(30) For a discussion on these factors see Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123.

(31) A simple Huckel molecular orbital calculation using the heteroatom model for the methyl substituent with the parameters $h_x = 2.0$ and $k_{C-x} = 0.8$ gives a similar plot, i.e., no improvement is observed.

(32) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, N.Y., 1969; pp 81, 112.

(33) References cited in Olah, G. A.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3137.

(34) Caution should be exercised in attributing a stabilizing effect to the methyl only as a result of a large ^{13}C deshielding of C_α upon substitution of hydrogen for methyl, as, e.g., the ethylbenzenium ion with $\Delta\delta_{C_\alpha}$ = 25 ppm.[35]

In the present report the deshielding for C(1) and C(3) of the naphthalenium ions, which are 22.5 and 30 ppm, respectively, are illustrative.

(35) Olah, G. A.; Porter, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6877.

(36) (a) Mackor, E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1958**, *54*, 66. Daudel, R.; Chalvet, O. *J. Chim. Phys. Phys.-Chim. Biol.* **1956**, 943.

Electron Transfer Reactions Involving Porphyrins and Chlorophyll *a*[1]

P. Neta,*[2] A. Scherz,[3] and Haim Levanon[4]

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and the Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel.
Received October 2, 1978

Abstract: Electron transfer reactions involving porphyrins (P) and quinones (Q) have been studied by pulse radiolysis. The porphyrins used were tetraphenylporphyrin (H_2TPP), its tetracarboxy derivative (H_2TCPP), the sodium and zinc compounds (Na_2TPP and ZnTPP), and chlorophyll *a* (Chl *a*). These compounds were found to be rapidly reduced by electron transfer from $(CH_3)_2\dot{C}O^-$. Reduction by $(CH_3)_2\dot{C}OH$ was rapid in aqueous solutions but relatively slow in *i*-PrOH solutions. Transient spectra of the anion radicals were determined and, in the case of $H_2TCPP^-\cdot$, a pK = 9.7 was derived for its protonation. Electron-transfer reactions from the anion radical of H_2TCPP to benzoquinone, duroquinone, 9,10-anthraquinone 2-sulfonate, and methylviologen occur in aqueous solutions with rate constants $\sim 10^7$–10^9 M^{-1} s^{-1} which depend on the pH and the quinone reduction potential. Reactions of $Na_2TPP^-\cdot$, $ZnTPP^-\cdot$, and Chl $a^-\cdot$ with anthraquinone in basic *i*-PrOH solutions occur with rate constants $\sim 10^9$ M^{-1} s^{-1}. The spectral changes associated with these electron-transfer reactions as observed over a period of $\sim$1 ms indicated, in some cases, the formation of an intermediate complex $[P\cdots Q^-\cdot]$.

Introduction

Electron-transfer reactions have been the subject of extensive studies in recent years. Particular attention has been drawn to those systems which bear specific relation to primary photosynthetic processes.[5-10] Two types of electron-transfer reactions are generally studies by fast kinetic techniques. In the system of porphyrins (P) and quinones (Q) these reactions are

$$P^* + Q \rightarrow P^+\cdot + Q^-\cdot \qquad (1)$$

$$P^-\cdot + Q \rightarrow P + Q^-\cdot \qquad (2)$$

In the first case, the donor molecule is promoted to an excited electronic state which subsequently undergoes an electron-transfer reaction with an acceptor molecule. Either the photoexcited singlet or the photoexcited triplet serves as precursor for the intermediate radical pair ($P^+\cdot Q^-\cdot$) which is formed following the excitation. It is expected that the efficiency of charge separation would be higher in the case of a triplet precursor, as indeed has been confirmed in recent studies on model compounds.[6,9-11] In bacterial photosynthesis, however, it is known that the preceding state for photochemistry is the singlet and the reason for this apparent contradiction is as yet unknown.

Another approach to the study of photosynthetic electron transfer reactions is to follow reaction 2. This type of reaction, although studied quite extensively in many systems, has rarely been applied to porphyrins and their biological analogues. It is the purpose of the present study to show some examples of electron-transfer reactions between anion radicals of various porphyrins and different acceptors in aqueous and alcoholic solutions. In the first part we discuss the reduction of porphyrins and the acid-base equilibria of some anion radicals. The second part deals with electron transfer to various acceptors. This electron transfer was found to be more complicated than that formulated in reaction 2. In order to account for our findings we invoke the possible participation of an intermediate complex $[P\cdots Q^-\cdot]$.

Experimental Section

The porphyrins used in this study were the following. Mesotetra(4-carboxyphenyl)porphyrin (H_2TCPP) was obtained from Strem Chemicals, and mesotetraphenylporphyrin (H_2TPP) from Aldrich. Zinc tetraphenylporphyrin (ZnTPP) was kindly supplied by Professor A. D. Adler, and chlorophyll *a* (Chl *a*) was extracted and purified by the method described.[12]

The H_2TCPP was used for experiments in aqueous solutions. It was dissolved (1×10^{-5} to 1×10^{-4} M) in slightly alkaline solutions (pH $\sim$11) which were then adjusted to the pH required for the experiments. Sodium phosphates and sodium tetraborate were used as buffers for pH 6-8 and 8-10, respectively. The solutions contained also 0.1-0.4 M of 2-propanol (*i*-PrOH) or *tert*-butyl alcohol (*t*-BuOH) as scavengers for OH radicals. The alcohols and the inorganic compounds were all Baker Analyzed reagents, and the water was doubly purified by a Millipore Milli-Q system.

