

Solvent Dependence of Photochemical Electron-transfer Rates in a Covalently Linked Porphyrin–Quinone Molecule

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The solvent dependence of intramolecular photochemical electron-transfer rate constants in a covalently linked porphyrin–amide–quinone molecule (PAQ) has been found in nine solvents to correlate reasonably well with the semiclassical formulation of Marcus theory. In making this correlation it is necessary to take into account the solvent dependence of both ΔG° , the Gibbs energy of the electron-transfer reaction from the excited state of the porphyrin to the quinone, and that of λ , the reorganisation energy. The former was estimated from the redox potentials of PAQ measured in each solvent, and the latter was estimated using Marcus' dielectric continuum model.

It is well known that the primary energy-storage step of photosynthesis is a photochemical electron transfer within a reaction-centre protein from the singlet excited state of a chlorophyll donor to an acceptor. Many simple models of the photosynthetic reaction centre have been synthesised by covalent linkage of an electron donor D to an acceptor A.¹ In most of these systems D is a porphyrin and A a quinone. Covalent attachment confers special features not readily attainable in intermolecular D+A systems. The effective concentration of the quencher is sufficiently high for reaction from short-lived singlet states to be possible. Moreover, D and A may be held in a more or less rigid molecular framework at a defined distance.

The porphyrin–amide–quinone molecule PAQ shown in fig. 1 was synthesised² as a model in which the porphyrin and quinone are close enough (centre-to-centre distance 1.5 ± 0.1 nm) to interact *via* electron transfer from the excited state(s), yet far enough apart that the electronic absorption spectrum shows no perturbation arising from interaction with the other chromophore. The space-filling structure shown in fig. 1 is only one of many in which the van der Waals interactions and bond strain are minimised. However, it is clear from molecular modelling that the quinone cannot fold back to interact with the porphyrin *via* π overlap. Thus although there is some flexibility in the amide linkage, it is rigid enough to maintain a fairly narrow range of centre-to-centre distances between the porphyrin and the quinone. This conclusion is consistent with the observation of single fluorescence lifetimes and no perturbations in the electronic spectra.

In a previous study, the kinetics of intramolecular photochemical electron transfer have been determined in more than twenty solvents of widely varying static and optical dielectric constant ϵ_s and ϵ_{op} .³ The rate constants vary by over two orders of magnitude from the worst to the best solvent. In this paper, further electrochemical data are

