Electron-Transfer Reactions of Chlorophyll *a* and Porphyrin Triplets with Radicals in Aqueous Micellar Solutions

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The reactivity of the photoexcited triplet states of chlorophyll *a* (Chl*a*), ZnTPP, and MgTPP (P^T) with radicals was studied in neutral micelles by pulse radiolysis and photolysis (PRAP) spectroscopy. Steady-state triplet concentration was produced by a 2-ms light pulse, and the system was then subjected to a 10-ns electron pulse to form the radicals $(CH_3)_2\dot{C}OH$, $Br_2^{-}\cdot$, and $MV^{+}\cdot$ from the proper solutes. The triplet states were found to undergo one-electron reduction by $(CH_3)_2\dot{C}OH$ and oxidation by $Br_2^{-}\cdot$ with second-order rate constants approaching the diffusion-controlled limit and significantly more rapidly than the reactions of the ground states. The reaction of the triplet states (P^T) with $MV^{+}\cdot$ radicals was found to result in an overall recovery of the ground-state P from P^T. The mechanism of this process is discussed in terms of two steps of electron transfer: $P^T + MV^{+}\cdot \rightarrow P^{-}\cdot + MV^{2+} \rightarrow P + MV^{+}\cdot$.

Introduction

The feasibility of combining pulse radiolysis and photolysis (PRAP) spectroscope to study reactions of photoexcited triplets with transient radicals has been demonstrated in several systems, i.e., pyrene in micelles[5] and porphyrins.[6,7] In recent studies[6,7] we have shown that one-electron reduction or oxidation of triplet porphyrins (P^T) by various radicals takes place more rapidly than the corresponding reactions with the ground state. In all systems examined the reactions with the triplet approached the diffusion-controlled limit (10^9–10^{10} M^{-1} s^{-1}).[7] This increased reactivity of the triplet can be predicted from its electronic configuration and, in fact, it has already been indicated that the triplet should be more reactive than the ground state both as a reductant and as an oxidant.[8,9] Most of the previous measurements were carried out with aqueous solutions which permit the study of a variety of well-known reducing and oxidizing radicals, e.g.

$$P^T + (CH_3)_2\dot{C}OH \rightarrow P^{-}\cdot + (CH_3)_2CO + H^+ \quad (1)$$

$$P^T + Br_2^{-}\cdot \rightarrow P^{+}\cdot + 2Br^- \quad (2)$$

as well as radicals that add rapidly to P^T

$$P^T + \dot{C}H_2C(CH_3)_2OH \rightarrow \dot{P}\text{-}CH_2C(CH_3)_2OH \quad (3)$$

even though the addition reaction with ground-state P is very slow and was not detected in the pulse experiment.[7] In order to investigate the reactivity of the triplets of the water-insoluble chlorophyll *a*, ZnTPP, and MgTPP with the same radicals, it was necessary to solubilize them in water by the use of micelles. The behavior of their triplets was found to parallel that of the water-soluble ZnTPPS[7] in reactions 1–3.

This study was further extended to investigate the reactivity of P^T with another well-known radical, i.e., the methylviologen cation radical, $MV^{+}\cdot$. This system is of interest because of the extensive solar photochemistry research on the interaction of triplet porphyrins with methylviologen,[10-17] where the important reaction is

$$P^T + MV^{2+} \rightarrow P^{+}\cdot + MV^{+}\cdot \quad (4)$$

In steady-state photolysis experiments, a competing process of $P^T + MV^{+}\cdot$ may interfere with the desired reaction 4. This process can be conveniently studied by the PRAP technique. The results suggest a rapid electron transfer to produce the porphyrin anion radical

$$P^T + MV^{+}\cdot \rightarrow P^{-}\cdot + MV^{2+} \quad (5)$$

a reaction which does not take place with ground-state P, followed by a back electron transfer to produce $P + MV^{+}\cdot$.

Experimental Section

The PRAP experimental setup has been described previously.[6,7] It consists of the computer-controlled pulse radiolysis apparatus[18] interfaced with an exciting light source. The pulse radiolysis utilized an ARCO LP-7 linear accelerator which supplied 10-ns pulses of 8-MeV electrons, each pulse producing 2–4 μM of solvent radicals, and a xenon lamp as an analyzing light source. The exciting light source was also a 1-kW Xe lamp which was pulsed for 1–10 ms to ~50 times its steady-state intensity. The use of separate analyzing and exciting sources allows an inde-

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[5] (a) Grätzel, M.; Henglein, A.; Janata, E. *Ber. Bunsenges. Phys. Chem.* **1975**, *79*, 475. (b) Frank, A. J.; Grätzel, M.; Henglein, A.; Janata, E. *Ibid.* **1976**, *80*, 294. (c) Frank, A. J.; Grätzel, M.; Henglein, A.; Janata, E. *Int. J. Chem. Kinet.* **1976**, *8*, 817. These authors have used the analyzing light source for production of triplets by pulsing it for 3.5 ms. In our experiments, however, we have applied an independent exciting light pulse as described in the text.

