

ELECTRON TRANSFER IN PHOTOEXCITED PORPHYRIN QUINONE CYCLOPHANES

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SUMMARY: The striking difference in fractions of fast versus slow components of electron transfer of the porphyrin mono- and bis-quinone cyclophanes are attributed to an orbital symmetry effect between the porphyrin and the quinone.

Introduction: The efficiency of the primary reactions of the photosynthetic process has prompted many attempts to duplicate these electron transfer reactions¹. The determination of the structure of the bacterial reaction center² has fueled this effort by showing several of the characteristics responsible for the rapid and efficient primary electron transfers which lead to charge separation across the photosynthetic membrane. Outstanding among these characteristics are the separation, and orientation, of the reacting molecules well beyond their van der Waals radii. The occurrence of an optimal distance of a few Angstroms on the yield-lifetime product as a function of distance of electron transfer by tunneling had been pointed out before³. Many molecules have been synthesized in which a porphyrin and a quinone are held together by a single flexible chain¹. This tether usually allows considerable conformational and orientational freedom. The cyclophane molecules considered in this paper have far more restricted motions: essentially the quinone can only rotate around the bridging axes above the plane of the porphyrin (Fig. 1). Their electron transfer rates can be compared with those of a polymacrocyclic co-planar porphyrin-quinone where the four bridges prevent this motion from occurring⁴. As expected, the electron transfer from the photoexcited porphyrin to the quinone in I and II is very rapid (1 ns to 50 ps). The electron must tunnel from the porphyrin to the quinone. The reaction is only weakly temperature dependent except at the glass point of the solvents. This is explained as

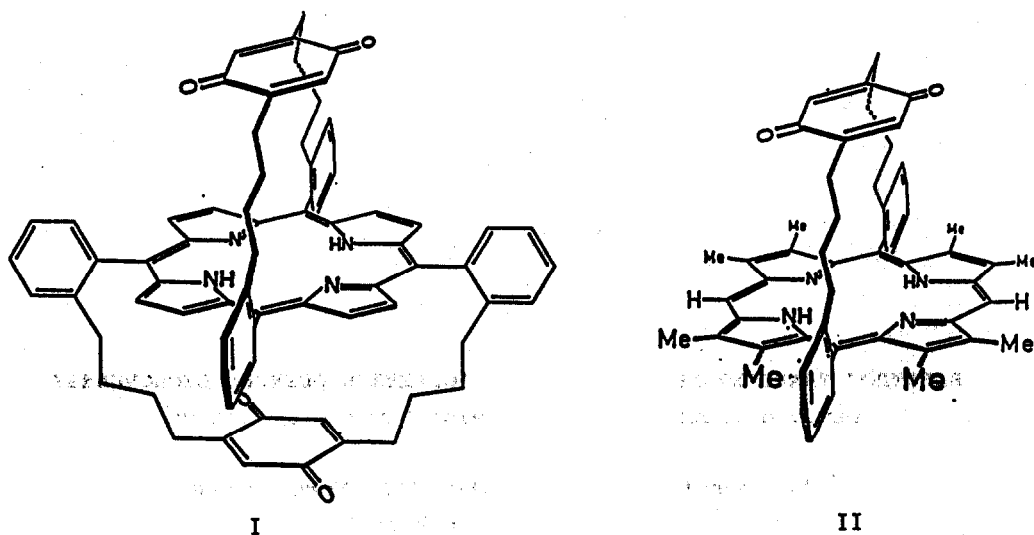


Figure 1. Structures of PQ₂ (I) and OMPQ (II).

slowing of the rotational motion of the quinone and thus as an orientation requirement for electron tunneling. The solvent dependent fraction of slow and fast electron transfer times of the monoquinone porphyrin cyclophane (II), in contrast to the single fast time constant of the bisquinone cyclophane (I), is explained by an orbital symmetry requirement for electron transfer.

Materials and Methods: The porphyrin quinones I and II (Fig. 1) were synthesized by methods reported elsewhere⁵. The structure of I, has been determined by x-ray crystallography⁶. The synthesis of the mixed quinone-dimethoxyphenyl analogue of I will be published elsewhere⁷.