The other porphyrins are not sufficiently soluble in water to allow meaningful radiolytic experiments. They were, therefore, studied only in alcoholic solutions. First they were dissolved in a minimal amount of tetrahydrofuran (THF, refluxed over $LiAlH_4$ and distilled). This solution was then diluted into a large volume of *i*-PrOH. A stock solution containing $\sim$0.1 M *i*-PrO^-Na^+, prepared by dissolving sodium metal in *i*-PrOH, was used for experiments in basic alcoholic solutions.

Since the porphyrins are quite sensitive to light, their solutions were

0002-7863/79/1501-3624$01.00/0

prepared fresh before each experiment and were protected from unnecessary light. During the pulse radiolysis experiments the analyzing light was passed through various cutoff filters. In the preliminary runs it was noticed that the kinetic traces were strongly dependent on the intensity and bandwidth of the analyzing light. It was also noticed that the light sensitivity of H_2TPP was especially high when dissolved in basic solutions. In order to minimize the undesired photochemical processes in our experiments, we found it necessary to use the analyzing xenon lamp in its steady state level without pulsing it. Cutoff filters were changed every ~50 nm when taking a spectrum. Further, all kinetic measurements were done with the light passing through interference filters which have a band-pass of 8–10 nm.

Anion radicals of porphyrins and chlorophylls are known to react with acids and bases.[13,14] These reactions, however, are substantially slower than the electron-transfer reactions with the acceptors studied here, and will be excluded from our discussion.

All solutions were deoxygenated by bubbling with pure N_2 or N_2O. The optical spectra of all solutions were measured before irradiation using Cary 14 or Cary 219 spectrophotometers. The kinetic spectrophotometric experiments were carried out with signal averaging using the computer-controlled pulse radiolysis apparatus described previously.[15-17]

Electron Transfer to Porphyrins and Chlorophyll *a*

The anion radicals of porphyrins can be produced in irradiated aqueous or alcoholic solutions by the reaction of the solvated electron, e.g.

$$P + e^-_{solv} \rightarrow P^- \cdot \qquad (3)$$

This type of reaction is diffusion controlled, $k_3 = (1\text{-}3) \times 10^{10}$ $M^{-1}\ s^{-1}$.[18] It is desirable, however, to increase the yield of the anion radical and to eliminate the reaction of the porphyrin with the other primary radicals. This is often achieved in aqueous solutions by the addition of 2-propanol.

$$(CH_3)_2CHOH + H \rightarrow (CH_3)_2\dot{C}OH + H_2 \qquad (4)$$

$$(CH_3)_2CHOH + OH \rightarrow (CH_3)_2\dot{C}OH + H_2O \qquad (5)$$

The $(CH_3)_2\dot{C}OH$ radical produced in reactions 4 and 5 is expected to reduce porphyrins:

$$P + (CH_3)_2\dot{C}OH \rightarrow P^- \cdot + (CH_3)_2CO + H^+ \qquad (6)$$

The anion radical is thus produced rapidly by reaction 3 and more slowly by reaction 6, and the total result is that all the primary radicals of water radiolysis are converted into (porphyrin)$^-$ ·. In order to follow the kinetics of reaction 6 it is advantageous to eliminate reaction 3 by saturating the solution with N_2O. This solute reacts with e^-_{solv} very efficiently to produce OH:

$$N_2O + e^-_{aq} \rightarrow N_2 + OH^- + OH \qquad (7)$$

which subsequently reacts with the alcohol (reaction 5). In the solutions used, reactions 7 and 5 are complete within <100 ns and reaction 6 becomes the only observable process on the microsecond time scale.

A parallel situation occurs in neat *i*-PrOH and reaction 6 again becomes the only important process, as found previously.[17]

H_2TCPP in Aqueous Solutions. The free base porphyrin H_2TCPP was used for experiments in aqueous solutions because it is soluble in water, when at least part of its four carboxyl groups are in the anionic form. All experiments were carried out at $6.8 < pH < 13$. Under these conditions the compound exists in one form only, namely, H_2TCPP, in which all four carboxyl groups are dissociated and two of the pyrrole nitrogens are protonated. The equilibria in the porphyrin skeleton can be formulated as follows.

$$H_4TCPP^{2+} \rightleftarrows H_3TCPP^+ \rightleftarrows H_2TCPP \rightleftarrows HTCPP^- \qquad (8)$$

The acid pK values are below 5 and the basic one is above 14.[19] The free base, although formulated as H_2TCPP, may actually exist in a dimeric form, especially at high ionic strength. The monomer-dimer equilibrium has been studied previously by monitoring the variations in the absorption spectra, and an equilibrium constant has been derived.[20] Using the previous data,[20] and examining the effect of ionic strength on the absorption spectra, we estimate that in our experiments 65–75% of the H_2TCPP was dimerized.

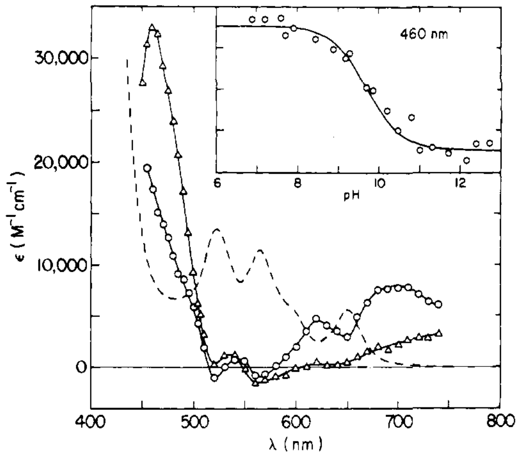

Figure 1. Transient absorption spectra of irradiated aqueous solutions of H_2TCPP and their pH dependence. The difference spectra were recorded with N_2O-saturated solutions containing 1×10^{-4} M H_2TCPP and 0.15 M *i*-PrOH at pH 12.1 (○) or 6.9 (△), and were not corrected for the bleaching of the parent compound. The spectrum prior to irradiation (- - -) is given for comparison. The insert shows the effect of pH on the 460-nm absorption. The curve was calculated from the limiting values and p*K* = 9.7.

