ$ concentrations, i.e., different values of $\bar{n}$. Optimum fit is obtained for $k_q = 5 \times 10^6$ s^{-1}. Figure 3 shows that the agreement between experimental points and the computed curves is convinc-

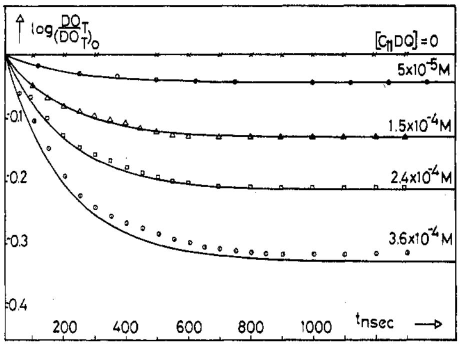


Figure 3. Decay of ZnP triplet at 840 nm at different $C_{11}DQ$ concentrations: [ZnP] = 5 × 10^{-5} M; 0 < [$C_{11}DQ$] < 3.6 × 10^{-4} M; [CTAC] = 5 × 10^{-2} M.

ingly good for this value of k_q, the deviations being within the error limits of the experiments. The value of k_q found is typical for intramicellar electron transfer occurring upon each encounter of the reactants.[9] It implies that the average time required for the redox reaction in micelles containing one ^3ZnP and one $C_{11}DQ$ each is 200 ns.

(*2*) *Acceptor DQ*. Here the ^3ZnP absorption decays also in two fractions. However, the second component is much faster than in the case of $C_{11}DQ$. The fast decay is attributed to intramicellar electron transfer as in the case of $C_{11}DQ$. To explain the second component another mechanism of electron transfer has to be evoked. Though sparsely soluble in water, the DQ molecules have to be envisaged as partitioning between the micellar and aqueous phase[10]

$$\text{DQ} + \bigcirc \underset{k'}{\overset{k_a}{\rightleftharpoons}} \text{(DQ)} \qquad (4)$$

where the circle represents a micelle with or without ZnP association. k_a is the second-order rate constant for the association with the micelle and k' is the first-order rate constant for dissociation from the micelles. Equation 4 allows for intermicellar migration of DQ molecules which can also contribute to the electron-transfer process. In fact, the slower decay of the 840-nm absorption is attributed to micelles containing initially only ^3ZnP, the quencher entering only after excitation. Such a model leads to the following time law for the ^3ZnP decay[8]

$$[^3\text{ZnP}]_t = [^3\text{ZnP}]_0 \exp\left[-\left(k + \frac{k_q k_a[\text{DQ}]_w}{k'+k_q}\right)t - \frac{Kk_q^2[\text{DQ}]_w}{(k'+k_q)^2}\left(1 - e^{-(k'+k_q)t}\right)\right] \qquad (5)$$

$[\text{DQ}]_w$ is the concentration of acceptor in the aqueous phase and is given by

$$[\text{DQ}]_w = \frac{[\text{DQ}]_{\text{total}}}{1 + K[\text{M}]}$$

where K, the association constant, can be expressed by $K = k_a/k'$ and $[\text{DQ}]_{\text{total}}$ is the total quencher concentration. For longer times and large values of k_q or k' expression 5 reduces to

$$\ln\frac{[^3\text{ZnP}]_0}{[^3\text{ZnP}]_t} = \left[k + \frac{k_a k_q[\text{DQ}]_{\text{total}}}{(k'+k_q)(1+KM)}\right]t + \frac{Kk_q^2[\text{DQ}]_{\text{total}}}{(k'+k_q^2)(1+K\,[\text{M}])} \qquad (6)$$

Figure 4 shows satisfactory agreement of the experimental points with the predictions of eq 5. At higher DQ concentrations and longer times positive deviations of the absorbance values from the theoretical line become noticeable. These are attributed to contributions of the reaction product ZnP^+ to the absorbance at 840 nm. Extrapolation of the linear position of the decay curves back to the origin and plotting of the intercept as a function of DQ concentration yields $Kk_q^2/(k'+k_q)^2(1 + K[\text{M}])$ while the slopes give $k_a k_q/(k'+k_q)(1 + K[\text{M}])$. Using for k_q the same value that was determined for $C_{11}DQ$, i.e., 5 × 10^6 s^{-1}, one obtains from this evaluation k' = 6 × 10^5 s^{-1}. The value k_a = 5 × 10^{10} M^{-1} s^{-1} is then derived from an optimalization of the theoretical curves with the experimental results. Finally, from the ratio k_a/k' one obtains K = 8.3 × 10^4 M^{-1} for the association constant. These values of the rate of entry and exit appear reasonable in the light of data obtained recently for molecules of similar size and hydrophobicity.[11] From solubility measurements K = 7.5 × 10^4 is derived, in good agreement with the kinetic results.