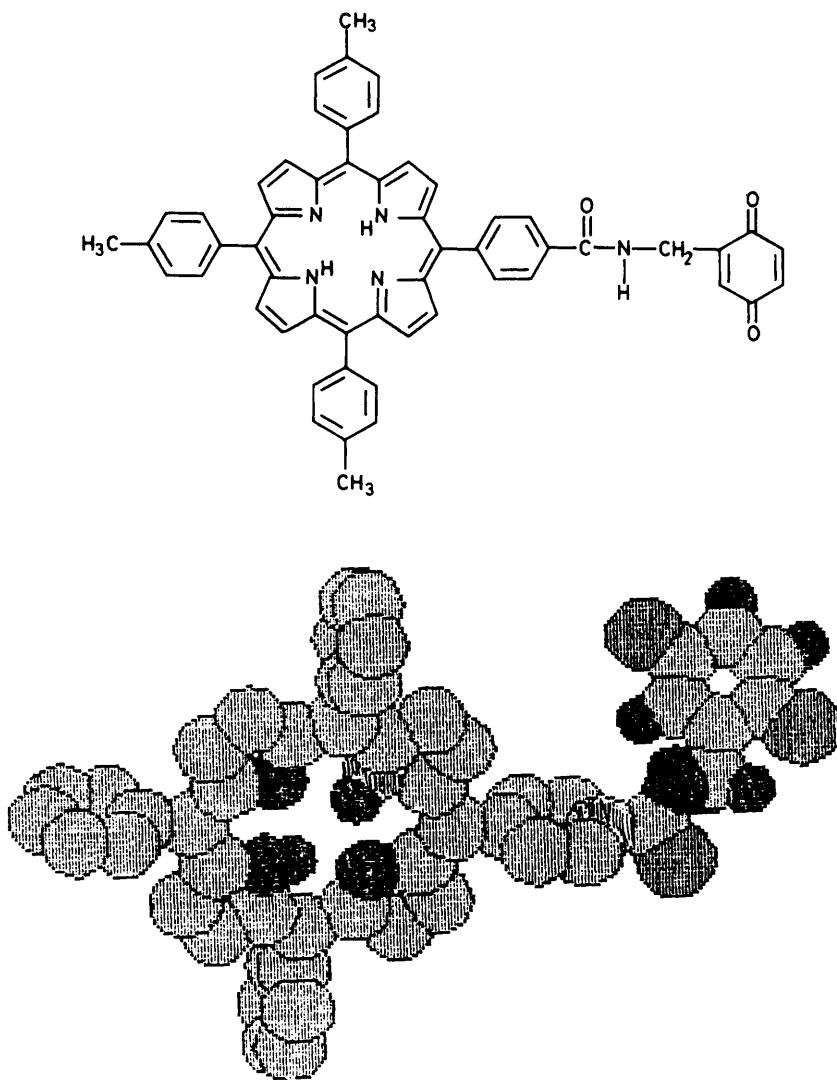


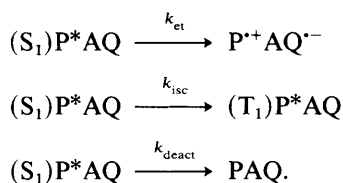
Fig. 1. Structures of PAQ.

reported, and the combined photochemical and electrochemical data are tested for conformity with Marcus theory and with various semiempirical theories of solvent polarity.

The solvent dependence of the electron-transfer kinetics was previously interpreted both in terms of Onsager's reaction-field theory^{4,5} and Marcus theory.⁵ In our earlier analysis, we found a better agreement with the former; however, we assumed ΔG° , the free energy of the forward electron transfer, to be solvent-independent in our Marcus treatment. When the solvent dependence of ΔG° is incorporated into the Marcus treatment, the agreement with experiment is dramatically improved, to the point where we now feel that this analysis is to be preferred to that using Onsager's theory.

Fluorescence quenching³ and other studies of PAQ and related molecules provide strong evidence for the following decay channels of $(S_1)P^*AQ$ following its production

by visible-light irradiation of the porphyrin:



The lifetime of the charge-separated state $P^{+}AQ^{-}$, which is also reached *via* intramolecular electron transfer from the triplet,⁴ is <1 ns and it undergoes rapid back electron transfer to the ground state.⁴ The charge-separated state, although transient, is assumed sufficiently long-lived to acquire its equilibrium conformation and solvation in each solvent.

The rate constant k_{et} is calculated from the fluorescence lifetimes τ_1 and τ_2 of $(S_1)P^*AQ$ and the corresponding hydroquinone-containing compound $(S_1)P^*AQH_2$. Electron transfer is energetically unfavourable in $(S_1)P^*AQH_2$ so, provided that k_{isc} and k_{deact} are the same for $(S_1)P^*AQ$ and $(S_1)P^*AQH_2$ in a given solvent,

$$k_{et} = 1/\tau_1 - 1/\tau_2. \quad (1)$$

The standard Gibbs energy ΔG_{\pm}° of the charge-separated state with respect to the ground state may be estimated from the difference between the first porphyrin ring oxidation potential O_1 and the first quinone reduction potential Q_1

$$\Delta G_{\pm}^{\circ} = e(O_1 - Q_1) - w_{pr} \quad (2)$$

where w_{pr} is a work term expressing the stabilisation by charge interaction of $P^{+}AQ^{-}$ with respect to the electrochemically produced species $P^{+}AQ$ and PAQ^{-} . The Gibbs energy change of the forward electron transfer reaction is given by

$$\Delta G^{o'} = U_{00} - \Delta G_{\pm}^{\circ} \quad (3)$$

where the prime indicates inclusion of the term w_{pr} . U_{00} is the singlet excitation energy of the porphyrin, provided that ΔS° , $\Delta V^{\circ} = 0$ for the porphyrin excitation $P \rightarrow (S_1)P^*$.

