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An ESR Study of Photo-Induced Electron Transfer Reaction between Zinc(II)-Tetraphenylporphyrin and *p*-Benzoquinone in Solutions

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Synopsis. The titled reaction was studied, by means of the ESR technique at room temperature, as a model reaction of the primary process in the photosynthesis. Two kinds of radicals were observed in dichloromethane upon illumination with light of the porphyrin excitation; the zinc-tetraphenylporphyrin cation radical and the semiquinone neutral radical.

Since Tollin and Green[1] first observed the ESR signal of the semiqunone anion radical, Q^-, upon the illumination of ethanolic solutions containing chlorophyl (Chl) and *p*-benzoquinone (Q) at room temperature, both rise and decay processes of intermediates have been investigated in order to clarify the primary process of the photo-induced one-electron transfer from Chl to Q by using either ESR or the flash-photolysis technique. However, now there is a large discrepancy in the intermediates observed by two groups of workers using the former and latter techniques;[2] the latter group[3] has observed both Chl$^+$ and Q^- radicals, while the former group[4] has not yet succeeded in detecting Chl$^+$ at room temperature. Accordingly, the following proposals for the electron-transfer mechanism in the systems have been advocated:

1) Both Chl$^+$ and Q^- are in reality produced by the direct electron transfer from Chl to Q, but the lifetime of Chl$^+$ is shortened by a fast decay process with either ethanol[3] or an unknown material, X.[2]

2) Q^- and solvent radicals are formed by the electron transfer within a ternary complex among Chl, Q, and ethanol in which Chl acts as a photosensitizer.[4]

The identification of Chl$^+$ by flash photolysis is complicated by the overlap of the spectra of other species, such as Chl^T and Q^-; therefore, the unambiguous identification of Chl$^+$ by ESR at room temperature seems to be desirable. It is considered that the use of an appropriate solvent, in which the Chl$^+$ formed can exist with a longer lifetime, will lead to the easy detection of Chl$^+$ by ESR. Moreover, in this study zinc(II)-tetraphenylporphyrin, ZnTPP, was used as a model compound for chlorophyl, because the ESR spectrum of the ZnTPP$^+$ cation radical had been reported to reveal a well-defined hyperfine structure.[5]

ZnTPP and its π-cation radical, ZnTPP$^+$, were prepared by the method of Fajer *et al.*[5] *p*-Benzoquinone was purified by sublimation. The ethanol and dichloromethane used as solvents were purified by distillation. Unless otherwise specified, the concentrations of ZnTPP and Q were 10^{-4} and 10^{-1} M respectively. All the samples were thoroughly degassed by repeated freeze-degas-thaw cycles on a vacuum line prior to the measurements. The ESR spectra were recorded on a JEOL PE-1X spectrometer at room temperature. In most of the measurements, the sample in the cavity of ESR spectrometer was illuminated with light of wavelengths longer than 520 nm from a 650 W tungsten filament lamp, using a colored glass filter (Toshiba V-052).

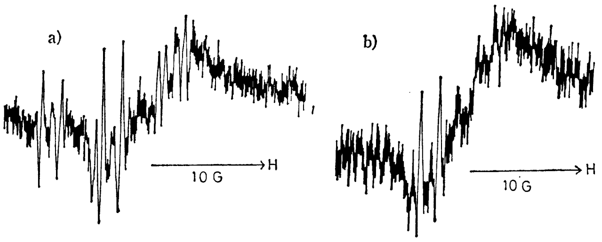

Fig. 1. ESR spectrum of the solution of ZnTPP and Q in dichloromethane upon illumination (>520 nm).
Modulation amplitude 0.63 G.
Microwave power: a) 4 mW, b) 20 mW.

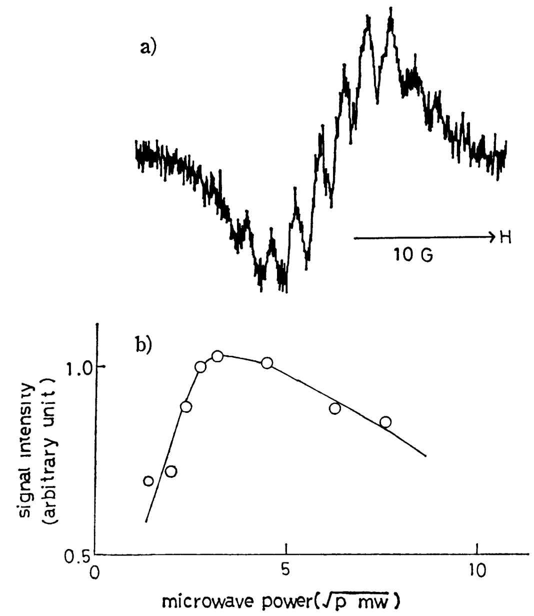

Fig. 2. a) Signal I with partially resolved hyperfine structure.
Modulation amplitude 1.0 G.
Microwave power 8 mW.
b) Saturation behavior of signal I.

