Time-Resolved Electron Spin Resonance Study of Photooxidation of Zinc Tetraphenylporphyrin by Benzoguinone

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The pulsed-dye laser-induced photooxidation of ZnTPP by benzoquinone has been studied with time-resolved direct-detected electron spin resonance (ESR). Spectra of free radicals can be obtained within 1 µs after the laser pulse. For the first time the ESR spectra of both the anion and cation radicals generated in the electron-transfer reaction have been observed. The time-resolved spectra show triplet and radical pair spin polarization (CIDEP) effects that can be linked to the mechanism of the photoinduced charge separation reaction. The CIDEP effects give semiquantitative data on rate constants.

Introduction

The reversible photooxidation of zinc tetraphenylporphyrin (ZnTPP) by 1,4-benzoquinone (BQ) has been subject of numerous spectroscopic studies.¹⁻⁷ The rates of forward and back electron transfer are close to diffusion controlled, so that most of the data on mechanism and kinetics of the reaction involving this system and similar donor-acceptor pairs is derived from flash photolysis measurements. The work reported here deals with the information that can be derived from direct-detected time-resolved CW ESR⁸ spectra.

Following laser excitation with an excimer-laser-pumped dye laser, direct detection (no field modulation) with a boxcar integrator gives the ESR signal produced by ZnTPP⁺ and BQ⁻ at a specific time after the laser pulse. The time delay between excitation and detection can be as short as $0.5 \ \mu s$. The spectra make it possible to identify free-radical products. Furthermore, chemically induced dynamic electron spin polarization (CIDEP)9 effects give a direct insight into the mechanism of the electron-transfer reaction and the role played by spin dynamics. CIDEP also gives semiquantitative kinetic data.

Detailed data on ZnTPP/quinone systems can be obtained as well by using a combination of pulsed laser excitation and time-resolved detection of transient free radicals with Fourier transform ESR (FT ESR).¹⁰ The application of the two ESR techniques in a study of the charge separation reaction involving porphyrins and quinones facilitates an evaluation of the relative merits of these methods.

Experimental Procedure

ESR measurements were performed with a VARIAN E-9 X-band spectrometer with variable-temperature accessory. In time-resolved measurements the signal from the preamplifier in the microwave bridge was fed into a PAR 162 dual channel boxcar integrator via a Hewlett Packard HP461A high-frequency amplifier. The boxcar signal served as input for the AD converter of a Nicolet 1180E computer. A Lambda Physik FL3001 dye laser (Rhodamine 6G, 580 nm, 1 mJ) pumped by a Lambda Physik EMG103MSC excimer laser (pulse width 15 ns, rate 40 Hz) was used as light source. Field measurements were performed with an AEG proton NMR gaussmeter and microwave frequency measurements with a Marconi Instruments 2440 counter.

ZTPP was synthesized following published procedures.¹¹ Deuterated benzaldehyde was used for the synthesis of phenyldeuterated ZnTPP. Benzoquinone (Aldrich) was purified by vacuum sublimation. Freeze-pump degassed samples of ZnTPP (concentrations ranging from 5×10^{-4} to 10^{-3} M) and BQ (10^{-3} to 10^{-2} M) in absolute ethanol were prepared on a vacuum line. In studies of the effect of acceptor concentration on the timeresolved spectra, a closed-loop flow system driven by argon gas was used. It is estimated that the radical ion concentration immediately following the laser pulse was in the range of 10⁻⁶-10⁻⁵ M. In the absence of BQ no ESR signals are detected. Furthermore, variations in ZnTPP concentration did not reveal any evidence of an effect of porphyrin-porphyrin interactions on the experimental results. Between measurements samples were stored in a freezer (-90 °C). They were used over a period of weeks without noticeable degradation of ESR signals.

Conditions for recording of the spectra were as follows: microwave power 1 mW, delay between excitation and detection 2 μ s, boxcar gate width 50 ns, field range 20 G, sweep time 300 s, and time constant 0.1 s.

Experimental Results and Discussion

Description of the Spectra. Irradiation of ZnTPP/BQ generates some BQ⁻ that is relatively long-lived and readily detected with conventional ESR.³ The spectrum, presented in Figure 1A, does not show the ZnTPP cation which must be generated if the anion stems from the photoinduced electron-transfer reaction:

$$ZnTPP^* + BQ \rightarrow ZnTPP^+ + BQ$$

The presence of long-lived BQ⁻ and absence of ESR evidence for the formation of the cation has been attributed to a side reaction in which a fraction of $ZnTPP^+$ is reduced by hydroquinone.^{5,12} This leaves some BQ⁻ that decays via a slow disproportionation reaction instead of fast reverse electron transfer. It is noteworthy that optical spectroscopy shows the formation of ZnTPP⁺. On the other hand, the transient BQ⁻ species cannot be identified unequivocally with this technique because of overlapping absorption bands.5

Figure 1B shows the room temperature ESR spectrum obtained

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Figure 1. ESR spectra of radicals generated by irradiation of a solution of ZnTPP (10^{-3} M) and BQ (10^{-2} M) in ethanol at room temperature. (A) Conventional detection using field modulation and lock-in amplifier, (B) Direct detection with boxcar integrator (delay time 2 μ s, window 50 ns).