Fluorescence lifetimes were determined by a short pulse (~300 ps) N₂ laser, a microchannel plate photomultiplier and a scan converter digitizer. The apparatus is described elsewhere^{8,4}. The rapidity of the measurements (20 sec per lifetime) allows large numbers of experiments to be run, including study over extensive temperature ranges. These were carried out in an Oxford dewar with homemade temperature control accurate to 1K. Hysteresis was determined by measuring both descending and ascending temperatures with a 10-min wait at each temperature for equilibration. Data analysis was by iterative deconvolution^{8,9}. Goodness-of-fit was by least-squares values and by inspection of residuals⁹. Solvents were of HPLC grade and solutions were flushed with N₂ before measurement.

Results: As expected the fluorescence lifetimes of the quinone porphyrins were

much shortened by electron transfer. However, we have no measure of the lifetime of the putative ion pair. Comparison of the lifetimes of the methoxy derivatives with those of the quinones provides the evidence for electron transfer. (Table I). The bis-dimethoxyphenyl porphyrin, $P(\phi\text{OMe})_2$ and the dimethoxyphenyl octamethyl porphyrin, $\text{OMP}\phi\text{OMe}$, have mono-exponential lifetimes in the range of 9-16 ns, the same as simple free-base porphyrins. The lifetimes are not solvent dependent to any great extent. In contrast, the

TABLE I

Fluorescence Lifetimes of Porphyrin-Quinone Cyclophanes

Solvent	$P(\phi\text{OMe})_2$	$\text{PQ}\phi\text{OMe}$	PQ_2		$\text{OMP}\phi\text{OMe}$	OMPQ
	τ_1	τ_1 (X_1)	τ_1	(X_1)	τ_1	τ_1 (X_1)
Heptane	-	1.4 (.81)	-	-	-	-
Toluene	13.3	0.64 (.83)	0.30 (.99)		9.8	0.5 (.93)
Methyl Tetrahydro- furan	9.5	0.31 (.66)	0.13 (.99)		-	-
Ethyl Acetate	9.1	0.42 (.47)	0.12 (.99)		-	-
Methylene Chloride	9.0	0.31 (.31)	0.26 (.84)		-	-
Propylene Carbonate	9.7	0.73 (.15)	0.27 (.86)		-	-
Ethanol:Methanol,4:1	9.1	0.36 (.14)	0.095(.95)		-	0.46 (.60)
Dimethyl Acetamide	13.0	0.40 (.10)	0.055(.99)		16.6	0.55 (.87)

The lifetimes are in ns and the value in parenthesis is the fractional amplitude of that component. The measurements were made near 25° and fit with two exponentials. The lifetimes of the longlived components were in the range of 2 - 7 ns for PQ_2 , 9 - 11 ns for $\text{PQ}\phi\text{OMe}$, and 3.5 - 4.5 ns for OMPQ . The lifetimes of $P(\phi\text{OMe})_2$ and $\text{OMP}\phi\text{OMe}$ were fit to > 99% single exponential by amplitude.

lifetime of the bis-quinone, PQ_2 (Fig.1,I) is 30 to 200 times shorter (Table I). With the exception of two solvents, methylene chloride and propylene carbonate, these lifetimes are > 95% single exponential by amplitude. The fast

lifetime of PQ_2 is the major and often the only component. It is slightly solvent dependent, decreasing over fivefold between toluene and dimethylacetamide (Table I). The lifetimes of the mixed quinone-dimethoxyphenyl porphyrin, PQ_2OMe , also vary over a fivefold range but with an appreciable and often a majority of a long lifetime component. This component lifetime is in the range 10 ± 1 ns, i.e. close to that of $P(\phi OMe)_2$. Since these lifetimes were all measured with the same purified sample of porphyrin in freshly prepared, purified solvents, the wide variation in the percentage of the long lifetime component (20-90%) cannot be caused by contamination of PQ_2OMe with $P(\phi OMe)_2$ or with $PQH_2\phi OMe$. The short lifetimes of $OMPQ$ (Fig.1,II) were similar to those of PQ_2OMe with a greater percentage of the longer lived component in the polar solvents. This effect may be caused by an undetected very short-lived component since there is a correlation with solvent polarity. The very low fluorescence quantum yield of the compound, $< 5 \times 10^{-5}$, suggests that this is the case.

The fluorescence yield of the Zn and Mg derivatives of $OMPQ$ could be measured but the short lifetimes of these metallo-porphyrin quinones were longer than those of the free-base derivatives. Thus again the measured fluorescence was mostly impurities. It is expected that the filled shell metallo-porphyrins are more readily photooxidized than the free base porphyrins¹⁰. In fact for the tetra-bridged-porphyrin-tetramethoxyquinone compound, reaction is observed only with the zinc chelate, not with the free-base derivative⁴.