Experimental

The synthesis of PAQ and the methodology of the fluorescence lifetime measurements have been described elsewhere,^{2,3} as have most of the electrochemical and materials purification procedures.^{6,7} The supporting electrolytes tetrabutylammonium hexafluorophosphate (TBAPF₆), tetrabutylammonium perchlorate (TBAClO₄), tetrabutylammonium tetrafluoroborate (TBABF₄), tetraethylammonium perchlorate (TEAClO₄) and tetramethylammonium perchlorate (TMAClO₄) were obtained from Southwestern Analytical. The solvent acronyms used in table 1 and elsewhere are 1,2-DME for 1,2-dimethoxyethane and 2-MTHF for 2-methyltetrahydrofuran. The redox potentials of 10^{-5} – 10^{-4} mol dm⁻³ PAQ in various solvent/supporting electrolyte combinations were determined by differential pulse voltammetry without *IR* compensation in the presence of *ca.* 10^{-4} mol dm⁻³ ferrocene (Fc) to act as an internal reference at a Pt quasi-reference electrode. A typical DPV is shown in fig. 2. The appearance of the DPV was itself a highly sensitive check on the purity of all cell constituents.

Results and Discussion

The redox potentials R_1 and R_2 of the first and second reductions of the porphyrin ring of PAQ, Q_1 and Q_2 of the first and second reductions of the quinone, and O_1 and O_2

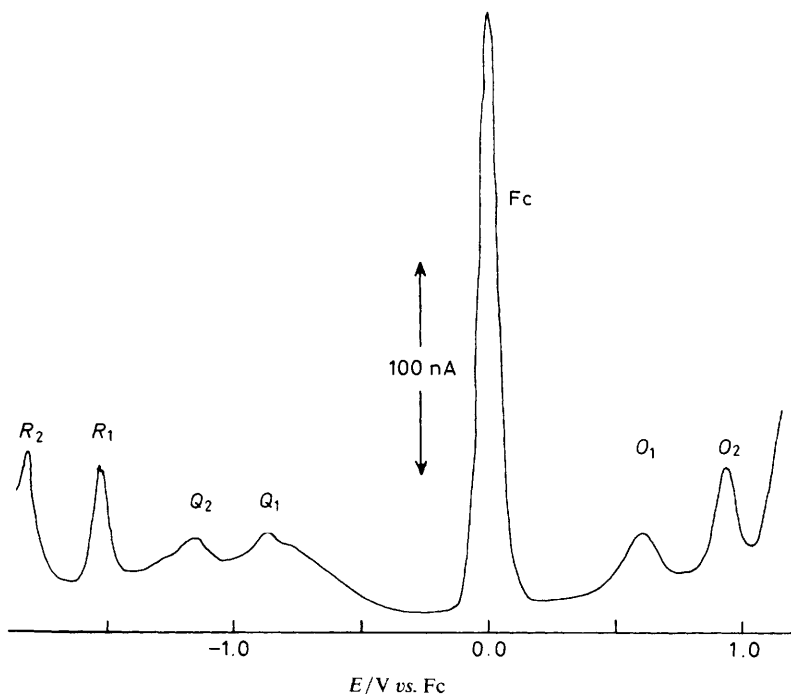


Fig. 2. Differential pulse voltammogram at a Pt electrode of PAQ in CH_2Cl_2 - 0.1 mol dm^{-3} tetraethylammonium perchlorate. Scan rate 5 mV s^{-1} ; pulse height 20 mV . The redox potentials R_1 and R_2 , and Q_1 and Q_2 , are the first and second reductions of the porphyrin ring and the quinone moiety, respectively; O_1 and O_2 are the first and second oxidations of the porphyrin ring. All potentials are referred to the ferricenium/ferrocene (Fc) couple used as an internal reference.