Figure 2. (A) Conventional ESR spectrum from chemically oxidized ZnTPP (phenyl deuterated) in ethanol. (B) Conventional ESR spectrum of BQ⁻ in ethanol. (C) Time-resolved ESR spectrum of photochemically generated free radicals from ZnTPP- d_{20}/BQ in ethanol. All at room temperature.

with the time-resolved detection technique. It consists of five narrow absorption peaks due to BQ^- ($a_H = 2.37$ G) and a broad resonance due to a radical with a slightly smaller g value. The spectrum can be detected with a delay time as short as 0.5 μ s. However, below 2 μ s severe line broadening is observed. This effect is attributed to the dynamics of the interaction between electron spins and microwave field.⁹

The broad signal is assigned to the ZnTPP⁺ radical. The assignment is confirmed by measurements on phenyl-deuterated ZnTPP. Deuteration strongly enhances spectral resolution by reducing broadening caused by unresolved proton hyperfine interactions.¹³ The ESR spectrum of ZnTPP⁺- d_{20} in anhydrous ethanol prepared by chemical oxidation is presented in Figure 2A. It shows nine hyperfine lines due to four equivalent pyrrole nitrogens ($a_N = 1.60$ G). The time-resolved spectrum from BQ/ZnTPP- d_{20} given in Figure 2C establishes that phenyl deuteration leads to the expected enhanced spectral resolution. In addition to the BQ⁻ resonances (cf. Figure 2B), peaks are observed that can be attributed unequivocally to ZnTPP⁺.

Spin Polarization Effects. The BQ^- spectra presented in Figures 1B and 2C exhibit a pattern that deviates markedly from the binomial intensity distribution found in the normal ESR





Figure 3. Temperature dependence of the time-resolved ESR spectrum given by ZnTPP (0.5 mM)/BQ (5 mM) in ethanol. Delay between laser pulse and boxcar detection, 2 μ s. Emission peaks point down.

SCHEME I



spectrum. The spectra given in Figure 3 show that the effect becomes more pronounced upon lowering the temperature. A reduction in temperature even causes some low-field hyperfine lines to turn into emission. Evidently, the time-resolved spectra show spin polarization (CIDEP) effects due to the fact that the delay between radical generation and detection is too short for establishment of thermal equilibrium.

The CIDEP effects can be linked in a straightforward way to the mechanism that has been proposed¹⁻⁷ for the electron-transfer process. As Scheme I shows, the reaction involves the following steps: (1) excitation of ZnTPP to a singlet excited state, (2) intersystem crossing (isc) to the lowest triplet state (${}^{3}ZnTPP^{*}$), (3) formation of a radical pair [ZnTPP⁺··BQ⁻] via an encounter complex [${}^{3}ZnTPP^{*}$ ··BQ], and finally (4) dissociation of the radical pair (RP) into separated redox ions. The time-resolved spectra are affected by spin selectivity of the isc process as well as the spin-state evolution during the lifetime of the radical pair.

ESR studies^{14,15} show that isc preferentially populates the (zero field) $|Z\rangle$ triplet spin state of ³ZnTPP*. In fluid solution and a

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Figure 4. Analysis of the time-resolved (delay $2 \mu s$) spectra recorded at 20 °C and -12 °C in terms of contributions from TM and RP spin polarization contributions. The inset displays the intensity patterns expected for pure TM (top) and pure RP (bottom) spin polarized BQ⁻ radicals. Emission peaks point down.

strong magnetic field this generates excess spin population in the (high field) $M_{\rm S} = -1$ level.^{16,17} Triplet spin polarization is carried over to doublet radicals if the rate of formation of the radical pair competes with the rate of relaxation $(T_{1\rm e}^{-1})$ of the triplets. If the ESR is measured before relaxation processes in radical ions establish thermal equilibrium an *enhanced* absorption signal is obtained. For ZnTPP/BQ in ethanol the rate constant of triplet quenching is reported⁵ to be 1.8×10^9 M⁻¹ s⁻¹. The triplet spin-lattice relaxation time is around 20 ns, and the doublet radical $T_{1e} \sim 10 \ \mu s.^{10}$ Therefore, with [BQ] $\sim 10^{-2}$ M, the triplet mechanism (TM) can be expected to affect the time-resolved ESR signals. This conclusion is supported by the concentration dependence of the ESR spectrum (vide infra).

