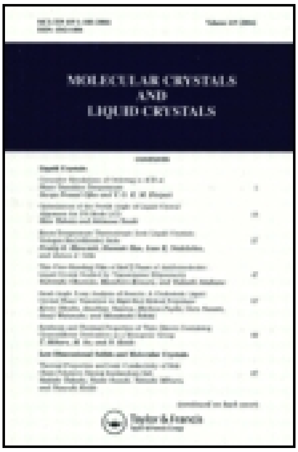

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CONFORMATIONAL CONTROL OF RATES OF INTRAMOLECULAR ELECTRON TRANSFER

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Abstract A series of porphyrins having a "viologen" appended via a short chain to a meso-aryl ring has been studied by time-resolved absorption and emission techniques. The viologen quenches porphyrin fluorescence but not the triplet state lifetime. Complex fluorescence decay profiles, which are observed for all compounds, are attributed to the presence of families of discrete ground-state conformers. Fluorescence quenching is interpreted in terms of intramolecular electron transfer, for which there is a modest thermodynamic driving force. However, charge separation (CS) is followed by rapid charge recombination (CR) such that long-lived redox products are not observed. Such behavior is consistent with recently introduced theoretical models dealing with conformational control of electron transfer rates. The rates of CS are almost insensitive to changes in temperature or solvent dynamics for alkanols.

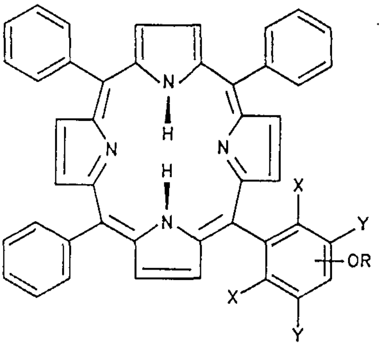
Keywords: Electron transfer, conformation, porphyrin, fluorescence, flash photolysis

INTRODUCTION

It has been established that the rate of intramolecular electron transfer proceeding through intervening σ-bonds can be affected by the configuration of the bridge.[1-3] Similarly, the magnitude of through-bond-interactions between spatially-remote terminal groups shows a marked dependence on the stereochemistry of the molecule.[4,5] Such findings have been used to suggest[6,7] the possibility that "gated" electron transfer may occur in certain cases where two conformations of the same donor-acceptor (D-A) molecule have discrete geometries. Indeed, a theoretical model has been developed recently by Brunschwig and Sutin[8] that describes the rates of intramolecular electron transfer processes within reactant and product conformations of varying stability. We have applied these ideas to understanding the photochemistry of covalently-linked porphyrin-viologen compounds where the connecting spacer group is flexible. These compounds, which cover only a limited range of D-A separation distances, retain very similar energetics for intramolecular electron transfer such that variations in rates cannot be explained in terms of thermodynamic changes or reorganization terms. Instead, these variations appear to relate to the ground-state structure of the compound.

EXPERIMENTAL

Structures for the porphyrin-viologen compounds are shown in Figure 1. The compounds were prepared as described before for related compounds.[9] Experiments were performed in N,N-dimethylformamide, unless stated otherwise.



X = Y = H; ortho, meta, para $H_2P\text{-}A\text{-}MV^{2+}$

X = H; Y = isopropyl

X = $C_3H_{10}CONH$; Y = H

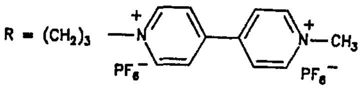


FIGURE 1 Structures of the porphyrin-viologens

General experimental methods were as described previously.[10,11] Singlet excited state lifetimes were measured by the time-correlated single-photon-counting technique using a mode-locked Nd-YAG laser synchronously pumping a cavity-dumped dye laser; for which the instrumental response function was 60 ± 10 ps. Flash photolysis absorption studies were made with a frequency-doubled, Q-switched Nd-YAG laser (pulsewidth 10-ns, 380 mJ). The laser intensity was attenuated and calibrated using tetraphenylporphyrin H_2TPP as standard[11] and deoxygenation was achieved by N_2-purging. Improved time resolution was achieved by employing a frequency-doubled, mode-locked Nd-YAG laser (pulsewidth 30-ps) as excitation source. Averaging procedures were used in which 300 laser shots were accumulated for each point. Computational studies were made with the CHEM-X modelling program (Chemical Design Ltd., Oxford, U.K.).