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pendent choice of wavelength regions for each light source. This light pulse produces a steady-state concentration of triplet porphyrin and the electron pulse is given when triplet steady state is approached. Typical time profiles of triplet formation and decay are shown in the inserts of Figures 1 and 7, from which the triplet concentration in each experiment was determined[7] (generally 10–40% ground-state conversion).

Differential triplet absorption spectra have been obtained by nanosecond laser photolysis employing a Nd:YAG laser (Quanta Ray). The computer-controlled setup in its present configuration has been described elsewhere.[19-21] ZnTPP and MgTPP were photolyzed at 532 nm (second harmonic) and Chl*a* at 640 nm (DCM dye pumped by the second harmonic).

The porphyrins (Midcentury Chemical Co.) and Chl*a* (prepared as described earlier)[22] were first dissolved in Triton X-100 (Accurate Chemical Co., analytical grade) and then diluted with aqueous solutions containing the other components of the system studied. Water was purified by a Millipore Milli-Q system and the other compounds were Baker Analyzed reagents. Methylviologen (Sigma) was used without further purification. The solutions were thoroughly deoxygenated by bubbling with pure N_2 or N_2O and were protected from light until they entered the irradiation cell. Both the PRAP and the laser photolysis experiments utilized cells connected to a flow system in order to supply a fresh sample for every pulse and to avoid secondary reactions.

Solubilization of Chl*a* and porphyrins in water was achieved by using neutral micelles of Triton X-100. This material is *p-tert*-octylphenoxypolyethoxyethanol (M_r 625) with a critical micelle concentration (cmc) of 0.15 g L^{-1} and an aggregation number of 140.[23,24] At the concentrations used (2–3 vol %) this surfactant is predominantly in micellar form and the concentration of micelles is 2×10^{-4}–3×10^{-4} M, i.e., in a large excess over the concentration of the porphyrin. Therefore, ~90% of the porphyrin molecule should be distributed in separate micelles with no appreciable aggregation (see calculations in ref 25). This was confirmed in the case of Chl*a*, where aggregates were observed at 3×10^{-4} M Chl*a* with 0.2% Triton but mostly monomers at 7×10^{-5} M Chl*a* and 2% Triton.[25] Added solutes may affect the cmc; however, under our experimental conditions the absorption spectra did not indicate any aggregation of Chl*a*.

On the basis of $k(\mathrm{OH} + \mathrm{Triton}) = 3.5 \times 10^9\ M^{-1}\ s^{-1}$,[25] $k(\mathrm{OH} + \mathrm{Br}^-) = 1 \times 10^{10}\ M^{-1}\ s^{-1}$,[26] $k(\mathrm{OH} + i\text{-PrOH}) = 2 \times 10^9\ M^{-1}\ s^{-1}$,[26] and 2% Triton solutions with either 0.1 M Br^- or 1 M alcohol, the fraction of OH radicals reacting with the Triton would be 0.1 and 0.05, respectively. The reaction of the Triton radicals with chlorophylls is somewhat slow (~$10^8\ M^{-1}\ s^{-1}$)[25] and has been shown not to interfere with the study of Br_2^- reactions with chlorophylls in conventional pulse radiolysis.[25,27] Similarly, it is not expected to interfere in the study of the $(CH_3)_2\dot{C}OH$ radicals. These considerations, however, may not hold for the PRAP experiment since the Triton radicals would probably react faster with P^T than with P and may interfere with the desired reactions. This possibility was also examined and will be discussed below.

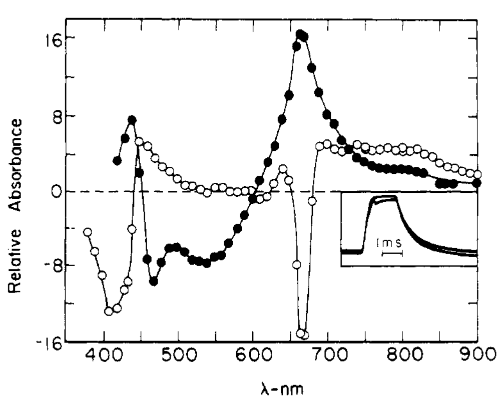

Figure 1. Differential absorption spectra recorded with Chl*a* in *i*-PrOH–Triton–aqueous solutions in conventional pulse radiolysis (○) and in the PRAP mode (●). The solution contained 2.5×10^{-5} M total Chl*a*, 1.3 M *i*-PrOH, 2% Triton X-100 at pH 7 with 1×10^{-3} M phosphate buffer and was saturated with N_2O. Spectrum ○ was recorded at 400–800 μs after the electron pulse. Spectrum ● was taken in the PRAP mode, 200 μs after the pulse, with 43% of the Chl*a* converted into the triplet state. One unit on the relative absorbance scale corresponds to $\Delta\epsilon = 1000\ M^{-1}\ cm^{-1}$ for species produced with a yield of $G = 6.0$ based on thiocyanate dosimetry. The insert shows the time profile of triplet formation, steady state, and decay and the effect of the electron pulse on it, recorded at 480 nm.