Theory¹⁸ predicts that, if triplet spin relaxation does not play a role, the signal enhancement due to the TM is about a factor of 20. TM signal amplification accounts in part for the remarkably high signal-to-noise obtained in these measurements.

The triplet CIDEP effect does not perturb the *relative* intensities of hyperfine lines. The deviation of the intensities of the five peaks from the binomial pattern is attributed to the radical pair (RP) CIDEP mechanism.^{9,19} It has been postulated^{5,6,20} that the fate of the charge-transfer complex [ZnTPP⁺...BQ⁻] is governed by spin selection rules: triplet character favors cage escape of redox ions, while singlet character favors back electron tranfer. Even though the radical pair is formed in the triplet state, it will acquire singlet character due to differences in Zeeman and hyperfine interactions experienced by the two unpaired electrons. As a consequence a nuclear spin state dependent spin polarization is generated in the free radicals. The RP intensity distribution can be calculated with the theoretical expression given by Adrian¹⁹ using experimental data on relative positions of BQ⁻ and ZnTPP⁺ resonance peaks. For the BQ⁻ radical the ratio of the RP in-



Figure 5. BQ concentration dependence of the time-resolved (delay $2 \mu s$) ESR spectrum generated by pulsed-laser excitation of an ethanol solution of ZnTPP and BQ at room temperature.

tensities (P_M^{RP}) , setting the absolute value of the center peak intensity equal to 6, from low field to high field is given by -1.8, -5.9, -6, -1.1, and +0.5. Here negative values denote emission signals.

Relative TM and RP Contributions. The observed signals will contain contributions from both CIDEP effects. For the Mth hyperfine component, where M (-2, -1, 0, 1, or 2) denotes the total nuclear spin state, the intensity is given by

$$S_{\rm M} = a P_{\rm M}^{\rm TM} + b P_{\rm M}^{\rm RP} \tag{1}$$

In this expression a and b give the relative weights of the TM and RP contributions. P_M^{TM} and P_M^{RP} represent the TM and RP spin polarization values. For BQ⁻ the *relative* values of P_M^{TM} are given by the binomial distribution 1:4:6:4:1. Figure 4 illustrates that peak intensities in the spectra can be accounted for quantitatively by summing TM and RP contributions.

The computer fits reflect a remarkably strong temperature dependence of the relative weights of TM and RP contributions. There are a number of possible explanations for this temperature effect. First, with a BQ concentration of 10^{-2} M the self-exchange reaction

$$BQ^- + BQ \rightarrow BQ + BQ^-$$

which has a rate constant of the order of $10^8 \text{ M}^{-1} \text{ s}^{-1}$,²¹ will tend to reduce the RP contribution.²² With decreasing temperature the effect of the self-exchange reaction will diminish, increasing a/b. However, measurements performed over a range of BQ concentrations show that this effect is too small to account for the strong temperature dependence. Second, a reduction in temperature can reduce the polarization carried over from ³ZnTPP* because of a reduction in rate of triplet quenching. Finally, the increase in correlation time of relative molecular motion of the radical ions captured in the solvent cage can produce an increase in RP spin polarization.¹⁹ The temperature dependence of a/b can be due to one of these effects or a combination of both.

[BQ] Variation. Figure 5 illustrates the BQ concentration dependence of the time-resolved spectra. Qualitatively the effect of a reduction in [BQ] is similar to the effect produced by lowering the temperature. The [BQ] dependence of the amplitude of the center line (S_0) and the difference in amplitudes of the two components flanking the center line $(\delta S = S_1 - S_{-1})$ is given in Figure 6. The decrease in S_0 and δS with increasing acceptor

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Figure 6. BQ concentration dependence of the center-line amplitude and difference in amplitudes of the pair of lines flanking the center line in BQ^- spectra recorded with 2 μ s delay time.

concentration for [BQ] > 6 mM is attributed to partial averaging of the RP contribution by the self-exchange reaction. With [BQ]< 6 mM there is an insufficient number of exchange events between radical generation and signal detection for this reaction to affect the ESR signal. Under those conditions, the [BQ]dependence of the intensity of individual hyperfine lines can be due to changes in $[BQ^-]$ as well as changes in the TM contribution. With a measurement of δS the TM effect is eliminated (cf. eq 1) so that an insight is obtained into the relation between [BQ]and $[BQ^-]$. δS is proportional to the value of b and radical ion concentration $[BQ^-]$ at the time of measurement. The acceptor concentration dependence of $[BQ^-]$ is given by

$$[BQ^{-}] = C[1 - \exp(-k_{et}[BQ]t)]$$

where C is a proportionality constant, k_{et} is the rate constant of formation of separated redox ions, and t is the time interval between laser excitation and signal detection. According to Figure 6, δS is constant within experimental uncertainty over a BQ concentration range from 1 to about 6 mM. The result establishes that, for [BQ] > 1 mM, k_{et} [BQ] $t \gg 1$ so that variation in acceptor concentration does not change the concentration of radical ions present 2 μ s after the laser flash. From this it can be concluded that the rate constant of radical ion formation must exceed 10⁹ M^{-1} s⁻¹. This finding is in complete agreement with published data^{5,6} on the kinetics of photooxidation of ZnTPP triplets by BQ.

