

Intramolecular Photochemical Electron Transfer to Acceptors in a β -Cyclodextrin linked to a Porphyrin

Monica C. Gonzalez, Alan R. McIntosh, James R. Bolton,* and Alan C. Weedon*

Photochemistry Unit, The University of Western Ontario, London, Ontario, Canada N6A 5B7

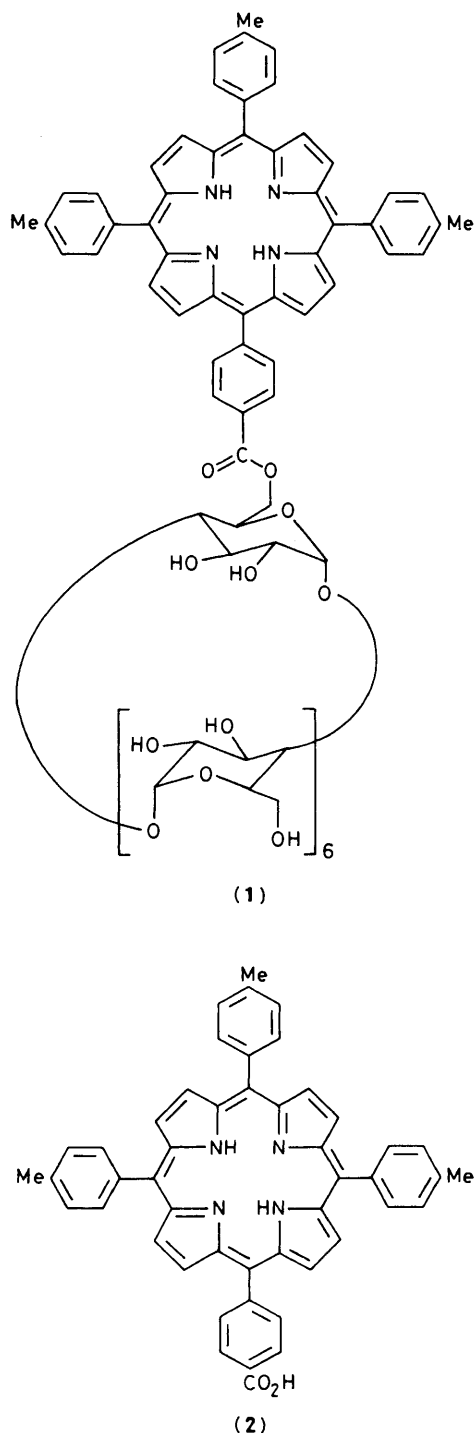
Evidence for intramolecular light induced electron transfer to acceptors (quinones and nitrobenzenes) complexed in a β -cyclodextrin linked to a porphyrin is presented, and the dependence of electron transfer efficiency upon the reduction potential of the acceptor is examined.

In an attempt to mimic the light induced electron transfer process in the reaction centre protein of photosynthesis, we have synthesized¹ and studied² the electron transfer properties of a series of linked donor-acceptor molecules in which a tetra-arylporphyrin is the electron donor and a *p*-benzoquinone is the electron acceptor. Our work represents one of several complementary investigations of linked donor-acceptor compounds³ aimed at understanding the factors controlling the efficiency of the light induced intramolecular electron transfer reaction.

One of the more important factors which might govern the efficiency of electron transfer is the reduction potential of the acceptor relative to the oxidation potential of the donor. A way in which to examine this parameter would be to synthesize a series of linked donor-acceptor compounds containing acceptors of varying reduction potential. In a strategy designed to avert the lengthy synthetic programme necessary

in such a study we have prepared[†] the linked porphyrin-cyclodextrin compound (**1**). This molecule takes advantage of the ability of cyclodextrins to complex hydrophobic species into their central cavity⁵ and allows the examination of the light induced electron transfer reaction between the porphyrin chromophore in (**1**) and acceptors of varying reduction potential held in the cyclodextrin cavity. We report here the results of such an examination which used e.s.r. spectroscopy to monitor the electron transfer reaction.

[†] Compound (**1**) was prepared in 50% yield from β -cyclodextrin and the acid chloride of 5-(*p*-carboxyphenyl)-10,15,20-(tri-*p*-methylphenyl)porphyrin (**2**) in pyridine. Compound (**1**) had satisfactory spectral data and gave a correct combustion analysis; that the cyclodextrin was linked through a primary hydroxy group was confirmed by the ¹³C n.m.r. spectrum (ref. 4).



Broad-band irradiation ($\lambda > 500$ nm) of a frozen solution of (1) and benzoquinone generated a single line e.s.r. signal ($g = 2.004$).[‡] This signal was very similar to the spectrum obtained by visible light irradiation of a frozen solution of 5-(*p*-carboxyphenyl)-10,15,20-(tri-*p*-methylphenyl)porphyrin (2) in the presence of a high concentration of benzoquinone.[‡]

[‡] Compound (1) (2.0×10^{-4} M) and the acceptor (5.0×10^{-4} M) were dissolved in a 50:50 mixture of glycerol and dimethyl sulphoxide and frozen to give a glassy solid at 200 K. A solution containing a mixture of (2) (2.0×10^{-4} M), β -cyclodextrin (2.0×10^{-4} M), and the acceptor (5.0×10^{-3} M) was used as a control.