Results and Discussion

The search for efficient photochemical charge separation has led to many studies on micellar solutions of porphyrins and other photosynthetic pigments. Although most investigations involved the study of photoelectron transfer, recent work on one-electron oxidation of ground-state chlorophylls by $Br_2^-\cdot$ in micellar systems has been reported.[25,27] In the present study we use the same neutral micelle and compare the reactions of ground and triplet states of Chl*a* and porphyrins with various radicals.

Reactions of P and P^T with Short-Lived Radicals. The production of the $(CH_3)_2\dot{C}OH$, $\dot{C}H_2C(CH_3)_2OH$, and $Br_2^-\cdot$ radicals by pulse radiolysis and their reactions with P and P^T in aqueous systems have been described earlier.[7,28] Similar conditions are used to study the reactions of these radicals in Triton–aqueous systems.

Chlorophyll a. The transient absorption spectra recorded with Chl*a* solutions upon reaction of the ground and triplet states with the $(CH_3)_2\dot{C}OH$ radical are presented in Figure 1. Both reactions lead to the formation of Chl*a*$^-\cdot$ (e.g., reaction 1). The differential spectrum for the ground-state reduction is in very good agreement with the spectra obtained in electrochemical studies.[29] The spectrum observed in the PRAP mode indicates conversion of Chl*a*^{T} to the anion radical, $\epsilon(P^-\cdot) - \epsilon(P^T)$. This is evident from a comparison of the experimental differential spectrum (Figure 1) with the spectrum of the anion radical,[29] $\epsilon(P^-\cdot)$, and the spectra shown in Figure 2, i.e., $\epsilon(P^T) - \epsilon(P)$ (laser photolysis) and $\epsilon(P)$. The fact that no bleaching of Chl*a* ground state is observed in this experiment indicates that the $(CH_3)_2\dot{C}OH$ radicals react selectively with the triplets even though the steady-state level was $[\mathrm{Chl}a^T] = 0.4[\mathrm{Chl}]_0$. Kinetic measurements at different wavelengths in the two experimental modes give $k(\mathrm{Chl}a + (CH_3)_2\dot{C}OH)$

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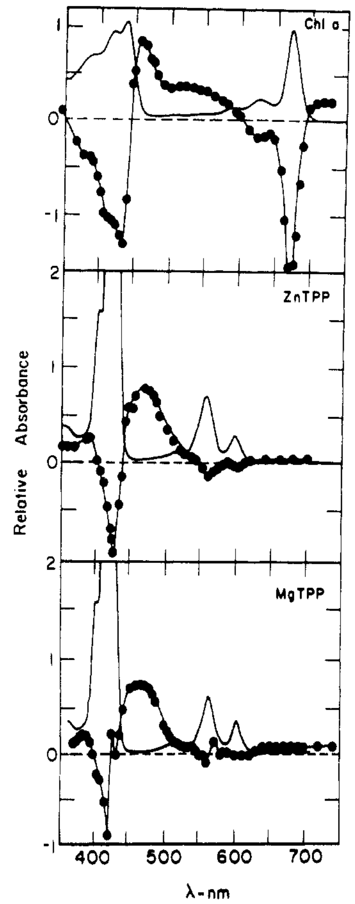

Figure 2. Ground-state absorption and triplet-triplet absorption (●, uncorrected for ground-state bleaching) spectra. The solutions contained 3 × 10^{-5}–6 × 10^{-5} M total porphyrin and 2% Triton in water. The absorbance scales for the ground and triplet states are different. The triplet states were produced by laser photolysis at 532 nm for ZnTPP and MgTPP and at 640 nm for Chl*a*.

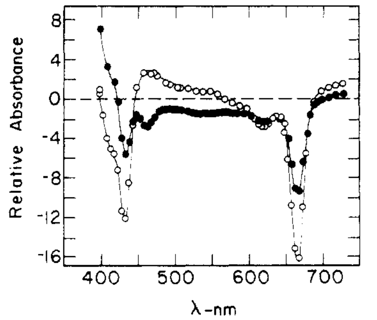

Figure 3. Differential absorption spectra recorded 300 μs after the pulse with Chl*a* in Br^-–Triton–aqueous solutions in conventional pulse radiolysis (O) and in the PRAP mode (●) (15% triplet conversion). The solutions contained 1.3 × 10^{-5} M total Chl*a*, 0.1 M NaBr, and the Triton, buffer, and N_2O as in Figure 1.