RESULTS AND DISCUSSION

Photophysical Properties

Fluorescence quantum yields (Φ_f), measured for the various compounds in polar solvents, were reduced with respect to H_2TPP showing that the appended viologen quenches the porphyrin excited singlet state. Quenching is attributed to intramolecular electron transfer from the excited singlet state of the porphyrin to the appended viologen.

$$(H_2P)\text{-A-}MV^{2+} \xrightarrow{h\nu} {}^*(H_2P)\text{-A-}MV^{2+} \rightarrow {}^+(H_2P)\text{-A-}MV^+ \quad (1)$$

Fluorescence decay profiles were complex and could not be analyzed satisfactorily in terms of a single-exponential process. Fitting the decay data to a Gaussian distribution of first-order rate constants about a mean value gave a fit only slightly better than that obtained with a single-exponential term. Increasing the number of exponential terms to two gave a significant improvement in the quality of the fit, as determined from the reduced chi-square parameters. Analyzing the decays as the sum of three-exponential terms did not significantly improve the quality of the fit. Consequently, the decay profiles were analyzed as the sum of two-exponential terms:

$$I_f(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (2)$$

This dual-exponentiality is attributed to the presence of two families of conformers that do not equilibrate on the ns-timescale. The derived lifetimes (τ_1 and τ_2) were used to calculate rate constants for intramolecular electron transfer (k_{et}^1 and k_{et}^2 respectively) by comparison to the lifetime of H_2TPP measured under identical conditions. The fractional amplitudes for the two components (A_1 and A_2) were used to derive the equilibrium constant ($K = A_2/A_1$) for the conformers.[12]

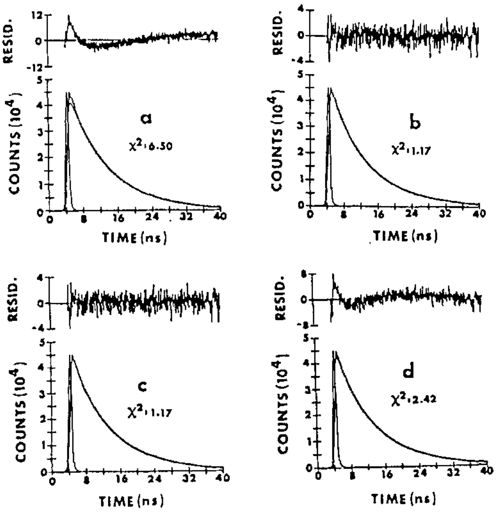


FIGURE 2 Fluorescence decay profiles for the meta isomer. The fits were computed for (a) one (b) two (c) three exponentials and (d) a Gaussian distribution.

The porphyrin excited singlet state could be detected immediately after excitation of the compounds with a 30-ps laser pulse (Figure 3a). The transient absorption profile recorded at different delay times ranging from 30 ps to 20 ns follows exactly that recorded for H_2TPP. Transient absorption spectra recorded 20 ns after excitation with a 30-ps laser pulse (Figure 3b) exhibit characteristics of the porphyrin excited triplet state, as shown by comparison with spectra recorded for H_2TPP. Thus, deactivation of the excited singlet state does not involve formation of a detectable yield of electron transfer products. Quantum yields for formation of the porphyrin triplet manifold were found to decrease with increasing levels of fluorescence quenching. This is taken to indicate that CS does not involve population of the triplet state but leads directly to formation of ground-state reactants via rapid CR. The triplet state decays via first-order kinetics, at low laser intensities, and the derived triplet lifetimes remain similar to that measured for H_2TPP.

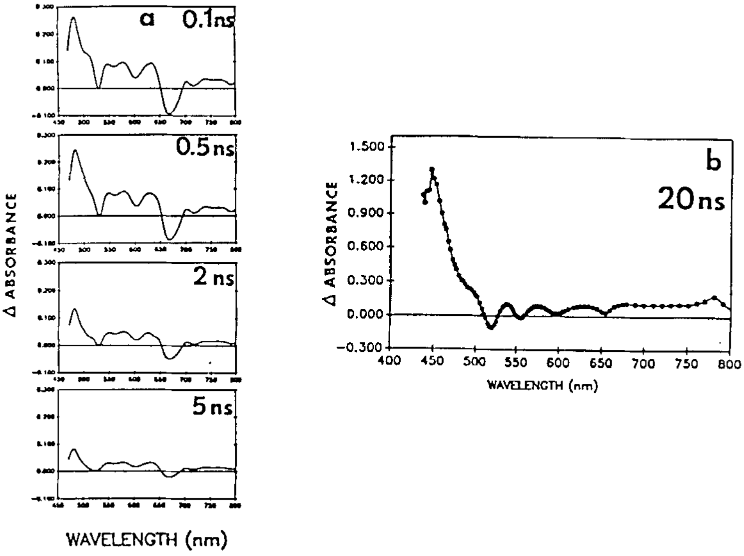


FIGURE 3 Transient differential absorption spectra recorded after excitation of the meta isomer with (a) a 30-ps and (b) a 10-ns laser pulse at 532 nm.