The spectral changes observed when the quinone concentration is reduced from 6 to 1 mM (cf. Figures 5 and 6) are entirely due to a diminishing TM contribution. The magnitude of this contribution is proportional to a (cf. eq 1). The concentration dependence of this parameter is expressed by

$$a = \Phi(k_{a}[BQ] / k_{a}[BQ] + k_{1e}) \{1 - \exp(-(k_{a}[BQ] + k_{1e})t)\}$$

where Φ is a proportionality constant, k_a is the rate constant of radical pair formation, and k_{1e} is the triplet spin-lattice relaxation rate constant. Because the exponential term is negligible, a is simply proportional to the fraction of triplet-state molecules quenched before relaxation

$$a = \Phi(k_{a}[BQ] / k_{a}[BQ] + k_{1e})$$

In principle, the increase in S_0 observed over the concentration range from 1 to 6 mM (cf. Figure 6) can be used to determine the relative magnitudes of k_a and k_{1e} . It is found that the concentration effect is compatible with $k_a = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and a triplet spin relaxation time of the order of 20 ns. However, the uncertainty in measured signal intensities was too high for a quantitative determination of the ratio of the two rate constants. The effect of [BQ] variation on the time-resolved spectra establishes unequivocally that TM spin polarization contributes significantly to signal intensities. From the change in S_0 observed over an acceptor concentration range from 1 to 6 mM it can be deduced that this polarization produces a signal enhancement of well over a factor of 8. Evidently, a spin polarization effect of similar magnitude is generated by the RP mechanism.

Comparison with FT ESR. The data presented show that time-resolved CW ESR measurements can be a valuable source of information on photoinduced electron-transfer reactions involving porphyrin/quinone donor-acceptor pairs. Redox ion products can be identified by using hyperfine and g-value data. An insight into the reaction mechanism is obtained through CIDEP effects. Specifically, the spectra show that porphyrin triplets are involved and that the rate of electron transfer is affected by spin dynamics in the transient radical pair. Furthermore, CIDEP effects give semiquantitative data on reaction kinetics. Work in progress shows that this is particularly useful in studies of effects of changes in the structure of donor or acceptor molecules or in solvent composition on the dynamics of the electron-transfer reaction. With some improvement in signal to noise, the method can give quantitative information on rate constants.

It is difficult to obtain quantitative kinetic data from timeresolved CW ESR by measurement of the signal as function of delay between laser pulse and boxcar detection.^{9,23} This is because the time evolution of the signal is determined in part by the interaction between electron spins and microwave radiation field. In the first 500 ns following the laser pulse this effect is particularly strong, giving rise to weak, very broad peaks. This precludes a direct determination of the rate of BQ⁻ formation through measurement of the delay time dependence of the ESR signal. This problem is not encountered in FT ESR measurements.

The basic principles of FT ESR are identical with those on which the FT NMR method is based. In FT ESR a short (10-20 ns) microwave pulse rotates the spin magnetic moment into the plane perpendicular to the external field. Following the pulse the free induction decay (FID) is measured. Fourier transformation of the FID gives the ESR signal. This signal reports on the condition (radical concentration, CIDEP effects) of the system at the time of the microwave pulse. Hence, the growth and decay of photogenerated radicals can be monitored by measuring FT ESR spectra over a range of laser pulse-microwave pulse delay times. Application of the method in measurement of the duroquinone (DQ) anion radical generated by photoinduced electron transfer from ZnTPP demonstrates that the delay time can range from 10 ns to more than 1 ms.¹⁰ With the pulse method, the time evolution of the signal is not perturbed by the microwave field. Therefore, the technique is particularly suited for quantitative studies of the kinetics of radical formation and decay. FT ESR spectra from ZnTPP/DQ has given values for the spin-lattice relaxation times of ³ZnTPP* and the DQ anion, and the rate constant of the electron-transfer reaction. FT ESR spectra did not reveal the presence of ZnTPP+ because of the large inhomogeneous line width. A comparison of signal intensities shows, as expected, that the pulsed method is superior to the CW method. With the latter technique the time evolution of the BQ⁻ signal could be followed only over about 10 μ s.

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