Table 1. Redox potentials in V^a vs. Fc of PAQ in various solvents with 0.1 mol dm^{-3} TBAPF₆ as the supporting electrolyte except where otherwise indicated

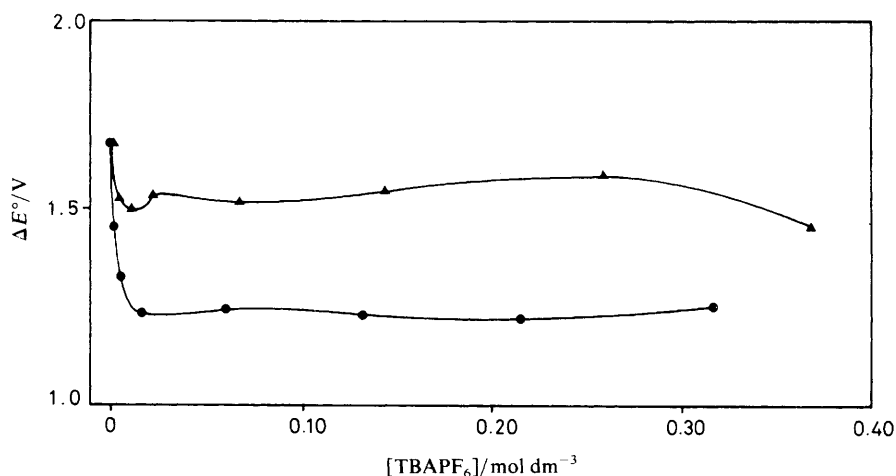
| solvent | R_2 | R_1 | Q_2 | Q_1 | O_1 | O_2 | ΔE° |
|--|--------|--------|-------|--------|-------|-------|------------------|
| 1,2-DME | ? | -1.590 | ? | -0.984 | 0.600 | ? | 1.58 |
| anisole-TBAClO ₄ ^b | -1.872 | -1.386 | ? | -1.056 | 0.516 | ? | 1.57 |
| CH ₃ COOC ₂ H ₅ | ? | -1.739 | ? | -1.175 | 0.364 | ? | 1.54 |
| CH ₃ COCH ₃ | ? | ? | ? | -0.908 | 0.600 | ? | 1.51 |
| C ₆ H ₅ CN | -1.53 | -1.290 | ? | -0.852 | 0.596 | ? | 1.45 |
| 2-MTHF-TBABF ₄ ^b | -1.536 | -1.304 | ? | -0.948 | 0.468 | 0.636 | 1.42 |
| CH ₃ CN | ? | ? | ? | -0.985 | 0.425 | ? | 1.41 |
| CH ₂ Cl ₂ | ? | -1.526 | ? | -0.906 | 0.496 | ? | 1.40 |
| CHCl ₃ | ? | ? | ? | -1.014 | 0.326 | ? | 1.34 |

^a Error in the relative values of any pair of potentials = $\pm 0.040 \text{ V}$; the values vs. Fc are less certain than this because the potential of the quasi-reference electrode was time-dependent. ^b TBAPF₆ is insoluble in these solvents.

Table 2. Redox potentials^a in V vs. Fc of PAQ in dichloromethane with various supporting electrolytes (0.1 mol dm⁻³ in concentration except where otherwise specified)

| electrolyte | R ₂ | R ₁ | Q ₂ | Q ₁ | O ₁ | O ₂ | ΔE° |
|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------------|
| TMAClO ₄ | -2.106 | -1.806 | -1.086 | -0.894 | 0.528 | ? | 1.42 ^b |
| TEAClO ₄ | -1.804 | -1.530 | -1.158 | -0.882 | 0.606 | 0.930 | 1.49 |
| TBAPF ₆ | ? | -1.526 | ? | -0.906 | 0.496 | ? | 1.40 |
| TBAClO ₄ | -1.668 | -1.182 | ? | -0.858 | 0.486 | 0.918 | 1.34 |
| TBABF ₄ | -1.758 | -1.462 | ? | -0.722 | 0.522 | ? | 1.24 |

^a See footnote a of table 1 for errors. ^b Saturated solution (<0.1 mol dm⁻³) TMAClO₄ in CH₂Cl₂.

