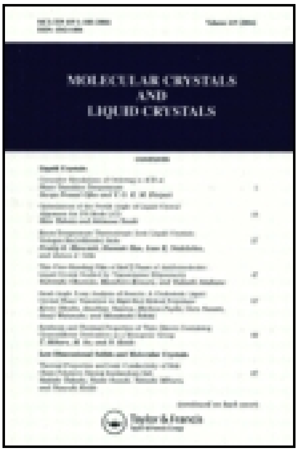

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FT-EPR Study of Photoinduced Electron Transfer in a Micellar System

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FT-EPR STUDY OF PHOTOINDUCED ELECTRON TRANSFER IN A MICELLAR SYSTEM

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Abstract Photoinduced electron transfer from Zn-tetraphenylporphyrin (ZnTPP) to benzoquinone (BQ) in micelles of cetyltrimethylammonium chloride (CTAC) has been investigated by time-resolved Fourier-Transform Electron Paramagnetic Resonance (FT-EPR). An analysis of the time-evolution of the FT-EPR signal from the BQ anion radical following laser excitation of ZnTPP gives the values of the forward and back electron transfer rate constants and for the BQ^- spin-lattice relaxation time. The data are compared with those obtained from ZnTPP/BQ in ethanol. The experimental data show that the forward reaction involves electron transfer from CTAC solubilized ZnTPP to BQ in the aqueous phase. Furthermore, attraction between the cationic headgroups of the surfactant molecules and BQ^- apparently promotes back electron transfer.

Keywords: FT-EPR, photoinduced electron transfer, porphyrins-quinones, micelles

INTRODUCTION

Photoredox processes in heterogeneous systems, such as micellar and vesicular solutions, have attracted attention because of potential applications in solar energy conversion. Studies of excited state electron transfer across boundaries between hydrophobic and hydrophilic domains also give a better understanding of the role played by membranes and vesicular structures in photoinduced biochemistry. It has been shown in artificial systems that the introduction of charged interfaces can lead to more efficient charge separation.[1-4]

With the development of Fourier Transform-Electron Paramagnetic Resonance (FT-EPR), it has become possible to study the spin dynamics of photo-generated free radicals with nanosecond time resolution. Recent publications[5-7] have illustrated the value of this novel technique in studies of the photo-oxidation of tetraphenylporphyrins by quinones in homogeneous solution. Because of the high spectral resolution, FT-EPR spectra can serve to identify unambiguously short-lived free radicals and determine the kinetics of their formation and decay. Chemically Induced Dynamic Electron Polarization (CIDEP) mechanisms play a key role in the time evolution of signal amplitudes. CIDEP effects provide insights into the photochemistry and physics of electron transfer reactions that complement the information given by other spectroscopic methods.

Here we report the application of time-resolved FT-EPR in the study of the reversible photooxidation of Zn tetraphenylporphyrin (ZnTPP) by benzoquinone (BQ) in a cetyltrimethylammonium chloride (CTAC) micellar system. The study establishes that FT-EPR can give information on the kinetics of excited state electron transfer in microheterogeneous systems as well as on the spatial organization of donor and acceptor molecules.

EXPERIMENTAL

ZnTPP was synthesized following published procedures.[8] BQ (Aldrich) was recrystallized from pentane and purified by vacuum sublimation. CTAC (Kodak) was used without further purification. Samples contained about 2×10^{-4} M ZnTPP and 2×10^{-3} M BQ in 25% (w/w) CTAC solution. The solubilization of ZnTPP was facilitated by first dissolving ZnTPP in 2-propanol, after mixing with the micelles, 2-propanol was removed at 60 °C by bubling argon through the solution. A similar procedure was used to introduce BQ. Samples were prepared in the dark under argon. Sonication in an ultrasonic cleaner was performed before and after sealing the sample. At the concentration of CTAC used, the micelles should be spherical and the micellar concentration is expected to be $\approx 8 \times 10^{-3} M$.[1,9] FT-EPR measurements show that this micellar system is stable over a period of weeks.

FT-EPR spectra were recorded with a home-built spectrometer similar to that described in reference 10. Typically 4000 quadrature phase detected free induction decays (FID, 2000 data points, 10ns/point) were averaged for each phase setting of a CYCLOPS phase cycling routine. A field-frequency lock was used in order to achieve optimum spectral resolution. The microwave pulse width was 15 ns. ZnTPP was excited with an excimer laser (Lambda Physik EMG 103 MSC) pumped dye laser (Lambda Physik FL 3001) operated at repetition rates of 25-50 Hz with 2 mJ pulse energy at 560 nm wavelength and approximately 15 ns pulse width. The measurements were performed at 295 K with delay times between laser pulse and microwave pulse ranging from 0 to 100 μs. Only the BQ anion radical is observable via the FID because of the short relaxation time (T_2) of the ZnTPP cation radical.