The transient absorption spectra recorded with irradiated neutral and alkaline solutions of H_2TCPP, along with the spectrum of the unirradiated solutions, are shown in Figure 1. The experimental points represent a difference spectrum and were not corrected for the bleaching of the parent compound. The band observed in the 700-nm region is a real absorption of the radical. Between 500 and 600 nm the spectrum of the radical is apparently similar to that of the parent compound. The Soret band appears to be red shifted in the radical.

In order to confirm reaction 6, i.e., that the radical from *i*-PrOH transfers an electron to H_2TCPP, the spectrum was recorded using either *i*-PrOH or *t*-BuOH as scavengers. In the latter case only the rapid reaction with e^-_{aq} is observed and the anion radical is produced with a yield of $G = 2.8$. When *i*-PrOH is used, the initial reaction of e^-_{aq} was followed by a slower process, which resulted in an identical spectrum but with a total yield over twice as high. The rate constant of reaction 6 was measured by following the formation of the $H_2TCPP^- \cdot$ at 460 and 700 nm. Solutions containing 0.2 M *i*-PrOH and saturated with N_2O were used for this purpose so that reaction 6 prevails. A value of $k_6 = (9 \pm 1) \times 10^8\ M^{-1}\ s^{-1}$ was determined at pH 7–11.

The difference between the transient spectra at pH 12.1 and 6.9[21] indicates that the radical undergoes an acid-base equilibrium in a pH region where the parent compound does not. The p*K* was determined from the change in the 460-nm absorbance (Figure 1, insert) and found to be 9.7. Since the p*K* of the anion radical is expected to be higher than that of the parent molecule,[22] we propose the following equilibrium in aqueous solution:

$$H_3TCP\dot{P} \xrightleftharpoons[pK\ =\ 9.7]{} H_2TCP\dot{P}^- + H^+ \qquad (9)$$

This formulation was also supported by conductometric pulse radiolysis experiments[23] which showed that at pH 10.5 the radical is mostly in the anionic form.

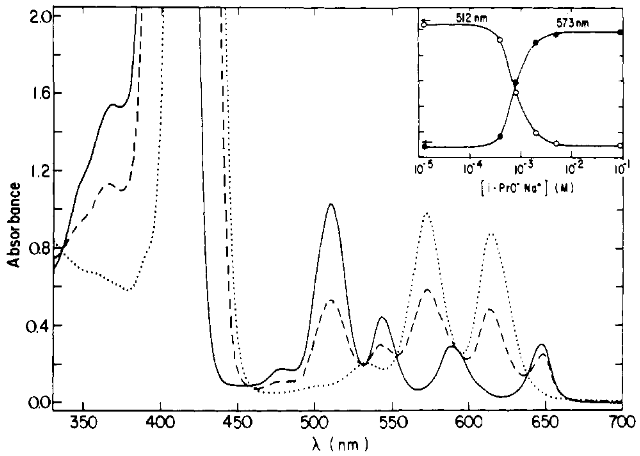

Figure 2. Absorption spectrum of 1×10^{-4} M H_2TPP in neutral and in basic *i*-PrOH: (—) neutral, (- - -) 8×10^{-4} M *i*-PrO^-Na^+, (···) 9×10^{-2} M *i*-PrO^-Na^+. The insert shows the effect of [*i*-PrO^-Na^+] on the absorption at 512 and 573 nm.

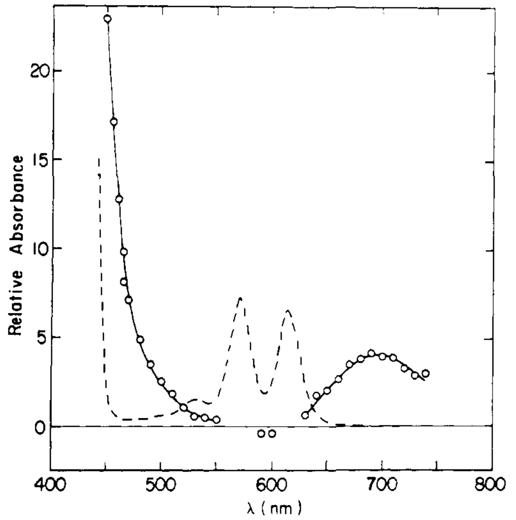

Figure 3. Transient absorption spectrum of irradiated H_2TPP (1×10^{-4} M) in basic *i*-PrOH (0.1 M *i*-PrO^-Na^+). If $G(Na_2TPP^- \cdot) = 6$, the relative absorbance scale can be converted into a scale of $\epsilon \times 10^{-3}$ (M^{-1} cm^{-1}). The spectrum of Na_2TPP prior to irradiation (- - -) is shown for comparison.

H_2TPP in 2-Propanol Solutions. Initial pulse radiolysis experiments in neutral *i*-PrOH solutions showed that H_2TPP is reduced by the solvent radical $(CH_3)\dot{C}OH$ relatively slowly. Since the dissociated form $(CH_3)_2{}^2\dot{C}O^-$ is known to react faster, experiments were carried out in basic solutions containing *i*-PrO^-Na^+. In addition, it was discovered that H_2TPP undergoes spectral changes in the presence of *i*-PrO^-Na^+. It was, therefore, decided to determine the nature of these changes before proceeding with the radiolytic reductions.