= (2.5 ± 0.5) × 10^8 M^{-1} s^{-1} and *k*(Chla^T + $(CH_3)_2\dot{C}OH$) = (2.3 ± 0.5) × 10^9 M^{-1} s^{-1}.

Similar experiments with *t*-BuOH indicate bleaching of Chla^T while no reaction was apparent with the ground-state Chl*a*.[30] As found previously with ZnTPPS[7] the reaction of $\dot{C}H_2C(CH_3)_2OH$ with Chla^T does not lead to formation of the anion radical but probably to an adduct (reaction 3).

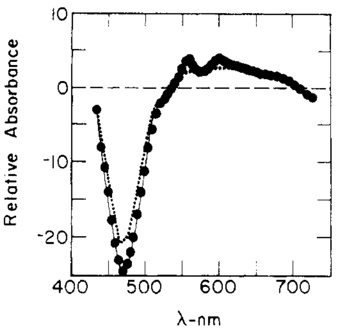

Figure 4. Differential absorption spectra recorded 30 (···) and 300 (●) μs after the pulse in PRAP experiment (12% triplet) with ZnTPP (5 × 10^{-5} M total) in Br^-–Triton–aqueous solutions as in Figure 3.

TABLE I: Rates of Reaction of Radicals with P and P^T in Micellar Solutions

P	radical	*k*,[a] M^{-1} s^{-1} P	*k*,[a] M^{-1} s^{-1} P^T
Chl*a*	$(CH_3)_2\dot{C}OH$	2.5 × 10^8	2.3 × 10^9
Chl*a*	$Br_2^-\cdot$	~2 × 10^9	~4 × 10^9
ZnTPP	$(CH_3)_2\dot{C}OH$	1 × 10^8	2.0 × 10^9
ZnTPP	$Br_2^-\cdot$	7 × 10^8	1 × 10^{10}
Chl*a*	$\dot{C}H_2OH$	<10^7	3 × 10^9
Chl*a*	$MV^+\cdot$		(8 × 10^3 s^{-1})[b]
ZnTPP	$MV^+\cdot$		(8 × 10^3 s^{-1})[b]

[a] Measured usually at one concentration only and are accurate to ±20–30%. The values for P may be slightly too high because of incomplete scavenging (see text).
[b] The experimental observations of these reactions (eq 9) permit only lifetime measurements.

The oxidation process as described by reaction 2 is manifested by the results shown in Figure 3. The differential spectrum obtained upon oxidation of ground-state Chl*a* by $Br_2^-\cdot$ is in good agreement with the spectra reported recently.[27] The spectrum recorded in the PRAP mode shows partial bleaching of ground-state Chl*a* at 670 and 430 nm along with the bleaching of Chla^T (450–550 nm). This result indicates that $Br_2^-\cdot$ does not react exclusively with the triplet. The reason for the low selectivity is the low triplet yield (15% in this experiment) and the ratio of the rate constants: *k*(Br_2^- + Chl*a*) ≈ 2 × 10^9 M^{-1} s^{-1} vs. *k*(Br_2^- + Chla^T) ≈ 4 × 10^9 M^{-1} s^{-1}. From these values it can be predicted that ~30% of $Br_2^-\cdot$ would react with Chla^T and, in fact, the bleaching levels at 670 nm are in agreement with this prediction.

ZnTPP. The behavior of $ZnTPP^T$ was similar to that of Chla^T discussed above and $ZnTPPS^T$ in aqueous solutions.[7] The differential spectrum observed upon reaction of $ZnTPP^T$ with $(CH_3)_2\dot{C}OH$ was very similar to that found in the aqueous system,[7] indicating bleaching of P^T (~475 nm) and formation of $P^-\cdot$ (~700 nm) in accordance with reaction 1. The kinetics were also similar and gave *k*(ZnTPP + $(CH_3)_2\dot{C}OH$) ≈ 1 × 10^8 M^{-1} s^{-1} and k_1($ZnTPP^T$ + $(CH_3)_2\dot{C}OH$) = (2.0 ± 0.5) × 10^9 M^{-1} s^{-1}, again indicating a high selectivity in the reaction of this radical with the triplet vs. ground state.

PRAP experiments under oxidative conditions ($Br_2^-\cdot$) also showed depletion of the triplet absorption at ~470 nm with concomitant formation of the cation radical absorption (~600–650 nm) in accordance with reaction 2 (Figure 4, earlier spectrum). The kinetics of this reaction was followed at 470 (P^T bleaching) and 575, 625, and 650 ($P^+\cdot$ formation) nm and found to be (9 ± 1) × 10^4 s^{-1} at all wavelengths, yielding k_2 = 1 × 10^{10} M^{-1} s^{-1}. Here again

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[30] The reaction of the $\dot{C}H_2C(CH_3)_2OH$ radical from *t*-BuOH with Chl*a* was shown to have a rate constant of 2.1 × 10^7 M^{-1} s^{-1}.[25] At the low concentrations of Chl used in this experiment (1 × 10^{-5}–2 × 10^{-5} M) and radical concentrations of 3 × 10^{-6}–5 × 10^{-6} M the radical–radical decay (*k* = 1.4 × 10^9 M^{-1} s^{-1}: Simic, M.; Neta, P.; Hayon E. *J. Phys. Chem.* **1969**, *73*, 3794) will predominate. Therefore, the reaction Chl + $\dot{C}H_2C(CH_3)_2OH$ was not observed in our case. A small concentration of Triton radicals may be formed in this system but their reaction with Chl*a* was not observed either.