**Fig. 3.** Dependence of ΔE° on the concentration of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆) in benzonitrile (▲) and in CH₂Cl₂ (●).

of the first and second oxidations of the porphyrin ring are given in table 1. The difference $\Delta E^\circ = O_1 - Q_1$ is an estimate of ΔG°_{\pm} , the standard Gibbs energy difference between the charge-separated state $P^{+}AQ^{-}$ and the ground state PAQ.

Most of the solvents we used have low to moderate static dielectric constants, so ion pairing with the counter-ion of the supporting electrolyte is quite probable. Ion association can shift redox potentials by several tenths of a volt, which poses a problem in combining the electrochemical data with electron-transfer rate constants measured in the absence of supporting electrolyte. We used supporting electrolytes with bulky ions in the hope of minimising such effects, but table 2 shows that they are still appreciable in CH₂Cl₂. The BF₄⁻ and ClO₄⁻ ions are smaller than PF₆⁻ and are likely to be more heavily ion-paired (with P⁺Q). Thus the results obtained with TBAPF₆ as the supporting electrolyte are probably the more reliable.

In solvents of lower dielectric constant, the nature of the supporting electrolyte will be still more significant, and further work is required. An uncertainty of ±0.1 eV in either ΔG° or λ leads to an error of ±1 ln unit at the low end of fig. 5 (see later), and ±0.3 at the high end.

Fig. 3 shows ΔE° as a function of supporting electrolyte concentration in dichloromethane and benzonitrile. There is little variation over the concentration range 0.02–0.30 mol dm⁻³, possible because incomplete dissociation provides a reasonably constant ionic strength medium. We ascribe the abrupt rise in ΔE° at very low supporting

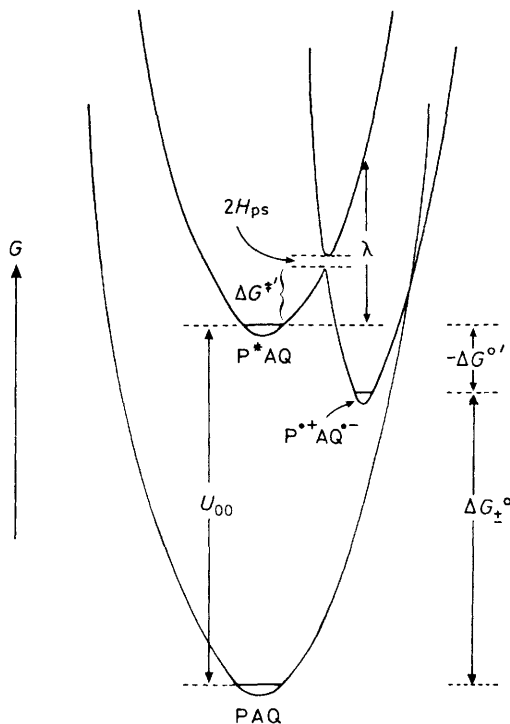


Fig. 4. Inferred Gibbs energy surfaces for the reactions of PAQ. U_{00} is the difference between the zero-point energies of the first excited singlet state P^*AQ and the ground state PAQ; λ is the reorganisation energy; ΔG^{*+} is the Gibbs energy of activation for forward electron transfer; $\Delta G^{o'}$ is the exergonicity of the reaction from P^*AQ to $P^{*+}AQ^{*-}$; ΔG_{\pm}° is the Gibbs-energy difference between $P^{*+}AQ^{*-}$ and PAQ and H_{ps} is the electronic coupling energy between P^*AQ and $P^{*+}AQ^{*-}$.

electrolyte concentrations to IR drop, and the imperfect agreement between corresponding ΔE° values in table 1 and fig. 3 to the imperfectly dry medium present in the experiment of fig. 3.