The spectrum of H_2TPP changes remarkably upon increasing the concentration of *i*-PrO^-Na^+ and the solution becomes much more sensitive to visible light. Careful experiments in the dark showed that the spectral changes are reversible when the basic solutions are neutralized. It was further shown that ionic strength (using *i*-PrOH saturated with LiCl) had little effect on these spectra. The spectrum of H_2TPP at high *i*-PrO^-Na^+ concentration (Figure 2) is very similar to that obtained previously[24] upon addition of sodium hydroxide in MeOH, which was assigned to Na_2TPP. It is concluded, therefore, that the spectral changes (Figure 2) are solely due to the equilibrium

Table I. Rate Constants for Electron Transfer from thc *i*-PrOH Radicals to Porphyrins and Chlorophyll *a*

compd	solvent	*k*, M^{-1} s^{-1}	
		$(CH_3)_2\dot{C}OH$	$(CH_3)_2\dot{C}O^-$
H_2TCPP	H_2O	$(9 \pm 1) \times 10^8$	
H_2TPP	*i*-PrOH	$\sim 1 \times 10^8$	
Na_2TPP	*i*-PrOH		$(2 \pm 0.4) \times 10^8$
ZnTPP	*i*-PrOH	$\sim 10^7$	$(6 \pm 1) \times 10^8$
Chl *a*	*i*-PrOH	$(7 \pm 3) \times 10^7$	$(6 \pm 1) \times 10^8$

$$H_2TPP + 2RO^-Na^+ \rightleftarrows Na_2TPP + 2ROH \qquad (10)$$

The inflection point is found at a concentration of 8×10^{-4} M *i*-PrO^-Na^+.

The reduction of H_2TPP in N_2O saturated basic solutions is in fact the reaction of the disodium compound

$$Na_2TPP + (CH_3)_2\dot{C}O^- \rightarrow Na_2\,TP\dot{P}^- + (CH_3)_2CO \qquad (11)$$

for which $k_{11} = (2 \pm 0.4) \times 10^8$ M^{-1} s^{-1} has been determined from the buildup of absorption of the anion radical at 700 nm. The transient difference spectrum of $Na_2TP\dot{P}^-$ is shown in Figure 3.

In neutral solutions, the reduction of the porphyrin should involve the two forms $H_2TPP + (CH_3)_2\dot{C}OH$. The formation of the anion radical under these conditions took place with a rate constant of $\sim 1 \times 10^8$ M^{-1} s^{-1}. This relatively low value, as compared with $k_6 = 9 \times 10^8$ M^{-1} s^{-1} for $H_2TCPP + (CH_3)_2\dot{C}OH$ in water (Table I), is in line with previous findings that this radical reacts more slowly in alcohol than in water.[17] The spectrum of the anion radical produced from H_2TPP in neutral *i*-PrOH resembles that observed in alkaline solutions, but the 700-nm band is less intense and appears to be broader. The spectrum may be assigned either to $H_2TP\dot{P}^-$ or $H_3TP\dot{P}$. By comparison with the results obtained with H_2TCPP in water, it appears likely that the neutral radical $H_3TP\dot{P}$ is observed in *i*-PrOH.

ZnTPP in 2-Propanol Solutions. This metalloporphyrin behaves in many respects similarly with Na_2TPP. The absorption spectrum of ZnTPP is identical in neutral and strongly basic *i*-PrOH. Reduction of this compound by $(CH_3)_2\dot{C}OH$ was found to be slow. As a result, experiments had to be carried out again in basic solutions, where reduction of ZnTPP by $(CH_3)_2\dot{C}O^-$ was found to have $k = (6 \pm 1) \times 10^8$ M^{-1} s^{-1}. The transient spectrum recorded upon reduction of ZnTPP is shown in Figure 4 along with that of the parent compound. The general features are similar to those observed upon reduction of Na_2TPP and H_2TCPP. The spectrum is in agreement with that reported previously[13] for $ZnTPP^-Na^+$ in THF, although the 700-nm band is broader in the present case.

Chlorophyll *a* in 2-Propanol. Chl *a* was found to be reduced to $Chl^- \cdot$ by e^-_{solv} ($k \geq 1 \times 10^{10}$ M^{-1} s^{-1}) and by $(CH_3)_2\dot{C}O^-$ ($k = (6 \pm 1) \times 10^8$ M^{-1} s^{-1}) in basic *i*-PrOH solutions. It is also reduced by $(CH_3)_2\dot{C}OH$ in neutral solutions, but with a much lower rate constant and to produce a lower yield. Apparently, this reaction is not sufficiently rapid to compete with the decay of the radicals. From the observed rate of buildup of $Chl^- \cdot$ absorption, and, from a comparison of the yield with that observed in basic solutions, it is estimated that reduction in neutral *i*-PrOH has a rate constant of $(7 \pm 3) \times 10^7$ M^{-1} s^{-1} (Table I).