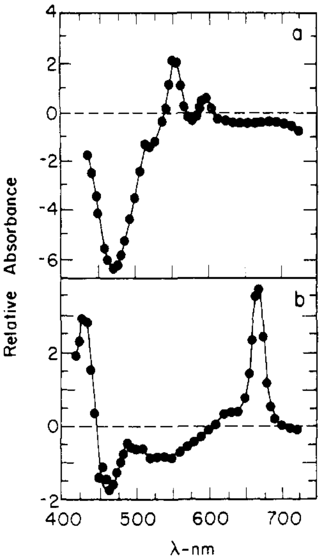

Figure 5. Differential absorption spectra recorded 800 μs after the pulse in a PRAP experiment with (a) ZnTPP, 5 × 10^{-5} M total, 12% triplet and (b) Chl*a*, 1.8 × 10^{-5} M total, 20% triplet in Triton–aqueous solutions saturated with N_2O.

the reaction of $Br_2^{-}\cdot$ with P^T is considerably faster that that with P ($k(Br_2^- + \text{ZnTPP}) = 7 \times 10^8\ M^{-1}\ s^{-1}$ under similar conditions, Table I). The yield of $P^{+}\cdot$ was estimated from the differential spectrum in Figure 4 and the spectrum of the triplet.[31] When ϵ values at several wavelengths are compared with those reported for the cation radical,[32] it is concluded that reaction 2 produces $P^{+}\cdot$ quantitatively.

Figure 4 also shows that the spectrum recorded at later times contains an additional contribution at 560 and 600 nm. These absorptions, superimposed on that of $P^{+}\cdot$, are formed about 1 order of magnitude more slowly ($k \sim 1 \times 10^4\ s^{-1}$) and are also accompanied by an additional triplet depletion (470 nm). The 560- and 600-nm maxima correspond to those of ground-state ZnTPP Q-band absorptions. This slower process can be thus ascribed to a partial recovery of P from P^T via a P^T + radical reaction. To study the origin of this process we have carried out a blank experiment with the system of ZnTPP–Triton–N_2O without Br^-. In the PRAP experiment this system exhibited P^T depletion with formation of P (560 and 600 nm) and no apparent reduction to $P^{-}\cdot$ or oxidation to $P^{+}\cdot$. Figure 5 shows the differential spectrum recorded with ZnTPP together with that obtained with Chl*a* under similar conditions. Both spectra indicate $P^T \rightarrow P$, and the yield of this recovery corresponds to ~10% of the total radical concentration for both ZnTPP and Chl*a*. The mechanism of the recovery may be a direct energy transfer from P^T to a Triton radical. The low yield results from the low probability of the radical to encounter a P^T during its lifetime since each one of these species is produced in a different micelle. It is also possible that only one type of Triton radical may engage in energy transfer. An alternative mechanism for $P^T \rightarrow P$ may be a reduction by one radical $P^T + R\cdot \rightarrow P^{-}\cdot + R^+$ followed by reoxidation with another radical $P^{-}\cdot + R'\cdot \rightarrow P + R'^{-}$. Since the latter electron transfer is expected to be slower than the first step and since no evidence for $P^{-}\cdot$ formation is found, the latter mechanism does not appear likely.

The slow recovery observed in the system of $\text{ZnTPP}^T + Br^-$ may be partially caused by Triton radicals. However, the yield of $P^T \rightarrow P$ in the presence of Br^- is only slightly less than that in its absence, while the yield of Triton radicals is only ~10%. Therefore, quenching by Triton radical can have only a minor contribution. An additional route for the recovery may involve the cation radical, i.e., $P^T + P^{+}\cdot \rightarrow P^{+}\cdot + P$, in which case $[P^{+}\cdot]$ is conserved and the net result is $P^T \rightarrow P$. In the case of the Chl*a* + Br^- system, the nature of the spectra does not indicate whether this slow recovery takes place. Even though the mechanism of the $P^T \rightarrow P$ process is of interest, its contribution in the above systems is small and does not mask the main reaction (eq 3).