Semi-classical Marcus theory, in its high-temperature limit, is a suitable model with which to analyse our results. This theory predicts that the electron-transfer rate constant is given by⁸

$$\ln k_{et} = \ln A - \frac{1}{2} \ln \lambda - \frac{(\Delta G^{o'} + \lambda)^2}{4\lambda kT} \quad (4a)$$

where

$$\ln A = \ln \frac{2\pi H_{ps}^2}{\hbar(4\pi kT)^{1/2}}. \quad (4b)$$

H_{ps} is the electronic coupling matrix element between the precursor state (prior to electron transfer) and the successor state (after electron transfer); H_{ps} is not expected to be solvent-dependent. λ is the reorganisation energy necessary to distort the precursor state to the equilibrium nuclear configuration of the successor state, and $\Delta G^{o'}$ [given by eqn (3)] is the Gibbs energy difference between the equilibrium states of the successor and precursor states. These parameters are shown in the schematic Gibbs energy surfaces of fig. 4.

Table 3. Comparison of calculated and experimental electron transfer rate constants for PAQ in various solvents using semiclassical Marcus theory

| solvent | ϵ_s | ϵ_{op} | λ/eV^a | $-\Delta G^{o'}/\text{eV}^b$ | $\ln k_{et}(\text{exptl})^c$ | $\ln k_{et}(\text{calcd})^d$ |
|---------------------------------|--------------|-----------------|-----------------------|------------------------------|------------------------------|------------------------------|
| CH ₃ CN | 37.5 | 1.806 | 1.12 | 0.52 | 17.69 | (17.69) |
| 1,2-DME | 7.20 | 1.907 | 0.87 | 0.45 | 16.81 | 18.96 |
| MTHF | 7.6 | 1.977 | 0.85 | 0.61 | 16.95 | 20.28 |
| CHCl ₃ | 4.81 | 2.091 | 0.67 | 0.76 | 21.51 | 20.94 |
| CH ₂ Cl ₂ | 9.14 | 2.028 | 0.87 | 0.61 | 20.50 | 20.17 |
| acetone | 20.7 | 1.847 | 1.06 | 0.44 | 17.18 | 17.32 |
| ethyl acetate | 6.02 | 1.882 | 0.84 | 0.52 | 16.91 | 19.76 |
| benzonitrile | 25.6 | 2.332 | 0.88 | 0.49 | 19.78 | 19.25 |
| anisole | 4.33 | 2.301 | 0.55 | 0.55 | 19.61 | 21.15 |

^a Calculated from eqn (5) and (6) with $B = 1.74 \text{ eV}$. ^b Calculated from eqn (2) and (3) with $U_{00} = 1.90 \text{ eV}$ and w_{pr} calculated using ϵ_s for the solvent. ^c All rate constants k_{et} in s^{-1} , taken from ref. (3). ^d Calculated from eqn (4) with $\ln A = -0.78$, calculated using CH₃CN as the reference solvent.

λ is usually divided into a solvent-independent inner term λ_i arising from internal bond-length changes between the precursor and successor states, and an outer term λ_o arising from the reorganisation of the surrounding solvent:

$$\lambda = \lambda_i + \lambda_o. \quad (5)$$

λ_o can be approximated by assuming that the solvent behaves as a dielectric continuum, yielding

$$\lambda_o = B \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (6)$$

where ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, respectively, and $\epsilon_{op} = n^2$, where n is the refractive index. The constant B depends on the electrostatic model chosen. If P^{+} and Q^{-} are assumed to be spheres with radii a_P and a_Q and centre-to-centre distance a_{PQ} , then⁸

$$B = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2a_P} + \frac{1}{2a_Q} - \frac{1}{a_{PQ}} \right). \quad (7)$$

λ_i is not expected to be large, since changing the redox state of P and Q does not greatly change the molecular geometry: we have arbitrarily set $\lambda_i = 0.2 \text{ eV}$. Taking $a_P = 0.8 \text{ nm}$, $a_Q = 0.4 \text{ nm}$ and $a_{PQ} = 1.5 \text{ nm}$, B is calculated to be 1.74 eV .

H_{ps} is difficult to calculate from first principles, so we fixed $\ln A$ in eqn (4) (and hence H_{ps}) by equating experimental and calculated rate constants for a chosen reference solvent (acetonitrile). Table 3 and fig. 5 show the results of the analysis. The data for six of the solvent systems are fairly well correlated by this treatment. 2-MTHF-TBABF₄ is deviant, possibly because of its different supporting electrolyte. Ethyl acetate is also deviant, possibly because it is attacked by $Q^{\cdot-}$. It is interesting that the correlation using ΔG^o values uncorrected for w_{pr} is better than for the 'corrected' $\Delta G^{o'}$ values. This may reflect the fact that the medium between P^{+} and $Q^{\cdot-}$ is not solvent, and hence the use of the bulk solvent ϵ_s to calculate w_{pr} is probably inappropriate.