Because of the possibility of varying quinone orientation and thus of rate constants, the data were also fit with a square distribution of time constants together with a single time constant. The least squares residue were about the same with this procedure. The reference compounds with essentially one lifetime were unchanged. The short single lifetimes of PQ_2 were in the narrow range 0.3 - 0.05 ns with $> 90\%$ contribution. The wide distributions of the longer lifetimes all overlap one another: 0.3 to > 10 ns. The single lifetimes of PQ_2OMe were in the 0.6 - 1.3 ns range but with amplitude of $< 10\%$. Thus the data will be interpreted with two exponential's, but it must be remembered that each of these is most likely a distribution¹¹.

The effect of temperature on the short lifetime of PQ_2 is small for fluid solvents. In ethanol-methanol, 4:1, the lifetime shows a very small activation energy of 0.5 kcal/mole over the range 300-150 K (Fig.2). Rapid transition through the glass-transition temperature or glass point (120 K) to liquid nitrogen temperature produces nearly the extrapolated lifetime. However, warming shows strong hysteresis in the glass. It is possible that since excitation was at 377 nm, photoexcited quinone could be reduced by sol-

vent, leading to formation of $PQ_2(OH)_2$ and a longer porphyrin lifetime in the glass. In 2-methyltetrahydrofuran, the activation energy is about 0.8 kcal/mole. The data could also be interpreted as a constant lifetime to 120K, followed by a rapid increase at $< 120K$. However, the 300K data point has a second convolution fit (of smaller least squares error but 2-fold larger than average time shift) at ~ 25 ps, below our error of 40 ps. This second fit falls on the extrapolated line and thus may be the correct number. The fraction of fast component in both solvents breaks away from 97% to much smaller values at the glass point. (Fig. 2, top). The slow lifetimes also increase from 3.7 to 10 ns as one passes through the glass point. Since 4:1 ethanol:methanol has a glass transition near $120 K^{12}$ and methyltetrahydrofuran at $100 K^{13}$ it seems that a parameter determining the fraction of fast component is viscosity. Note that the lifetimes (1 ns) are independent of solvent in the glass.

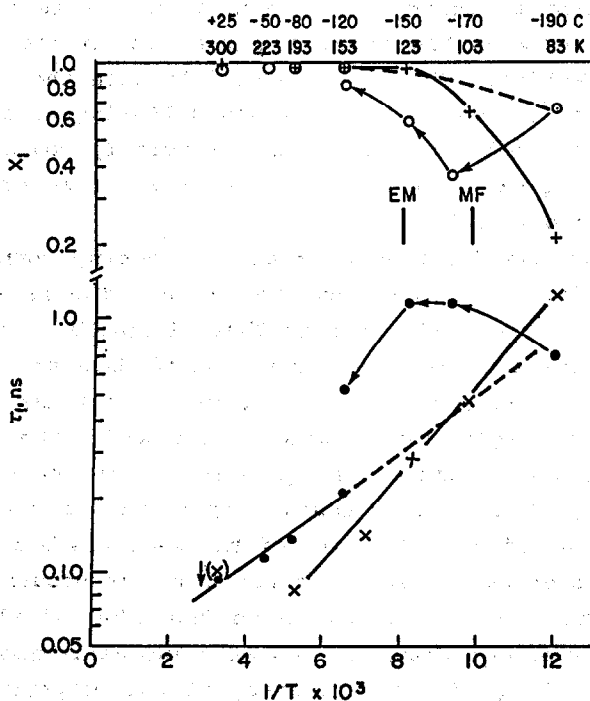


Figure 2. Lower section. The fast electron transfer time constant τ_1 of PQ_2 is plotted versus the reciprocal temperature in 4:1 ethanol-methanol, EM (\bullet), and 2-Methyltetrahydrofuran, MF (\times). The points following the arrows in the former are data on warming from 83 K, showing hysteresis. Upper section. The fraction of this fast component, X_1 , is plotted for the same solvents: EM (\circ) and MF ($+$). The glass transition temperatures points of the solvents EM¹² and MF¹³ are indicated by bars.