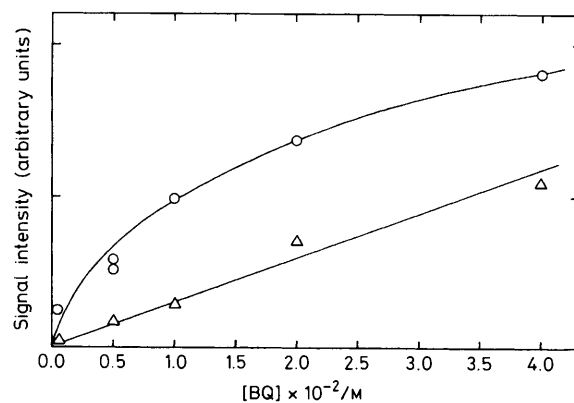


Figure 1. Dependence of signal intensity (in arbitrary units) on the concentration of benzoquinone for the linked porphyrin-cyclodextrin (1) (O) and the unlinked porphyrin (2) (Δ) as obtained from the light induced ($\lambda > 500$ nm) e.s.r. spectra of 2.0×10^{-4} M frozen solutions of porphyrin in glycerine-dimethyl sulphoxide at 200 K.

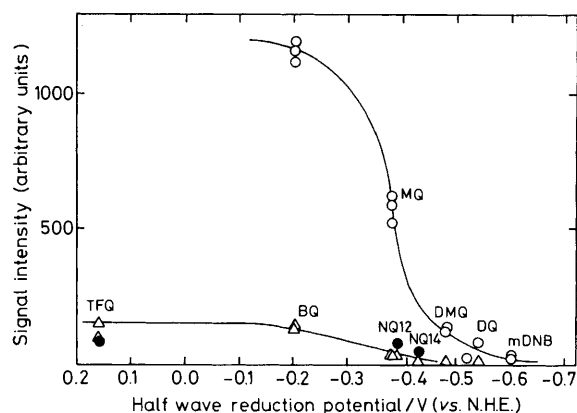


Figure 2. Dependence of light induced ($\lambda > 500$ nm) e.s.r. signal intensity (in arbitrary units) upon reduction potential for 2.0×10^{-4} M frozen (200 K) solutions of porphyrins (1) and (2) containing a 25 fold excess of acceptor. O: Solutions of (1) and acceptors small enough to fit readily into the cyclodextrin cavity; ●: solutions of (1) and larger acceptors; Δ : solutions of (2) and acceptors. Acceptors: TFG, tetrafluoro-*p*-benzoquinone; BQ, *p*-benzoquinone; MQ, methyl-*p*-benzoquinone; DMQ, 2,5-dimethyl-*p*-benzoquinone; NQ12, 1,2-naphthoquinone; NQ14, 1,4-naphthoquinone; DQ, duroquinone; mDNB, *m*-dinitrobenzene.

which has been interpreted as arising from an equal concentration of the porphyrin cation radical and the quinone radical anion.²

The dependence of the e.s.r. signal intensity upon the benzoquinone concentration for the solution of (1) and for the control[‡] is shown in Figure 1. The solutions of (1) exhibited consistently stronger e.s.r. signals compared with the controls; we interpret this as being due to the formation of an inclusion pocket in which the quinone is held in the hydrophobic pocket of the cyclodextrin, in close proximity to the porphyrin.

In the case of the control, the signal intensity increased linearly with the concentration of quinone, corresponding to an increasing probability of a quinone molecule being close enough to the porphyrin in the frozen matrix for electron transfer to occur. In the case of (1), however, the signal intensity initially increased rapidly and then more slowly, and at the same rate as the control, as the quinone concentration was increased. The initial rapid increase in electron transfer efficiency can be attributed to complexation of benzoquinone

by molecules of (1) which adopt a conformation on freezing in which intramolecular electron transfer can occur, whilst the lower rate of increase may correspond to intermolecular quenching of the excited state of complexes of (1) with benzoquinone in which the molecule exists in unfavourable conformations such that intramolecular transfer cannot occur.

A series of experiments were carried out using acceptors possessing reduction potentials [relative to the normal hydrogen electrode (N.H.E.)] varying from 0.2§ to -0.7 V[§] and the results are plotted in Figure 2. In all cases, the solutions containing (1) and an acceptor exhibited e.s.r. signals which were 3 to 4 times larger than those obtained with the controls. As in the case of benzoquinone discussed above, this increased signal intensity can be interpreted as arising from inclusion complexes in which the acceptor is in the hydrophobic pocket of the cyclodextrin and thus able to receive an electron from the photoexcited porphyrin at a higher efficiency than if randomly placed in the frozen glass matrix. In support of this hypothesis acceptors such as naphthoquinone and fluoroquinone, which are larger than the others examined and may not fit into the cyclodextrin cavity as efficiently, do not give rise to an e.s.r. signal significantly larger than that of the control, even though they possess reduction potentials sufficiently positive for electron transfer to occur.

The results shown in Figure 2 suggest that the lowest acceptor reduction potential for optimum efficiency of intramolecular light induced electron transfer from the porphyrin in (1) is *ca.* -0.3 V. Since the reduction potential of the

porphyrin radical cation is *ca.* $+1.2$ V,⁶ this implies that the maximum energy that can be stored by charge separation from the 1.90 eV (650 nm) porphyrin excited state is *ca.* 1.5 eV. Electron transfer may also occur for acceptors with reduction potentials more negative than -0.2 V, but possibly the activation barrier for back electron transfer may then be too small to allow observation of a radical ion pair.

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§ For more positive reduction potentials stable ground state complexes between the porphyrin and the acceptors were formed as evidenced by the observation of strong e.s.r. signals in the dark.