The spectral analysis was performed with the conventional Fast Fourier Transform (FFT) method and with a linear prediction singular value decomposition (LPSVD) routine.[11] The results obtained with the latter method were used to evaluate kinetic parameters.

RESULTS

Figure 1 displays FT-EPR spectra obtained for a series of delay time settings between laser pulse and microwave pulse. For most delays a five line spectrum is observed due to the hyperfine coupling between the unpaired electron and the four equivalent protons in BQ^-. It is noteworthy that the spectral resolution is excellent. Linewidths correspond closely to those reported for BQ^- in homogeneous aqueous solution.[12] With a 0.01 μs delay, the five hyperfine lines are in absorption. Then, as the delay time increases, one by one the four high frequency (low field) lines turn into emission. This effect is due to the competition between triplet mechanism (TM) and radical pair mechanism (RPM) CIDEP effects. The TM originates in the spin selective intersystem crossing process which generates spin polarized ZnTPP triplets (^{3}ZnTPP). If electron transfer to BQ occurs before ^{3}ZnTPP has relaxed to thermal equilibrium, triplet spin polarization is carried over to the anion radicals. TM CIDEP gives rise to enhanced absorption signals, since it does not depend on the nuclear spin state, the binomial (1:4:6:4:1) intensity distribution of the five hyperfine lines is maintained. RPM CIDEP reflects the time evolution of the

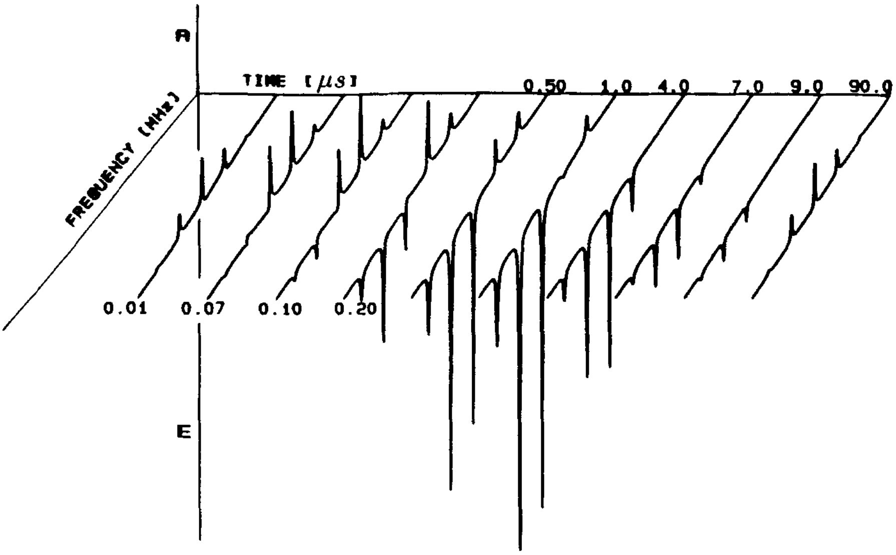

FIGURE 1. LPSVD reconstructed EPR spectra of photogenerated BQ^- as function of delay time (μs) between exciting laser pulse and microwave pulse. Absorption peaks point up, emission peaks down. Sample temperature 295 K.

spin state of the $[ZnTPP^+..BQ^-]$ radical pair.[13-16] It produces a contribution to the BQ^- spectrum in which the four high frequency (low field) lines are in emission and the remaining line is in absorption. The experimental spectra reflect the fact that with increasing delay time the RPM signal contribution becomes more dominant.

It is remarkable that the low frequency (m=2) hyperfine line decreases in intensity below the detection limit for delay time settings between 3-9μs, then reappears and remains detectable at 100 μs delay. This phenomenon is attributed to the effect of the homogeneous electron transfer reaction,

$$BQ^- + BQ \rightleftarrows BQ + BQ^-.$$

In this process spin polarization is transferred from one nuclear spin state to another. If the RPM dominates, the process will drive signal intensities to a binomial distribution with all five lines in emission. This accounts for an emissive contribution to the m=2 peak which, in the mentioned time interval, counterbalances the absorptive contribution.