Reactions of P^T *with the Methylviologen Radical.* Methylviologen radicals ($MV^{+}\cdot$) were produced by pulse radiolytic reduction of the parent compound (MV^{2+}) with $\dot{C}H_2OH$ radicals

$$\dot{C}H_2OH + MV^{2+} \rightarrow CH_2O + H^+ + MV^{+}\cdot \quad (6)$$

The $\dot{C}H_2OH$ radical was chosen for this purpose, rather than $(CH_3)_2\dot{C}OH$, since k_6 was reported to be $3.0 \times 10^8\ M^{-1}\ s^{-1}$,[33] and the reaction $\dot{C}H_2OH + P \rightarrow CH_2O + H^+ + P^-$ is expected to be much slower than that of $(CH_3)_2\dot{C}OH$,[28,34] probably $\leq 10^7\ M^{-1}\ s^{-1}$, so that it will not compete with reaction 6. Indeed, a pulse experiment with $\dot{C}H_2OH$ and P without MV^{2+} showed no apparent reaction. In the presence of ground-state P, with ≥5 times excess MV^{2+}, reaction 6 was nearly quantitative and the resulting $MV^{+}\cdot$ exhibits a spectrum (see below) identical with that reported previously.[33,35] This radical was found to be very long-lived with no indication of a reaction of $MV^{+}\cdot$ + P. This is expected since electron transfer occurs predominantly in the opposite direction,[34] i.e.

$$P^{-}\cdot + MV^{2+} \rightarrow P + MV^{+}\cdot \quad (7)$$

In the PRAP experiment $MV^{+}\cdot$ was also produced nearly quantitatively by the electron pulse via the predominant reaction 6. However, the possible reaction of $\dot{C}H_2OH$ with P^T should also be considered:

$$\dot{C}H_2OH + P^T \rightarrow CH_2O + H^+ + P^{-}\cdot \quad (8)$$

Kinetic measurements indicate that $k(\dot{C}H_2OH + P^T) \approx 3 \times 10^9\ M^{-1}\ s^{-1}$. At the concentrations of P^T (3–10 μM) and MV^{2+} (100–150 μM) generally used in these experiments we estimate that 70–80% of the $\dot{C}H_2OH$ radicals react directly with the MV^{2+}. However, those reacting with P^T form $P^{-}\cdot$ (reaction 8) which in turn will rapidly reduce MV^{2+} to $MV^{+}\cdot$ (reaction 7).[36]

Reaction 7 takes place quantitatively with no evidence for a reverse reaction of $MV^{+}\cdot$ with ground-state porphyrin. In the present study using the PRAP mode we find, however, that the reaction of $MV^{+}\cdot$ with the triplet P^T does occur (reaction 5) and is followed by reaction 7.

$$MV^{+}\cdot + P^T \xrightarrow{k_5} MV^{2+} + P^{-}\cdot \xrightarrow{k_7} MV^{+}\cdot + P \quad (9)$$

The net result of these two successive reactions is the recovery of P from P^T with no net change in $[MV^{+}\cdot]$ in the case of Chl*a* but some decrease in $[MV^{+}\cdot]$ with the two metalloporphyrins.

The spectral data obtained with the system of Chl*a* and MV^{2+} are shown in Figure 6. Conventional pulse ra-

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[36] Some $\dot{C}H_2OH$ radicalsy may also react via a radical–radical decay. We estimate that this process may consume 15–20% of the $\dot{C}H_2OH$ radicals.

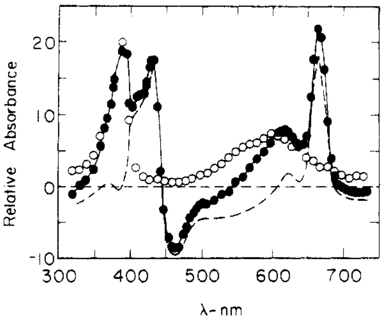

Figure 6. Differential absorption spectra recorded with Chl*a* (2.1 × 10^{-5} M total) in MeOH (1.5 M)-MV^{2+} (1.2 × 10^{-4} M)-Triton (2%)-aqueous solutions (pH 7, N_2O saturated) in conventional pulse radiolysis (O, 100 μs after the pulse) and in the PRAP mode (17% triplet; ●, 800 μs after the pulse). The dashed line is obtained by substracting spectrum O from spectrum ● and corresponds to $\epsilon(P) - \epsilon(P^T)$ (compare with Figure 2).