The transient spectrum observed with irradiated solutions of Chl *a* in basic *i*-PrOH is shown in Figure 5. In the region of 640-680 nm, where Chl *a* has an intense absorption, the monitoring light was insufficient for the determination of the difference spectrum. In the regions of 450-600 and 700-850

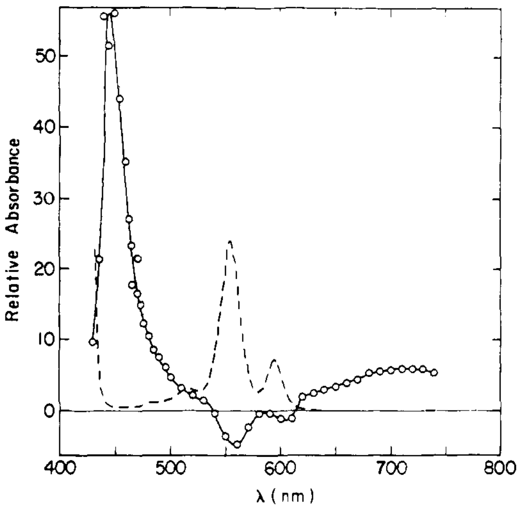

Figure 4. Transient absorption spectrum of irradiated ZnTPP (1×10^{-4} M) in basic *i*-PrOH (0.1 M *i*-PrO$^-$Na$^+$). The relative absorbance scale is the same as in Figure 3. The spectrum prior to irradiation (---) is shown for comparison.

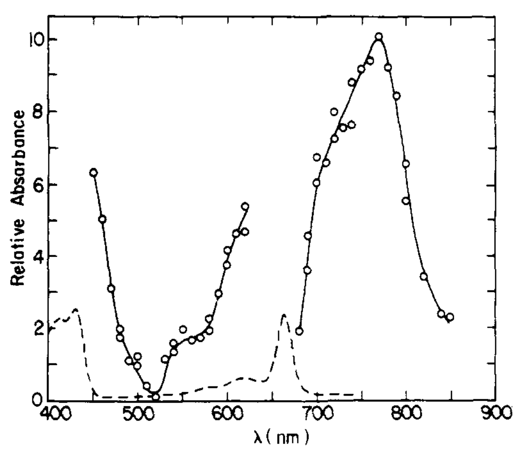

Figure 5. Transient absorption spectrum of irradiated Chl *a* (1×10^{-4} M) in basic *i*-PrOH (0.1 M *i*-PrO$^-$Na$^+$). The relative absorbance scale is the same as in Figure 3. The spectrum prior to irradiation (---) is shown for comparison, but on a compressed absorbance scale (the maxima at 430 and 665 nm have $\epsilon \sim 8 \times 10^4$ M^{-1} cm^{-1}).

nm the difference spectrum is very similar to that determined recently in DMF solutions.[25] If we assume that the overall *G* value for reduction in *i*-PrOH is similar to that in water, the extinction coefficient of the 770-nm peak is 1×10^4 M^{-1} cm^{-1}. This extinction coefficient is also in agreement with those reported in DMF[25] and in γ-irradiated MTHF glasses.[26]

Electron Transfer from the Anion Radicals of Porphyrins and Chlorophyll a

The anion radicals of the porphyrins and Chl *a* are expected to serve as electron donors in reactions with various acceptors which have higher reduction potentials. Of particular interest are the quinones.

$$P^- \cdot + Q \rightarrow P + Q^- \cdot \quad (2)$$

In attempting to demonstrate such reactions, it is necessary that the primary reduction step occurs preferentially with the porphyrin rather than with the quinone.

$$\dot{R}OH + P \rightarrow P^- \cdot \quad (12)$$

$$\dot{R}OH + Q \rightarrow Q^- \cdot \quad (13)$$

It has been demonstrated in the previous section that the rates of electron transfer to porphyrins depend on the solvent and on the basicity of the solution. The rates of the subsequent electron transfer to the quinones are also expected to be affected by the medium. Furthermore, it is not experimentally feasible to monitor the secondary electron transfer in neutral *i*-PrOH solutions, where the primary reduction is quite slow. In aqueous solutions, however, the electron transfer could be studied over a wide range of pH and with various acceptors.

Porphyrin-Quinones in Aqueous Solutions. In order to monitor the electron transfer reaction 2, experiments were carried out with solutions containing 1×10^{-4} M H_2TCPP and varying lower concentrations of several quinones. The rate constant k_2 was determined by following the first-order decay of the absorption at 460 and 700 nm as a function of the quinone concentration (Figure 6). Supporting evidence for reaction 2 may be obtained by following the formation of the $Q^- \cdot$ absorption as well. The only quinone which appeared to be promising for this purpose was 9,10-anthraquinone-2-sulfonate (AQS), whose anion radical absorbs intensely at 505 nm.[27]

The spectral changes observed upon electron transfer are shown in Figure 7. The spectrum monitored after completion of reactions 12 and 13 (30-40 μs after the pulse) is mostly that

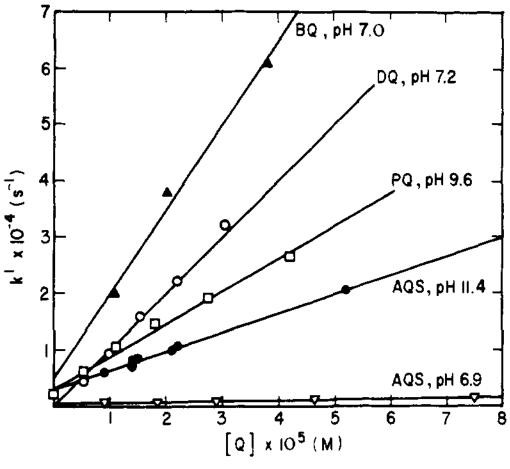

Figure 6. Dependence of the rate constant (k') for the decay of $H_2TCPP^- \cdot$ or $H_3TCPP\cdot$ on the concentration of various acceptors, monitored mostly at 460 and 700 nm.

