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Importance of reactant conformation upon the rates of rapid electron transfer reactions in homogeneous solution

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Abstract - Steady-state and time-resolved fluorescence spectroscopy, together with laser flash photolysis, has been employed to derive kinetic data for intramolecular electron transfer from the excited singlet state of a porphyrin to an appended viologen in homogeneous solution. For systems of fixed thermodynamic driving force, it is seen that the rate of electron transfer depends critically upon the conformation of the porphyrin-viologen molecule.

INTRODUCTION

Electron transfer reactions, which are of the utmost importance in innumerable chemical and biological processes, can occur on extremely diverse timescales, ranging from fs to hours. The rate of an electron transfer step k(r) is regulated by the electron tunneling matrix element V(r), the Franck-Condon weighted density of states FC, and solvent dynamics (ref. 1).

$$k(r) = (2\pi/h)[V(r)]^2(FC) \quad (1)$$

The electron tunneling matrix element depends strongly upon the intermolecular reactant separation distance r according to

$$[V(r)] = [V(\sigma)]^2 \exp[-\sigma(r-a)] \quad (2)$$

where σ is the sum of the molecular radii for the reactant pair and a is a constant having a value of ca. 0.11 nm^{-1}. The magnitude of V(r) is affected by the relative orientation of the reactants; orthogonal geometries favouring rapid electron transfer. From such considerations, it becomes clear that the rate of electron transfer should depend upon the thermodynamic driving force, the reactant separation distance and mutual orientation, and upon the nature of both reactants and medium (ref. 2).

This paper considers the case of photoinduced intramolecular electron transfer occurring within a series comprising an isomeric free-base porphyrin covalently linked to a viologen moiety via a short flexible chain. Within the series, the relative rates of electron transfer (k_{et}) will depend only upon differences in separation distance and mutual orientation of the porphyrin and viologen subunits. These geometric factors are controlled by the conformation of the molecule and by the rate at which specific conformers equilibrate. Since it has been shown that equilibration does not occur on the ns timescale (ref. 3), it should be possible to probe the conformational distribution of such molecules by measurement of electron transfer rates occurring within discrete families of conformers provided k_{et} is faster than conformational equilibration.

EXPERIMENTAL

The isomeric porphyrin-viologen complexes were prepared and purified as described elsewhere (ref. 4) and their structures are given in Fig. 1. All

solvents were spectroscopic grade and were analysed for fluorescing impurities before use. Fluorescence quantum yields (ϕ_f) were determined for optically dilute solutions and singlet excited state lifetimes (τ_s) were measured with a mode-locked, Nd-YAG synchronously-pumped, cavity-dumped rhodamine 6G dye laser (λ = 590 nm, response time = 280 ps). Transient absorption spectra were recorded with a frequency-doubled, mode-locked Nd-YAG flash photolysis apparatus (λ = 532 nm, pulse duration = 30 ps). Data analysis was made by computer least-squares minimising iterative procedures.

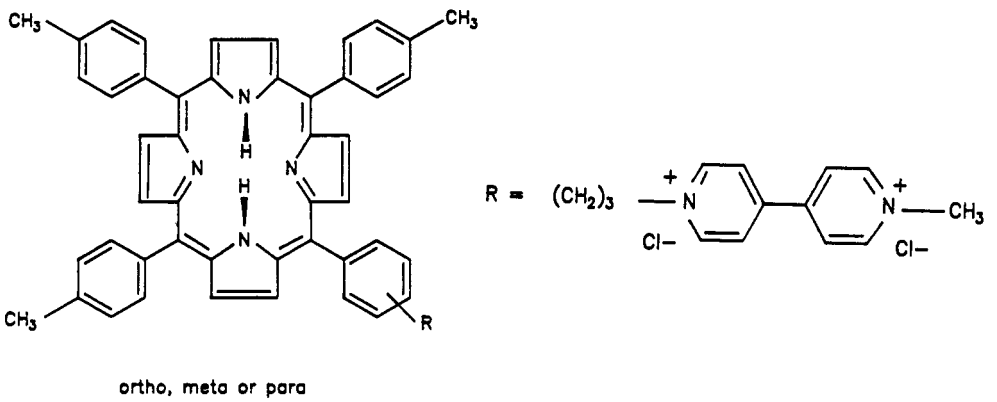

Fig. 1. Structures of the isomeric porphyrin-viologen complexes.