We have also examined the correlation of $\ln k_{et}$ with Kosower's Z parameter,¹⁰ Dimroth's E_T parameter,¹¹ and the A and B parameters of Swain *et al.*¹² None of these parameters provides a significant correlation.

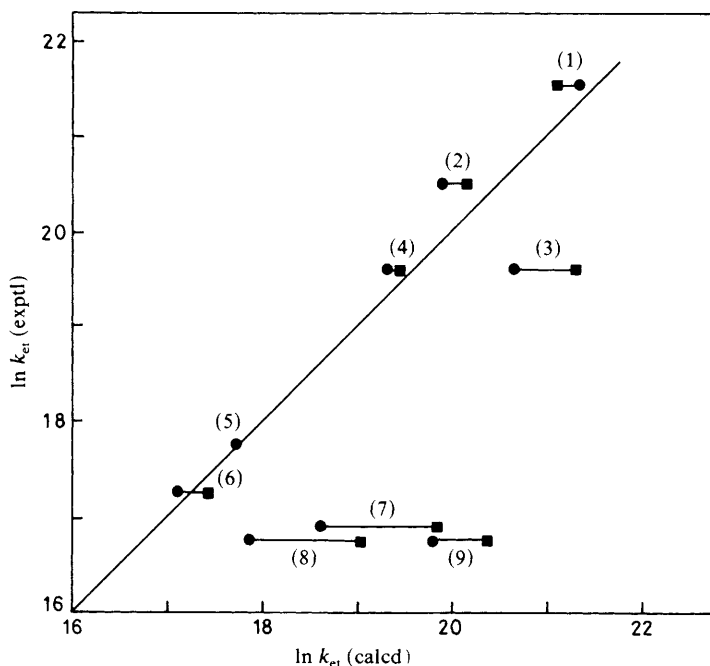


Fig. 5. Correlation of experimental values of $\ln k_{et}$ with values calculated from eqn (4); ●, using experimental values of ΔG° uncorrected for w_{pr} ; ■, ΔG° corrected by w_{pr} according to eqn (2). (1) CHCl_3 , (2) CH_2Cl_2 (3) anisole-TBAClO₄, (4) benzonitrile, (5) CH_3CN , (6) acetone, (7) ethyl acetate, (8) 1, 2-DME, (9) 2-MTHF-TBAPF₄.

Conclusions

Clearly it will be necessary to study several more solvents and to examine with more care the effect of supporting electrolyte on ΔG° , particularly in low dielectric constant solvents, before the applicability of Marcus theory to the rate of photochemical electron transfer from P^{*}AQ can be properly tested. Experiments are underway to provide further data. Nevertheless, it is possible to derive some preliminary conclusions from this study. (1) The solvent dependence of k_{et} shows a reasonable correlation with the semiclassical formulation of Marcus theory. (2) ΔG° is markedly solvent-dependent, and the variation of ΔG° with solvent does not correlate with either ϵ_s or ϵ_{op} . Thus the modified form of the Born equation, derived by Rehm and Weller,¹³ cannot be used to calculate ΔG° from an experimental value for one solvent, as Irvine *et al.*¹⁴ have done. (3) Since k_{et} for intramolecular electron transfer is strongly solvent-dependent, the nature of the surrounding medium must be taken into account as, for example, in the analysis of electron transfer in proteins.⁸ This requires not only an estimate of λ but also of ΔG° , since we have shown that the use of redox potentials calculated by the Born or a similar equation from one experimental result in a single solvent is likely to provide misleading values of ΔG° . (4) We have not yet done so, but k_{et} should be estimated from kinetic data obtained in the same solvent/supporting electrolyte system as used in the measurements of ΔG° .

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