of the porphyrin radical, with a small contribution by the quinone anion radical. After ~300 μs, during which time reaction 2 has taken place, the absorption of $H_2TCPP^- \cdot$ has disappeared and the remaining spectrum is very similar to that of $AQS^- \cdot$. The absorption under these conditions is slightly lower than that observed in the pure AQS solution. The experiments were such that this difference can be attributed to partial decay of $H_2TCPP^- \cdot$ in processes other than reaction 2. The absorption maximum, however, is shifted to lower wavelengths by ~10 nm. This shift is not caused by a contribution from $H_2TCPP^- \cdot$ absorption. It may be, therefore, suggested that the porphyrin anion radical is scavenged by the quinone to produce a complex

$$H_2TCPP^- \cdot + AQS \rightarrow [H_2TCPP \cdots AQS^- \cdot] \quad (14)$$

In such a complex most of the unpaired electron density should be on the quinone part to result in an optical absorption similar to that of $AQS^- \cdot$. It is not evident from our experiments whether the complex is only an intermediate which precedes the separation of the two species to produce free $AQS^- \cdot$ and H_2TCPP. Attempts to monitor the formation of free $AQS^- \cdot$ did not succeed because of subsequent disproportionation of these radicals.

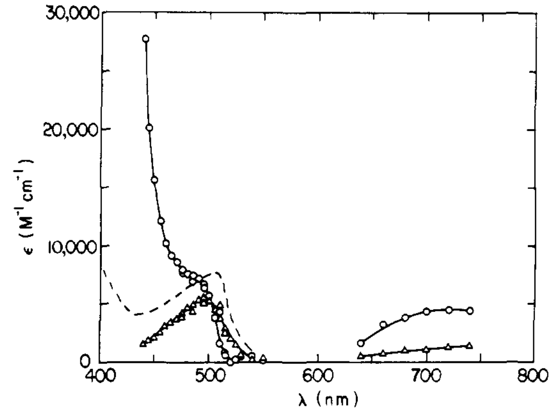

Figure 7. Spectra recorded with irradiated aqueous solutions of H_2TCPP (6.4×10^{-5} M) and AQS (1.4×10^{-5} M) at pH 11.5. The solution also contained 0.15 M *i*-PrOH and was N_2O saturated: (○), spectrum taken 30-40 μs after the pulse; (△), ~300 μs later; (---), spectrum of $AQS^- \cdot$ from ref 27.

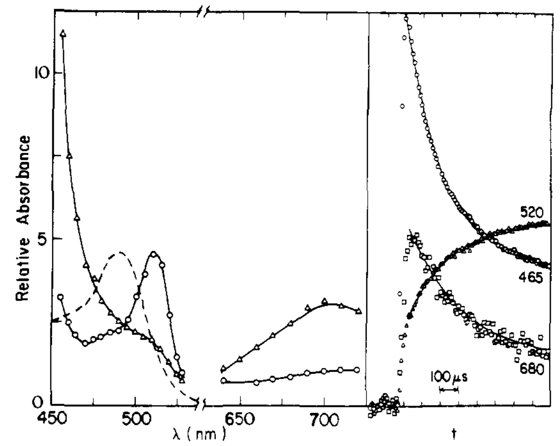

Figure 8. Spectral changes and time profile of the reaction between $Na_2TPP^- \cdot$ and AQ. The solution contained H_2TPP (1×10^{-4} M), AQ (6×10^{-6} M), *i*-PrO^-Na^+ (0.1 M), and 5% THF in *i*-PrOH and was N_2O saturated. The spectra were recorded ~60 (△) and ~800 μs (○) after the pulse. The pure spectrum of $AQ^- \cdot$ (---) has been determined with 1×10^{-4} M AQ solution under similar conditions. The time profiles at 465, 520, and 680 nm are also shown.

Another possible acceptor for the demonstration of the electron-transfer reaction was thought to be 4,4′-dimethyldipyridinium dication (methylviologen or paraquat, PQ^{2+}). This compound has a reduction potential[28] only slightly lower than that of AQS[27] and its reduced form exhibits an intense absorption at ~600 nm,[29] where the porphyrin radical absorption is very weak (Figure 1). Experiments were carried out with H_2TCPP solutions containing varying concentrations of PQ^{2+} at pH 7.2. The PQ^{2+} competes for the alcohol radicals very efficiently ($k = 3.5 \times 10^9$ M^{-1} s^{-1}) and the initial spectrum recorded was a superposition of those of $H_3TCPP\cdot$ and of $PQ^+\cdot$. The absorption at all wavelengths decayed with approximately the same rate (~10^4 s^{-1}) regardless of the concentration of PQ^{2+} and no indication of $PQ^+\cdot$ buildup was obtained. It appears that the electron transfer to PQ^{2+} is relatively slow ($<10^8$ M^{-1} s^{-1}) while the decay is attributed to radical-radical reactions between $H_3TCPP\cdot$ and $PQ^+\cdot$.