Reaction dynamics

Photoinduced intramolecular electron transfer from excited state porphyrin to appended viologen is thermodynamically feasible only for the excited singlet state. The calculated driving forces for the singlet state reactions are -0.36 ± 0.06; the driving force for triplet reaction is less favorable by 0.48 eV. Of the two fluorescence lifetimes, one (τ_1) is similar to, but invariably shorter than, that found for H_2TPP under identical conditions. The other (τ_2) is shorter and shows more dependence on the nature of the connecting chain. As such, τ_1 may be associated with a porphyrin species in which the appended viologen is positioned at a site unfavorable for rapid electron transfer whereas τ_2 is assigned to a porphyrin species having the viologen more favorably positioned.

It has been reported[8] that the stability of reactant or product conformations can markedly affect the rates of electron transfer. For intramolecular electron transfer between two redox sites occurring with a low driving force, a two-step mechanism, involving intermediate formation of an unstable conformer, may compete with the direct (concerted) mechanism, involving only stable reactant and product conformers. Such mechanisms could account for the dual-exponential fluorescence behavior observed with our compounds provided interconversion of the conformers is slower than fluorescence decay.

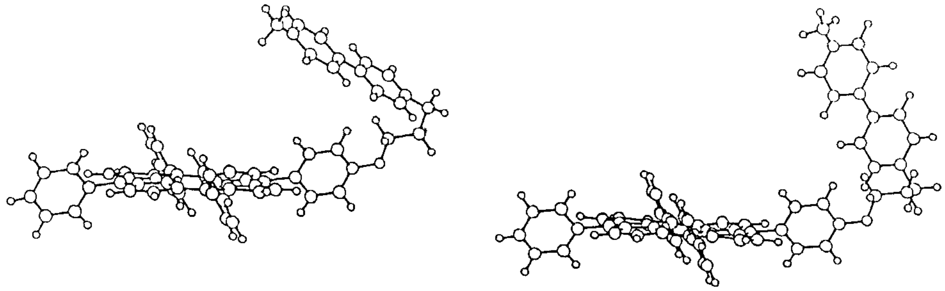


FIGURE 4 Computed structures for the two most stable conformers of the para isomer.

Computer calculations, based on the MM2 molecular mechanics program, were used to probe possible preferred conformations for the porphyrin-viologen compunds. For the H_2P-A-MV^{2+} isomers, the most stable conformations were found to have the porphyrin and viologen subunits quite well separated; the computed center-to-center separation distances (R^2) are given in Table 1. For each isomer there was a second group of conformations of slightly higher energy and shorter center-to-center separation distances (R^1) (Table 1). The computed structures obtained for the para isomer are displayed in Figure 4. The calculations gave estimated activation energies for interconversion between the two conformers of 40, 31, 46 kJ mol^{-1} for the ortho, meta, and para isomers respectively.

TABLE 1 Rate constants for intramolecular electron transfer, equilibrium constants, and computed separation distances for the various conformers.

Isomer	K	R^1 (nm)	$k_{et}^1/10^7$ (s^{-1})	R^2 (nm)	$k_{et}^2/10^8$ (s^{-1})
Ortho	1.2	0.58	2.3	0.86	7.5
Meta	0.9	0.62	1.3	0.96	2.3
Para	1.0	1.10	1.6	1.52	1.6
m-Propyl	>10	-	-	1.48	1.4
o-amide	>10	-	-	1.59	1.9

The various conformers appear to equilibrate on nmr timescales and, in order to clarify their structures, para isomers were synthesized in which steric blocking groups were inserted into the appropriate meso-phenyl ring. The compounds so-formed, meta-propyl and ortho-amide, gave fluorescence profiles that could be analyzed in terms of single exponential components that gave relatively high k_{et} values. For these compounds, the MM2 calculations were consistent with a single group of relatively extended structures (Table 1).