RESULTS AND DISCUSSION

Fluorescence emission from the isomeric P-MV complexes is quenched relative to that observed from meso-tetraphenylporphyrin (TPP) under identical conditions. In both N,N-dimethylformamide (DMF) and dimethylsulphoxide (DMSO) solutions, the measured fluorescence yields indicate that the appended viologen modulates deactivation of the porphyrin excited singlet state (Table 1). The quenching efficiency increases in the order para<meta<ortho and can account for more than 50% of the total decay process. In all cases, fluorescence quenching is attributed to photoinduced electron transfer from the porphyrin excited singlet state to the appended viologen unit.

$$^{*}P\text{---}MV \rightleftharpoons {}^{+}P\text{---}MV^{-} \qquad (3)$$

This charge separation process involves a free energy change of ca. -35 kJ mol^{-1} (ignoring corrections for Coulombic repulsive forces) and is followed by rapid charge recombination, for which the free energy change is ca. -145 kJ mol^{-1}. It should be noted that the corresponding triplet state reaction is thermodynamically unfavourable since the calculated free energy change is +8 kJ mol^{-1}.

TABLE 1. Fluorescence quantum yields and excited singlet state lifetimes determined for the isomeric P-MV complexes in DMF and DMSO solutions

isomer	DMF				DMSO			
	ϕ_f	τ_s^1	A_1	τ_s^2	ϕ_f	τ_s^1	A_1	τ_s^2
ortho	0.027	9.2	45	1.21	0.036	9.7	22	1.38
meta	0.050	10.2	53	3.25	0.055	10.9	46	3.40
para	0.074	9.8	51	4.10	0.082	10.2	49	4.72

From time-resolved studies, it was found that the fluorescence decay profiles could not be analysed satisfactorily in terms of a single exponential process or as a Gaussian distribution of first-order rate constants. Fits to the sum of two exponentials were much more satisfactory whereas increasing the number of exponential terms to three did not increase the quality of the fit. This situation is exemplified by Fig. 2 which gives typical analytical fits to fluorescence decay curves obtained for the para isomer in DMF solution. For all the isomers, fluorescence decay profiles were analysed as follows

$$I_f(t) = A_1\exp(-t/\tau_s^1) + A_2\exp(-t/\tau_s^2) \quad (4)$$

and the derived lifetimes and relative amplitudes are collected in Table 1.

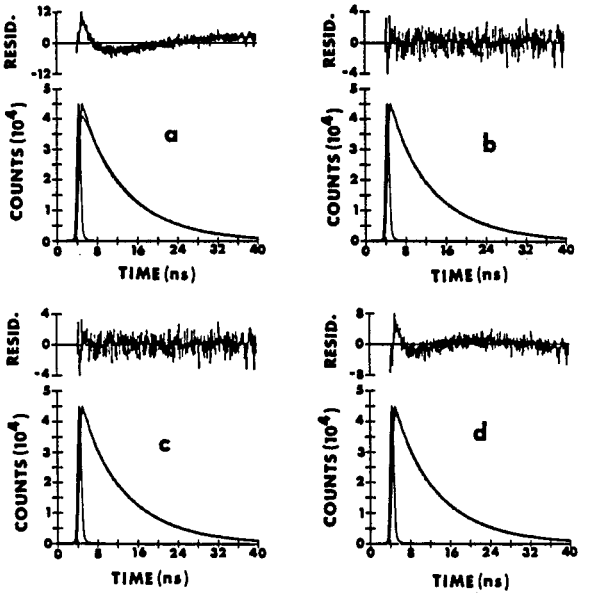

Fig. 2. Typical fluorescence decay profiles observed for the para isomer in DMF solution together with the instrument response function, an analytical fit and the weighted residuals. The fits are calculated for (a) one exponential (b) two competing exponentials (c) three competing exponentials and (d) a Gaussian distribution of first-order rate constants about a mean value with γ = 0.38.

Transient absorption studies confirmed the increased rate of decay of the porphyrin excited singlet state upon appending the viologen unit. It was found, however, that the rapid charge separation process was followed by even faster charge recombination such that long-lived redox products were not observed. The difference in rates of charge separation and recombination is in keeping with the derived thermodynamic driving forces and, for this system, charge recombination is not inhibited by the inverted Marcus effect (ref. 2) despite the large energy gap.