In order to make a quantitative analysis, we can consider the signal intensity of the m^{th} hyperfine line at time t ($S_m(t)$) as a sum of three contributions,

$$S_m(t) = af(m)[BQ^{-*}_{TM}] + bf'(m)[BQ^{-*}_{RP}] + cf(m)[BQ^{-}_{B}], \tag{1}$$

where the * indicates spin polarization and $[BQ^{-*}_{TM}]$, $[BQ^{-*}_{RP}]$, and $[BQ^{-}_{B}]$ are the concentrations of triplet mechanism polarized, radical pair mechanism polarized and non-polarized (Boltzmann) benzoquinone anion radicals, respectively. The function $f(m)$ takes the values 1,4,6,4,1 for m=-2,-1,0,1,2 respectively, reflecting the degeneracy of the nuclear spin states. The values -1.8, -5.9, -6, -1.1, and +0.5 were calculated[17] for $f'(m)$ using the theoretical expression given by Adrian.[16] In this evaluation, the hyperfine interaction of the unpaired electron with the four protons of the benzoquinone radical, and the hyperfine interaction with the four nitrogens in the ZnTPP radical were taken into account. The fact that contributions of $[BQ^{-*}_{TM}]$ and $[BQ^{-}_{B}]$ to hyperfine components with opposite projections of the nuclear spin are equal, allows us to study separately the RPM contribution, by using the relation,

$$S_m(t) - S_{-m}(t) = b(f'(m) - f'(-m))[BQ^{-*}_{RP}]. \tag{2}$$

where

$$\frac{d[BQ^{-*}_{RP}]}{dt} = \frac{1}{3}k_{et}[BQ][^3ZnTPP] - \frac{1}{T_1^R}[BQ^{-*}_{RP}] - k_R[ZnTPP^+][BQ^{-*}_{RP}] \tag{3}$$

with

$$[^3ZnTPP] = [^3ZnTPP]_0 exp(-k_{et}[BQ]t) \tag{4}$$

and

$$\frac{d[ZnTPP^+]}{dt} = k_{et}[BQ][^3ZnTPP] - k_R[BQ^-][ZnTPP^+]. \tag{5}$$

Here, $[^3ZnTPP]_0$ is the concentration of triplet precursor after laser excitation and $[BQ^-] = [ZnTPP^+]$ is the total concentration of BQ anions. As can be seen in eq.(3), $[BQ^{-*}_{RP}]$ depends on the pseudo first order electron transfer rate constant $k'_{et} = k_{et}[BQ]$, the spin lattice relaxation time of BQ^-, T_1^R, and the rate constant for the back electron transfer k_R. The factor 1/3 in eq.(3) takes into account the fact that the three spin levels of ^{3}ZnTPP are approximately equally populated at room temperature, and that at high magnetic field only the S-T_0 mixing is important for the RPM.[13] The T_{-1} and T_{+1} levels of the triplet give rise to BQ^{-*}_{TM} or to BQ^{-}_{B} depending on the time at which the electron transfer occurs relative to the spin-lattice relaxation time of the triplet precursor (T_1^T). A non-linear least-squares fit of the experimental data to eq.(2) gives the values of k'_{et}, T_1^R, $k_R[^3ZnTPP]_0$ and b. The fitting of the experimental data for the micellar system to eq.(2) is shown in Figure 2. The quality of the fittings for the ethanol homogeneous systems is the same. Table I summarizes the values obtained. In the determination of k_R, it has been assumed that photoexcitation leads to quantitative oxidation of ZnTPP. Therefore, values for k_R represent lower limits. Besides, in this analysis we have neglected the effect of homogeneous electron transfer. Inclusion of this effect would tend to increase the values for T_1^R. The value of b is a measure of the RPM polarization.

DISCUSSION

The FT-EPR data give an insight into the distribution of acceptor and donor molecules in this microheterogeneous system. Table I shows that the forward electron transfer rate constant is significantly smaller than that in homogeneous solution (ethanol) at 288 K and similar to the value found for the ethanol system at 223 K. This indicates that electron transfer is from micelle solubilized excited ZnTPP to BQ in the aqueous phase. Under the conditions of the experiment the micelle concentration is of the order of 10^{-2}M. If the BQ were confined to the hydrophobic phase, electron transfer would be extremely slow since the probability of finding donor and acceptor molecules in the same micelle is very small. A mechanism involving electron transfer across the interface also accounts for the fact that no evidence is found for singlet excited state electron transfer.