diolysis results in the formation of $MV^{+\cdot}$ radicals by reaction 6 followed by a very slow decay, not affected by the presence of Chl*a*. The differential spectrum in the PRAP mode indicates bleaching of Chl*a*^{T} as seen at 450–550 nm and formation of ground-state Chl*a* absorptions at 430 and 670 nm. An additional component contributing to this spectrum is the absorption of $MV^{+\cdot}$ (maxima at 390 and 600 nm) which does not change during the $P^T \rightarrow P$ recovery, i.e., reactions 6, 5, and 7. The sum of these three reactions corresponds to the net result $\epsilon(MV^{+\cdot}) + \epsilon(P) - \epsilon(P^T)$. Therefore, if we subtract the contribution of $MV^{+\cdot}$ (O) from the overall differential spectrum in the PRAP mode (●), the result should correspond to $\epsilon(P) - \epsilon(P^T)$. The dashed line obtained by the above procedure is found to be in very good agreement with the differential spectrum of $\epsilon(P^T) - \epsilon(P)$ obtained in the laser photolysis experiment (compare Figures 6 and 2). The overall yield of $P^T \rightarrow P$ as estimated from the absorption formed at 670 nm and the bleaching at 480 nm, by comparison with the spectra of Chl*a* and Chl*a*^{T},[37] and assuming $G(MV^{+\cdot}) = 6.0$, corresponds to only 35–40% of the radicals. This incomplete yield may be due to a back-reaction $P \rightarrow P^T$ caused by the exciting light pulse during the steady-state period (see Figures 1 and 7).

The rate of the $P^T \rightarrow P$ recovery by $MV^{+\cdot}$ (under the conditions of Figure 6) was found to be 8×10^3 s^{-1} from measurements of both P^T disappearance and P formation. Since k_7 is expected to be $\sim 1 \times 10^9$ M^{-1} s^{-1} (ref 34) and $[MV^{2+}] = 1.2 \times 10^{-4}$ M, the rate of reaction 7 is $\sim 1 \times 10^5$ s^{-1}, which is much faster than the overall rate observed for reaction 9. Therefore, we attribute the observed rate to the first stage in the $P^T \rightarrow P$ recovery (reaction 5) and calculate a second-order rate constant for this "quenching" process of $\sim 2 \times 10^9$ M^{-1} s^{-1}.

Similar experiments with ZnTPP and MgTPP indicate a somewhat similar behavior. The spectra presented in Figure 7 show again the bleaching of P^T with formation of P, with lifetimes similar to those found with Chl*a* and with a yield corresponding to ~50% of the $MV^{+\cdot}$ formed in the pulse radiolysis. With these porphyrins, however, during the $P^T \rightarrow P$ recovery process the concentration of $MV^{+\cdot}$ decreases considerably. The reason for this decrease may lie in reaction 7, in which in the case of ZnTPP and MgTPP a complex ($P\cdot MV^{+\cdot}$) is the final product. The spectral features of this complex are similar to those of P without a contribution from the 600-nm absorption of the free $MV^{+\cdot}$. Invoking this complex formation is in line with a previous independent study[34] where the electron-transfer

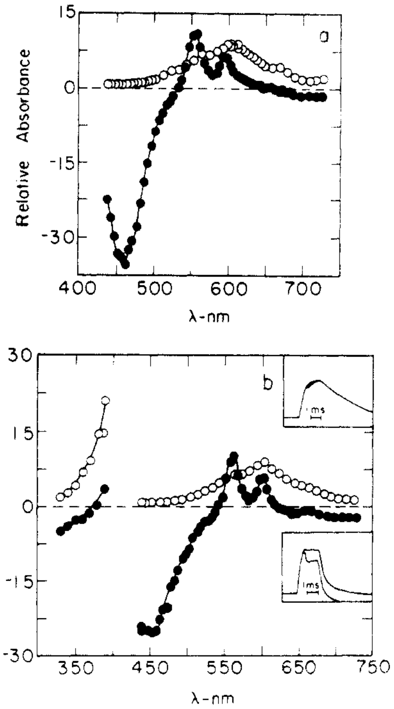

Figure 7. Differential absorption spectra recorded with (a) ZnTPP and (b) MgTPP (both 7 × 10^{-5} M total) under conditions as in Figure 6. The inserts show the time profiles of triplet buildup and decay in the absence (top) and presence (bottom) of MV^{2+} and the effect of the electron pulse.

reaction process between $ZnTPP^{-\cdot}$ and MV^{2+} has been investigated. The disappearance of $P^{-\cdot}$, in that study, was not accompanied by the concomitant formation of the 600-nm absorption of $MV^{+\cdot}$ as expected from reaction 7. It is concluded, therefore, that reaction 7 applied for ZnTPP and MgTPP proceeds in the formd of[38]

$$ZnTPP^{-\cdot} + MV^{2+} \rightarrow (ZnTPP\cdot MV^{+\cdot}) \qquad (7a)$$

The results observed upon reaction of $MV^{+\cdot}$ with P^T should be compared with those obtained upon reaction of the Triton radicals with P^T. In both cases the net result is $P^T \rightarrow P$, but the efficiency of this process is much higher with $MV^{+\cdot}$ than with the Triton radicals. The yield of Triton radicals in the presence of MeOH and MV^{2+} is very small so that their contribution to the overall process in the MV^{2+} system is negligible.