According to the above analyses, each isomer can be approximated as existing in two discrete families of conformations. One conformation must have the porphyrin and viologen subunits either held relatively far apart or in an orientation that is unfavourable for rapid electron transfer. The resulting singlet state lifetime (τ_s^1) remains quite similar to that measured for TPP under identical conditions (τ_s = 11.7 for DMF and 12.8 for DMSO). The other conformation is much more appropriate for fast electron transfer, either because of a shorter separation distance or because of a more orthogonal orientation. The excited singlet state lifetimes for this conformer (τ_s^2) are significantly reduced wrt TPP and they follow the order para>meta>ortho. As noted from Table 1, the two components contribute almost equally to the total fluorescence. Sincce the shorter-lived components differ significantly between the various isomers, it is clear that the electron transfer act proceeds via solvent modes and does not occur through the sigma bonds of the connecting sidechain.

^{1}H-Nmr studies carried-out at room temperature showed that these two families of conformers equilibrate on such timescales. Instead, estimates of their probable structures were obtained from computer simulations (ref. 4). It was found that extreme conformations, having porphyrin and viologen subunits either in very close proximity or fully extended, were unfavourable. The most preferred structures are drawn in Fig. 3. For the ortho isomer, the reactants are held relatively perpendicular at a centre-to-centre (ctc) separation distance of 0.86 nm (Fig. 3a). The meta isomer, on the other hand, favours a wide distribution of almost isoenergetic conformations having a

more orthogonal structure around an average ctc separation of 0.96 nm (Fig. 3b). The most preferred structure for the para isomer involves a somewhat extended conformation with a ctc separation of 1.52 nm (fig. 3c). For this isomer the porphyrin and viologen subunits can become almost orthogonal at a ctc separation of 1.11 nm (Fig. 3d) by rotating the C_1C_2 bond in the sidechain.

The longer-lived components observed in the fluorescence decay profiles are attributed to families of conformers in which the porphyrin and viologen subunits are inappropriately situated to facilitate rapid electron transfer. ost likely, this situation arises because the subunits are too far apart for electron transfer to compete with inherent nonradiative deactivation of the porphyrin excited singlet state. In contrast, the shorter-lived components are assigned to conformations in which the close proximity of the reactants permits rapid intramolecular electron transfer. The fact that the decay profiles are better represented as the sum of two exponentials rather than a Gaussian distribution about some mean value suggests that the families of conformers do not equilibrate on the ns timescale. From the shorter lifetimes, k_{et} values for the two solvents follow the order para<meta<ortho and the trend is in general agreement with the computer calculated ctc separation distances, but does not account for any variations in orientation, and with the observed nmr shifts. Thus, the site of attachment is the controlling factor in regulating the rate of intramolecular electron transfer. Overall, it seems that the sidechain maintains the porphyrin and viologen subunits within a family of conformations at discrete average ctc separation distances but allows sufficient degrees of freedom for there to be no preferred orientations.

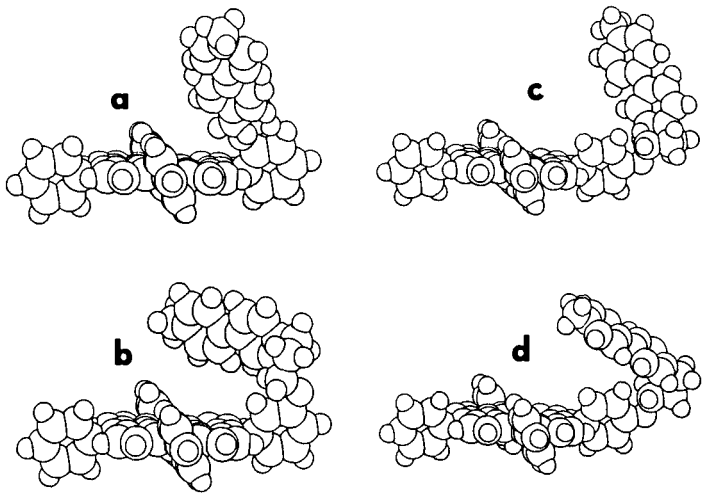

Fig. 3. Computer simulated structures for the most preferred conformations of (a) ortho (b) meta and (c) para isomers and (d) for the most closely-spaced conformation favoured by the para isomer.

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