The linewidths at half intensity calculated from the dampings of the FIDs are 0.32 MHz and 0.40 MHz for the m=0 and m=±1 signals, respectively. These values are in close agreement with the value of 0.39 MHz reported[12] for BQ^- in aqueous solution containing 5 M 2-propanol and 1 M acetone at pH 7. The microviscosity of the micellar interior in CTAC micellar solution at 293 K is in the range of 10-31 cP.[1] For ZnTPP-BQ in ethanol at 223 K ($\eta \simeq 6.8$ cP) measured linewidths are ≈ 0.7 MHz, reflecting incomplete averaging of g and hyperfine anisotropy. From the linewidths data it is evident that in the CTAC system BQ^- is solubilized in the aqueous phase. The conclusion that both BQ and its anion are found in the aqueous phase agrees with the finding that

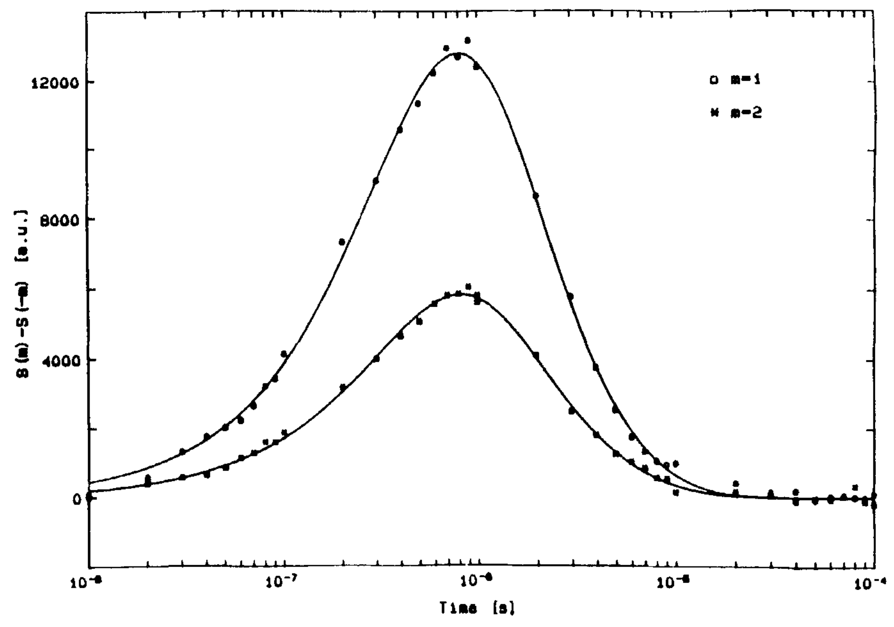

FIGURE 2. Time evolution of the differences in amplitude between hyperfine lines with opposite projections of the nuclear spin, $S_m(t) - S_{-m}(t)$, obtained in a ZnTPP-BQ-CTAC micellar system. The solid lines are obtained with a non-linear least-squares fit of the data to eq.(2).

TABLE I. Values obtained for the electron transfer rate constant k_{et}, the spin lattice relaxation rate of the acceptor radical T_1^R, the rate constant for the back electron transfer k_R and the proportionality constant b, with the procedure described in the text by using the m=+1 and -1 hyperfine components. For comparison, data on ZnTPP (10^{-4}M), BQ (10^{-3}M) in ethanol are also included. The values given within parentheses correspond to the fitting of the $S_2(t) - S_{-2}(t)$ data.

	CTAC at 295 K	ethanol at 288 K	ethanol at 223 K
k_{et} [$10^9\ M^{-1}s^{-1}$]	1.08 (1.06)	4.16 (3.85)	0.78 (0.76)
T_1^R [μs]	6.1 (6.7)	2.8 (3.7)	6.3 (6.7)
k_R [$10^9\ M^{-1}s^{-1}$]	3.5 (3.5)	2.8 (4.4)	0 (0)
b [a.u.]	12.6 (11.9)	8.6 (7.3)	22.4 (21.7)

homogeneous electron transfer has a noticeable effect on the time evolution of the EPR signal.

Despite the phase separation of the redox ions, there is a remarkably fast back reaction. This suggests that the anions remain constrained to the micellar-water interphase due to interaction with the cationic headgroups.

CONCLUSION

This is, to our knowledge, the first FT-EPR study of a photoinduced electron transfer reaction in a micellar system. The results demonstrate that the technique can provide valuable mechanistic and structural information. A study of excited state electron transfer in other types of microheterogeneous systems, such as neutral and anionic micelles, is currently in progress.

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