The mechanism of the $P^T \rightarrow P$ recovery is formulated in reaction 9. The first reaction in this mechanism (reaction 5) is thermodynamically allowed since the redox potential for the couple $MV^{2+}/MV^{+\cdot}$ is −0.45 V vs. NHE[39] (−0.69 V vs. SCE) and that for $P^T/P^{-\cdot}$ is estimated to be +0.22 to +0.27 V vs. SCE.[9] The second reaction in this mechanism is also favorable ($E(P/P^{-\cdot}) = -1.11$ to −1.35 V vs. SCE)[9,40] and has been experimentally shown to take place rapidly.[34] These considerations, together with the fact that $[MV^{2+}] > [P]_0$, support the electron-transfer mechanism for the $P^T \rightarrow P$ conversion (reaction 9). Nevertheless, in view of the results obtained with the Triton radicals, we cannot rule out the possibility that the reaction of $MV^{+\cdot}$ with P^T proceeds by energy transfer to result in $MV^{+\cdot}$ + P in the case of Chl*a* or in a complex

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($P{\cdot}MV^{+}{\cdot}$) in the case of the metalloporphyrins.

We have demonstrated in this and previous studies that the reactivity of the photoexcited triplet state of porphyrins and chlorophylls with radicals is substantially higher than that of the corresponding ground states. This behavior, not limited to the porphyrin moiety only, was found also with pyrene,[5] whose photoexcited triplet exhibits similar chemical reactivity toward transient radicals. The experimental results clearly indicate that PRAP spectroscopy is most suitable in studying reactions of photoexcited states with short-lived radicals. With regard to stable radicals such as $MV^{+}{\cdot}$, the advantage of employing this method, over conventional laser photolysis, is less substantial. Nevertheless, in the PRAP mode the interference due to a possible absorption overlap between the photoexcited triplet and that of the stable radical can be avoided as the triplet state is prepared prior to the radical production.

Electron Spin Resonance and Optical Detection of Manganese(IV) Tetraphenylporphyrin

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Radiation-chemical one-electron oxidation of (tetraphenylporphinato)manganese(III) ($ClMn^{III}TPP$) was carried out in tetrachloroethane (TCE) at 77 K. The ESR and optical absorption spectra of γ-irradiated solutions revealed that oxidation occurs not at the porphyrin ring but at the central metal, giving manganese(IV) porphyrin. The spin state of the manganese(IV) porphyrin was assigned to be 3/2 from the analysis of the highly anisotropic ESR spectra.

Introduction

Physical and chemical properties of metalloporphyrins and related compounds have been increasingly investigated with the aim of understanding their functions in biological systems and also of utilizing them as mediators for chemical and photochemical redox reactions. Manganese porphyrins are particularly interesting in this respect because of their possible involvement in the photosynthetic liberation of oxygen from water and also because of the possibility that they act as catalysts for electron transfer reactions. There have been experimental studies on their chemical[1,2] and photochemical[3] redox reactions in fluid solution and a review by Boucher.[4] A detailed theoretical study on their electronic structures has also been reported recently.[5] The possible valence states of manganese in porphyrin complexes are considered to be 2+, 3+, and 4+. Among these valence states, 3+ is the most stable. The reduction of manganese(III) porphyrins yields manganese(II) porphyrins, which are stable only in the absence of oxygen and water. No reliable evidence for the existence of manganese(IV) porphyrins, however, has never been reported and a few papers report[6,7] evidence for the existence of the cation radicals of manganese(III) porphyrins produced in fluid solutions. Such reports suggest that manganese(IV) porphyrins do not exist or they are unstable in fluid solutions, in which the chemical or electrochemical oxidation of manganese(III) porphyrins is carried out. If oxidation could be done in low-temperature matrices, manganese(IV) porphyrins might be stabilized. We have a good method to perform such an experiment, i.e., one-electron oxidation of solute molecules by radiolysis of alkyl halide matrices.[8,9] The oxidation takes place through electron abstraction from solute molecules by solvent cation radicals produced by ionizing radiation. When radiolysis is carried out at liquid-nitrogen temperature, oxidation proucts are usually stabilized because of the rigidity of the low-temperature matrices. The application of this method has been reported for the formation of cation radicals of chlorophylls[10] and copper[11] and lead[12] porphyrins. As another successful application of this technique to trap labile metalloporphyrins, this paper reports the first clear evidence for the existence of the manganese(IV) porphyrin.

Experimental Section

$ClMn^{III}TPP$ was prepared by the method reported in the literature[13] and purified by column chromatography using Sephadex LH-20. Commercially available TCE was used without further purification. Sample solutions of 10^{-3} M were degassed by repeated freeze-pump-thaw cycles. The cobalt-60 γ irradiation was carried out at a dose rate of ca. 4.5×10^{4} rd/min for 70-100 min.

ESR spectra were recorded on a JEOL FE-3AX spectrometer operating in the X band with 100-kHz modulation. Optical absorption spectra were taken on a Cary Model 14 spectrophotometer. Both irradiation and spectral measurements were made by placing sample cells in

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