A slow transfer was also observed with AQS at pH 6.9 while at pH 11 the anion radical $H_2TCPP^- \cdot$ reacted with AQS rapidly. PQ^{2+} cannot be studied at high pH because of its instability, so experiments were carried out at pH 9.6, where half of the porphyrin radicals are in the anionic form (eq 9). At this pH the absorption at 460 and 700 nm decayed by first-order kinetics attributed mainly to the electron-transfer reaction

$$H_2TCPP^- \cdot + PQ^{2+} \rightarrow H_2TCPP + PQ^+ \cdot \quad (15)$$

From the dependence on the PQ^{2+} concentration (Figure 6) $k = 6 \times 10^8$ M^{-1} s^{-1} was determined. This rate constant cannot be assigned exclusively to reaction 15 since $H_3TCPP\cdot$ is also present and it reacts with $PQ^+\cdot$ rather than with PQ^{2+} as discussed above. These complications interfered with our attempts to observe buildup of $PQ^+\cdot$ absorption concomitant with decay of $H_2TCPP^-\cdot$. In a few cases such a buildup was observed but the yield was incomplete. Therefore, it was not possible to verify whether the final spectrum was identical with that of $PQ^+\cdot$.

The rates of electron transfer from $H_3TCPP\cdot$ to benzoquinone (BQ) and duroquinone (DQ) were also measured as shown in Figure 6. Since the absorption maxima of $BQ^-\cdot$ and $DQ^-\cdot$ are at 430 and 445 nm, respectively, and are less intense than that of $H_3TCPP\cdot$ at the same wavelength, the kinetics were determined only from the decay of the 460- and 700-nm absorptions. The results are summarized in Table II. The rates of electron transfer in neutral solutions increase in the order PQ ~ AQS < DQ < BQ, corresponding to the changes in their reduction potentials.[27,28,30]

Porphyrins-Quinone in 2-Propanol. Electron-transfer experiments with H_2TPP, ZnTPP, and Chl *a* were carried out only with anthraquinone (AQ) in basic solutions. The BQ and DQ were found to be extremely unstable in basic *i*-PrOH solutions even at [*i*-PrO^-Na^+] = 10^{-5} M. In neutral solutions, the initial reduction step is too slow and the solubility of the porphyrins too low to allow experimental observation of the electron transfer to quinones.

The spectral changes and their time profiles with solutions of Na_2TPP + AQ are shown in Figure 8. The decay of $Na_2TPP^-\cdot$ (465 and 680 nm) is accompanied by buildup of $AQ^-\cdot$ (520 nm) with the same rate. The rate constant calculated from the concentration dependence is $(1.8 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. The final spectrum is red shifted by ~18 nm compared with that of $AQ^-\cdot$ produced in *i*-PrOH without H_2TPP. As in the case of H_2TCPP above, we attribute this shift to an intermediate complex formation (reaction 14). Such a complex is not produced in solutions containing excess AQ, i.e., $AQ^-\cdot$ was not found to react with H_2TPP, probably because the redox potentials are such that the reaction in this direction is extremely slow.

The rate constants for the electron transfer from $ZnTPP^-\cdot$ and $Chl^-\cdot$ to AQ were determined by following the decay at 700-780 nm. Buildup of absorption around 500-550 nm was

Table II. Rate Constants for Reactions of Porphyrin Radicals with Various Acceptors

donor	acceptor[a]	solvent	pH	k, M^{-1} s^{-1}
$H_3TCPP\cdot$	BQ	H_2O	7.0	$(1.3 \pm 0.3) \times 10^9$
$H_3TCPP\cdot$	DQ	H_2O	7.2	$(1.0 \pm 0.2) \times 10^9$
$H_3TCPP\cdot$	AQS	H_2O	6.9	$(1.1 \pm 0.3) \times 10^7$
$H_2TCPP^-\cdot$	AQS	H_2O	11.4	$(3.3 \pm 0.5) \times 10^8$
$H_3TCPP\cdot$	PQ^{2+}	H_2O	7	$<10^8$
$H_3TCPP\cdot$ + $H_2TCPP^-\cdot$	PQ^{2+}	H_2O	9.6	$(6 \pm 1) \times 10^8$
$Na_2TPP^-\cdot$	AQ	*i*-PrOH	0.1 M *i*-PrO^-Na^+	$(1.8 \pm 0.5) \times 10^9$
$ZnTPP^-\cdot$	AQ	*i*-PrOH	0.1 M *i*-PrO^-Na^+	$(2.6 \pm 0.5) \times 10^9$
Chl $a^-\cdot$	AQ	*i*-PrOH	0.1 M *i*-PrO^-Na^+	$(8 \pm 2) \times 10^8$

[a] BQ, benzoquinone; DQ, duroquinone; AQS, anthraquinone-2-sulfonate; PQ, paraquat (methylviologen); AQ, anthraquinone.

qualitatively observed but detailed spectra in this region were not recorded because of experimental limitations. We cannot verify, therefore, whether the product of the electron-transfer reaction has the same spectrum as that observed with Na_2TPP. The rate constants, however, are similar, near 10^9 M^{-1} s^{-1} (Table II).

Conclusion

The present study is an attempt to demonstrate electron transfer from porphyrin anion radicals to various acceptors (reaction 2). The systems employed here exhibited spectral changes which led to the suggestion of an intermediate complex formation ($P\cdots Q^- \cdot$). A previous study utilizing the photoexcitation route (reaction 1) has also invoked the formation of an intermediate complex in the chlorophyll-photosensitized one-electron oxidation of water by benzoquinone.[31] In addition, the reactions studied here were found to be affected by environmental parameters. In the case of free-base porphyrins, there is a strong effect of pH on the electron-transfer reactions (Table II) which is caused by acid-base equilibria. Anion radicals of the type $H_2P^- \cdot$ react with acceptors about an order of magnitude more rapidly than their protonated form $H_3P \cdot$. This protonation cannot occur in metalloporphyrins so that their anion radicals behave similarly to $H_2P^- \cdot$. However, anion radicals of conjugated systems can also protonate on a carbon atom in a process which depends on solvent and acidity.[32] In the few cases studied here, such protonation was not apparent. All of the effects discussed above emphasize the importance of the microenvironment in determining the course of electron-transfer reactions in vivo.