Conclusions: The weak dependence on solvent and the independence of temperature of the electron-transfer times inferred from the shortened fluorescence lifetimes of these porphyrin-quinones are in agreement with the view that the process is one of simple non-adiabatic electron tunneling. By this we mean that during the lifetime of the porphyrin excited state the electron tunnels to the polarizable quinone where it is trapped by relaxation to the final quinone anion. The reorganization energy for the P^* to P^+ transition is very small⁴ but that of Q to Q^- is larger; it has been estimated to be about 0.2 eV¹⁴. Since we claim the reorganization change follows tunneling^{3,4} the activation energy will be zero provided sufficient free energy of reaction is available to form P^+Q^- from the P^* state, as it is in the present case. Similarly, solvent effects will be minimal, but will be more significant as the trapping time itself becomes limiting. In contrast, these results are less compatible with adiabatic transition-state theory¹⁵. In that view a zero activation energy requires a balance between the total reorganization energy and the energy available for the reaction. This is incompatible with the observation of near zero activation energy of PQ_2 in two solvents differing widely in polarity and hydrogen bonding. The small solvent effects (Table I) would also be difficult to explain with that model. The same conclusion was reached in studies on the tetracyclic porphyrin-quinone^{4,16}.

The difference in the fraction of rapidly reacting components of PQ_2 and PQ_2OMe in various solvents is striking (Table 1). The rapid reaction of PQ_2 averages $94 \pm 6\%$ in all solvents whereas that of PQ_2OMe decreases from 83% to 10% with increasing solvent polarity. The limited data on $OMPQ$ are similar to those on PQ_2OMe . It is likely that these data reflect the effect of orbital symmetry on the electron-transfer reaction. The N-H protons of the porphyrin define a symmetry axis and reduce the D_{4h} symmetry of the dianion or metallo-porphyrin to (ideally) D_{2h} . This causes a splitting of previously degenerate energy levels as evidenced by a doubling of the weak visible bands and broadening of the allowed Soret band. The electron transfer occurs from the half occupied "LUMO" of the excited porphyrin to the LUMO of the quinone. This quinone orbital is symmetric along the C=O axis and antisymmetric perpendicular to this axis. The lifting of the degeneracy of the porphyrin LUMO by the N-H bonds makes the orbitals symmetric/antisymmetric about the N-H axis^{17,18}. Thus electron transfer from excited state of the porphyrin to the quinone will be allowed for one orientation of the quinone C=O axis parallel (or perpendicular) to the porphyrin N-H axis and forbidden for the other. Because of its electron density on the nitrogens, the " e_{gx} " orbital is expected to be lower in energy and thus the allowed transition will be with C=O and N-H axis aligned. The situation is quite analogous to that in cofacial chlorin-quinones discussed

previously⁴. Since the N-H...N exchange requires 10^{-4} s at 300 K¹⁹, the orientation in a particular configuration will be frozen during the 1 - 10 ns lifetime of the singlet state. It is also assumed that the quinone cannot rotate on the few ns time scale. This assumption is supported by the lack of activation energy in methyltetrahydrofuran until the glass point is reached.

Thus if the two NH-CO configurations were of equal energy, the prediction is that PQ ϕ OMe would have a fast lifetime of one-half amplitude and the other half at the slow lifetime of the non-quinone molecule, whereas PQ₂ would have a single fast lifetime. The inevitable wobble in the angle of the porphyrin and quinone axes because of the flexible alkane bridges would cause the forbidden configuration to become somewhat allowed and thus decrease the normal lifetime. To a good approximation this can be observed in Table 1. The variation in the fraction of fast reacting conformer in PQ ϕ OMe with solvent can be explained as a solvent effect on the total energy of the PQ ϕ OMe molecule in its two configurations. An estimate of this energy via the observed solvent effect (Table I) on dipoles in an Onsager cavity²⁰ produced a value of 1 kcal/mole. This is a reasonable value for the difference in energy of the N-H configuration with respect to the CO axis and supports the hypothesis.

The limited data on OMPQ (Table I) show some decrease of the rapid component with increasingly polar solvents but less than that of PQ ϕ OMe. The lack of symmetry of this molecule with one side of the porphyrin open to direct solvation may account for the weaker effect. The tunneling rate constants for OMPQ are almost the same as for PQ ϕ OMe as expected.

It is worth noting how misleading can be comparisons of rate constants at a single temperature. Figure 2 shows a dramatic example of quite different temperature behaviour of quenching constants which are almost identical at 300 K.

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