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When the solution of ZnTPP and Q in ethanol was illuminated with yellow light (>520 nm), only an ESR signal of the semiquinone anion radical, $Q^{\overline{\cdot}}$, was observed; this is in agreement with Quinlan's results.[6]

On the other hand, upon the illumination (>520 nm) of the solution of ZnTPP and Q in dichloromethane, the ESR spectrum shown in Fig. 1a was obtained. It was composed of two overlapped signals—one with a broad singlet (Signal I, $g=2.0027$) on the high-field side on the spectrum, and another with a rather well-resolved hyperfine structure (Signal II, $g=2.0046$) on the low-field side. The existence of the two kinds of radicals was confirmed by the method of microwave-power saturation; at higher microwave power levels, the intensity of Signal I increased, whereas that of Signal II decreased and its hyperfine structure became obscure (Fig. 1b). Both signals decayed completely within a second after light-off. In the dark, none of the signals were detected. Also, no signals were observed in either solvent with either ZnTPP or Q alone upon illumination with yellow light. More than a threefold increase in the porphyrin concentration resulted in a change in the spectrum of Fig. 1 to that in Fig. 2a, in which Signal I appeared as a partially resolved spectrum. Signal I did not saturate until moderately high microwave power levels (20 mW) as is shown in Fig. 2b. This saturation behavior clearly differs from that of the semiquinone radical saturable at higher levels than 4 mW, and rather resembles that of $ZnTPP^{+}$. The hyperfine coupling constant, which is inaccurate because of the poor S/N ratio, was estimated to be 1.7 G and compared with that of $ZnTPP^{+}$ ($g=2.0025$, $a=1.6$ G) prepared by electrochemical oxidation in dichloromethane. In a preliminary experiment by flash photolysis, an intermediate species with a lifetime of a few milli seconds was detected; its absorption spectrum was not inconsistent with that of $ZnTPP^{+}$ reported previously.[5] Thus, Signal I was reasonably assigned to $ZnTPP^{+}$.

On the other hand, *p*-benzoquinone alone in dichloromethane showed an ESR signal assignable to the neutral semiquinone radical, QH ($g=2.0046$, 18-line signal), upon illumination with light longer than 420 nm. This signal showed a well-resolved 15-line hyperfine structure at the modulation amplitude of 0.63 G, as is shown in Fig. 3, and its ESR parameters were in good agreement with those of Signal II.

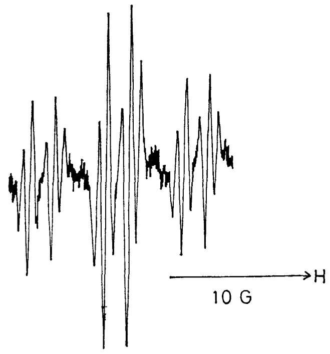

Fig. 3. ESR spectrum of the solution of Q in dichloromethane upon illumination (>420 nm).
Modulation amplitude 0.63 G.
Microwave power 4 mW.

As has been described above, on the illumination (>520 nm) of the solution of ZnTPP and Q in dichloromethane, the $ZnTPP^{+}$ and QH radicals are produced, whereas in ethanolic solutions only the *p*-benzoquinone anion radical is observed. These facts imply that there is a great difference in the lifetimes of the $ZnTPP^{+}$ produced in the two solvents, *i.e.*, a difference in the decay processes of $ZnTPP^{+}$. Barashkov and Chibisov[3] have proposed the following decay processes of Chl^{+} and Q^{-} in ethanol on the basis of the kinetic results obtained by flash photolysis:

$$Chl^{+} + Q^{\overline{\cdot}} \longrightarrow Chl + Q, \quad k = 2.0\times10^{9}\,M^{-1}\,s^{-1}, \tag{1}$$

$$2Q^{\overline{\cdot}} \longrightarrow Q + Q^{2-}, \quad k = 2\times10^{7}\,M^{-1}\,s^{-1}, \tag{2}$$

$$Chl^{+} + Q^{2-} \longrightarrow Chl + Q^{\overline{\cdot}}, \quad k = 5.5\times10^{5}\,M^{-1}\,s^{-1}, \tag{3}$$

$$Chl^{+} + C_2H_5OH \longrightarrow Chl + C_2H_5OH^{+}, \quad k = 8.6\times10^{2}\,M^{-1}\,s^{-1}. \tag{4}$$

Therefore, we examined the reactivity of $ZnTPP^{+}$, prepared by electrochemical oxidation in dichloromethane, toward both ethanol and hydroquinone in view of the similarity of Chl and ZnTPP. On the addition of hydroquinone to the solution, $ZnTPP^{+}$ was quickly reduced to reproduce ZnTPP stoichiometrically. Therefore, a decay process similar to (3) seems to be operative in our system, also. However, in the case of ethanol, only a trace amount of $ZnTPP^{+}$ decreased rapidly to reproduce ZnTPP. This fact indicates that a decay process similar to (4) is not important, but some decay process other than (4), such as a reaction with an unknown material, X, proposed by Hales and Bolton[2] may play a role in an ethanolic solution:

$$Chl^{+} + X \longrightarrow Chl + X^{+}, \quad k > 10^{3}\,s^{-1} \text{ (with X in excess)}. \tag{5}$$

The lifetime of $ZnTPP^{+}$ in ethanol may be shortened by a process similar to (5), but in dichloromethane the absence of decay processes similar to (4) and (5) may explain why $ZnTPP^{+}$ is not detected in an ethanolic solution.

Our present results indicate that the decay processes differ greately in the solvents used; that is, they depend on the environment of the primarily produced radicals. A similar investigation using micellar systems in which ZnTPP is incorporated is now in progress.

References

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