As such, the faster rates of intramolecular electron transfer (k_{et}^2) are assigned to the more extended conformations whereas the slower rates (k_{et}^1) are assigned to the more closed structures. The differences in rate constants between the various isomers is attributed to the different separation distances and geometries of the two subunits within a given conformer. According to Brunschwig and Sutin,[8] the driving force for CR could be sufficiently high for the rate of electron transfer to be independent of the geometry of the conformer, thus ensuring rapid reactions for all conformations. Intermediate formation of unstable conformers during CR could mask any reduction in rate of electron transfer expected for direct formation of stable conformations, hence explaining the apparent lack of an inverted Marcus effect.

Solvent and temperature effects

Solvent and temperature influence chemical reactions in various ways.[13] The solvent, in particular, can affect the relative energies of products and/or reactants and, by virtue of frictional forces, exert a more dynamic effect. The rate constant for intramolecular electron transfer can be expressed in the usual form

$$k_{et} = A\exp(-\Delta G^*/k_BT) \qquad (3)$$

where k_B is the Boltzmann constant and T is the temperature such that static solvent effects operate on the activation free energy ΔG^* and dynamic effects appear in the frequency factor A. It was found that the fluorescence decay profiles recorded for the various porphyrin-viologen compounds depended on solvent. On restricting the solvents to a series of linear alcohols, it was observed that both k_{et}^1 and k_{et}^2 decreased with increasing longitudinal dielectric relaxation time (τ_L) of the solvent, after correction[14] for solvent-induced changes in ΔG^*. This effect was not pronounced, however, and with low-friction alcohols the rate of electron transfer was almost independent of solvent dynamics. This behavior is shown in Figure 5 for the ortho isomer. Similarly, the rate of electron transfer in ethanol solution was not sensitive to changes in temperature over the range -70 to 40°C. Such findings imply that, at least in low friction media, electron transfer involves a nonadiabatic electron tunnelling process.

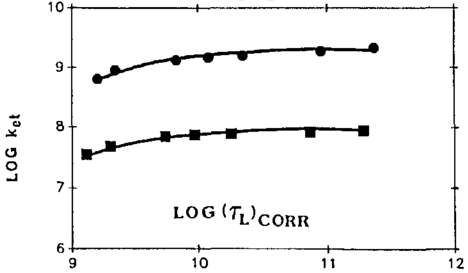


FIGURE 5 Logarithm plot of the derived rates of electron transfer versus reciprocal longitudinal relaxation time of the alkanol solvent for the ortho isomer.

REFERENCES

1. R. Hoffman, A. Imamura and W.J. Hehre, J. Am. Chem. Soc., 90, 1499 (1968).
2. A.M. Oliver, D.C. Craig, M.N. Paddon-Row, J. Kroon and J.W. Verhoeven, Chem. Phys. Lett., 150, 366 (1988).
3. G.L. Closs, M.D. Johnson, J.R. Miller and P. Piotrowiak, J. Am. Chem. Soc., 111, 3751 (1989).
4. K. Ohta, G.L. Closs, K. Morokuma and N.J. Green, J. Am. Chem. Soc., 108, 1319 (1986).
5. R. Bechtold, C. Kuehn, C. Lepre and S. Isied, Nature (London), 322, 286 (1986).
6. B.M. Hoffman and M.R. Ratner, J. Am. Chem. Soc., 109, 6237 (1987).
7. R.J. Guey, A.J. Hendry and A.M. Sargeson, J. Chem. Soc., Chem. Commun., 1646 (1989).
8. B.S. Brunschwig and N. Sutin, J. Am. Chem. Soc., 111, 7454 (1989).
9. A. Harriman, G. Porter and A. Wilowska, J. Chem. Soc., Faraday Trans. 2, 80, 193 (1984).
10. M. Gubelmann, A. Harriman, J.-M. Lehn and J.L. Sessler, J. Phys. Chem., 94, 308 (1990).
11. J.D. Batteas, A. Harriman, Y. Kanda, N. Mataga and A.K. Nowak, J. Am. Chem. Soc., 112, 126 (1990).
12. J.K. Delaney, D.C. Mauzerall and J.S. Lindsey, J. Am. Chem. Soc., 112, 957 (1990).
13. M. Maroncelli, J. MacInnis and G.R. Fleming, Science, 243, 1674 (1989).
14. G.E. McManis, R.M. Nielson, A. Gochev and M.J. Weaver, J. Am. Chem. Soc., 111, 5533 (1989).