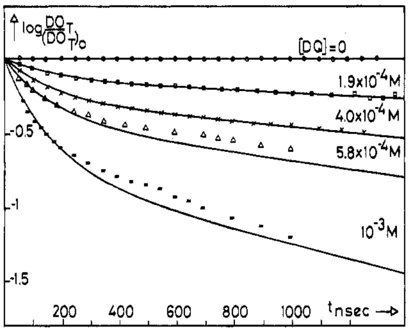


Figure 4. Decay of ZnP triplet at 840 nm at different DQ concentrations: [ZnP] = 5 × 10^{-5} M; 0 < [DQ] < 10^{-3} M; [CTAC] = 5 × 10^{-2} M.

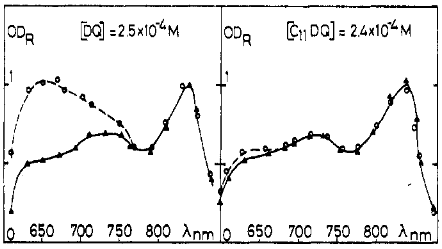


Figure 5. Relative triplet–triplet absorption spectrum obtained 100 ns (—) and 800 ns (---) after the laser pulse. All the spectra are normalized at 840 nm: [ZnP] = 5 × 10^{-5} M; [DQ] = [$C_{11}DQ$] = 2.5 × 10^{-4} M; [CTAC] = 5 × 10^{-2} M.

In the case of $C_{11}DQ$ the quenching of ZnP is not accompanied by the formation of the ZnP^+ absorption (Figure 5). Only a weak absorption around 650 nm is produced. Apart from the unfavorable influence of the statistics on the ZnP^+ yield, we attribute this effect to the immediate back transfer of the electron to the ZnP^+ ion which is favored by the fact that $C_{11}DQ^-$ is retained in the micelle. (DQ^-, due to electrostatic interactions, should also be retained in cationic micelles. However, the additional hydrophobic forces operative in the case of $C_{11}DQ^-$ are lacking here, rendering its exit more facile.) However, a small proportion of ZnP^+ seems to escape from the micelle into the aqueous phase. In the cationic aggregates this process is favored by local electrostatic interactions.[12,13] Hence, in this case the photoredox reaction is not completely reversible. In Figure 6 is shown the decay of the 460-nm absorption of $C_{11}DQ$, once for ZnP and next for ZnTPP as a donor; in the case of ZnP the original absorption decays to a plateau which is stable on a comparatively long time scale. However, if ZnTPP is used, the decay is quantitative, the signal returning entirely to the baseline. It appears that $ZnTPP^+$ is so hydrophobic that

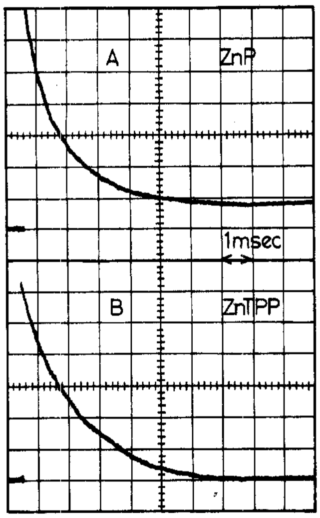


Figure 6. Decay of transient observed at 460 nm at long time (1 ms/div) after the laser pulse: [ZnP] = [ZnTPP] = 5×10^{-5} M; [$C_{11}DQ$] = 3.5×10^{-4} M.

its exit from the cationic aggregates requires more time than the back electron transfer, rendering the back reaction quantitative.

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Raman Spectra of Cobalt Molybdenum Oxide Supported on Silica

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Three series of cobalt molybdenum oxide catalysts supported on silica have been studied by Raman spectroscopy. All series had been characterized previously by various techniques. An interaction species which is described as a two-dimensional polymolybdate is observed, which is relatively weakly bound to the support. Addition of Co leads to a detachment of this species and to the formation of $CoMoO_4$. "Free" MoO_3 and Co_3O_4 are also detected, the relative amounts of the various supported compounds depending on the atomic ratio $r = Co/(Co + Mo)$ and the total transition metal oxide loading. The present Raman data principally confirm the previously reported characteristics of the catalysts, but in addition Raman spectroscopy demonstrates the existence of supported compounds which were not previously detected by X-ray analysis because of their small particle size and high dispersion.

1. Introduction

The nature of the carrier very strongly influences the interactions between the oxidic Co–Mo phase and the support. Moreover, the strength of this interaction governs the compound formation in the various systems. This behavior becomes evident on comparing γ-Al_2O_3- and SiO_2-supported molybdena catalysts. Thus, it has been proposed that a CoMo bilayer was being formed in γ-Al_2O_3-supported systems,[4] this bilayer probably being the precursor of the active sulfided phase of hydrodesulfurization catalysts.[5] When SiO_2 is used as the carrier, the interaction of the molybdena phase with the support has been found to be much weaker.[1-3] The interaction species have been described as polymolybdate-like two-dimensional structures, in which Mo^{6+} most probably occurs in octahedral coordination,[1,2] though the occurrence

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