References and Notes

(1) The work described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1936 from the Notre Dame Radiation Laboratory.
(2) University of Notre Dame.
(3) Hebrew University. Participated in preliminary experiments as a summer student at the University of Notre Dame.
(4) Hebrew University. Visiting Professor at the University of Notre Dame.
(5) For a recent review on the energetics of electron transfer reactions of chlorophyll see G. R. Seely, *Photochem. Photobiol.*, **27**, 639 (1976).
(6) G. Tollin, *J. Chem. Phys.*, **80**, 2274 (1976), and references cited therein.
(7) D. Holten, M. W. Windsor, W. W. Parson, and M. Gouterman, *Photochem. Photobiol.*, **28**, 951 (1978), and references cited therein.
(8) D. Holten and M. W. Windsor, *Annu. Rev. Biophys. Bioeng.*, **7**, 189 (1978).
(9) D. Holten, M. Gouterman, W. W. Parson, M. W. Windsor, and M. G. Rockley,
(10) M. Gouterman and D. Holten, *Photochem. Photobiol.*, **25**, 85 (1977).
(11) In that respect, the charged acceptor methylviologen is an exception. It has been shown that charge separation proceeds via the singlet precursor.
(12) H. H. Strain and W. A. Svec in "The Chlorophylls", L. P. Vernon and G. R. Seely, Eds., Academic Press, New York, 1966.
(13) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 818 (1963).
(14) R. H. Felton, G. H. Sherman, and H. Linschitz, *Nature (London)*, **203**, 637 (1964).
(15) L. K. Patterson and J. Lilie, *Int. J. Radiat. Phys. Chem.*, **6**, 129 (1974).
(16) R. H. Schuler, P. Neta, H. Zemel, and R. W. Fessenden, *J. Am. Chem. Soc.*, **98**, 3825 (1976).
(17) P. Neta and H. Levanon, *J. Phys. Chem.*, **81**, 2288 (1977).
(18) See, e.g., Y. Harel and D. Meyerstein, *J. Am. Chem. Soc.*, **96**, 2720 (1974).
(19) P. Hambright in "Porphyrins and Metalloporphyrins", K. V. Smith, Ed., Elsevier, Amsterdam, 1975.
(20) R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francescoui, E. Gibbs, P. Fasella, G. C. Venturo, and L. de C. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972).
(21) In order to minimize possible changes in the monomer–dimer equilibrium, these experiments were carried out with solutions at high ionic strength. Under these conditions, the pH variations affect the monomer–dimer equilibrium only slightly.
(22) See, e.g., P. Neta, *Adv. Phys. Org. Chem.*, **12**, 223 (1976).
(23) Using the experimental setup described by J. Lilie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).
(24) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315 (1951).
(25) I. Fujita, M. S. Davis, and J. Fajer, *J. Am. Chem. Soc.*, **100**, 6280 (1978).
(26) H. Seki, S. Arai, T. Shida, and M. Imamura, *J. Am. Chem. Soc.*, **95**, 3404 (1973).
(27) D. Meisel and P. Neta, *J. Am. Chem. Soc.*, **97**, 5918 (1975).
(28) E. Steckhan and T. Kuwana, *Ber. Bunsenges. Phys. Chem.*, **78**, 253 (1974).
(29) J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, **314**, 372 (1973).
(30) Y. A. Ilan, G. Czapski, and D. Meisel, *Biochim. Biophys. Acta*, **430**, 209 (1976).
(31) J. R. Harbour and G. Tollin, *Photochem. Photobiol.*, **20**, 271 (1974).
(32) H. Levanon, P. Neta, and A. M. Trozzolo, *Chem. Phys. Lett.*, **54**, 181 (1978).

Total Synthesis of Optically Pure Nucleoside Q.[1] Determination of Absolute Configuration of Natural Nucleoside Q

Tadaaki Ohgi, Tadao Kondo, and Toshio Goto*

Contribution from the Department of Agricultural Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan. *Received December 1, 1978*

Abstract: Two diastereomers of 7-(3,4-*trans*-4,5-*cis*-4,5-dihydroxycyclopent-1-en-3-ylaminomethyl)-7-deazaguanosine having the β-D-ribosyl group were synthesized, one of which, having the 3*S*,4*R*,5*S* configuration in its cyclopentenyl side chain, was proved to be identical in all respects, including ORD and CD, with natural nucleoside Q, thus determining the absolute and anomeric configurations of the latter.

In 1968, nucleoside Q was discovered in the first position of the anticodon of *Escherichia coli* tRNA^{Tyr}.[2] Later Q was also found in the same position of *E. coli* tRNA^{His}, tRNA^{Asp}, and tRNA^{Asn}.[3] Recently, it has become clear that Q is widely distributed in tRNA's of plants and animals.[4]

In 1975, Kasai et al.[5] proposed structure **1** (without assignment of stereostructure of the cyclopentene side chain) for the nucleoside Q, which was one of the most unique and complex nucleosides thus far known; it is a deazaguanosine derivative having a dihydroxycyclopentenylamine side chain at the 7 position. Later, nucleoside Q* (**2**), which was isolated from rabbit liver, was determined to be a mixture of mannosyl and galactosyl derivatives of Q.[6] Hitherto three antibiotics belonging to the 7-deazaadenosine, i.e., tubercidin (**3**),[7] toy-

0002-7863/79/1501-3629$01.00/0