

J. Chem. Soc., Faraday Trans. 1, 1989, **85**(5), 1027–1041

Intramolecular Photochemical Electron Transfer

Part 5.—Solvent Dependence of Electron Transfer in a
Porphyrin–Amide–Quinone Molecule

John A. Schmidt, Jing-Yao Liu and James R. Bolton*

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

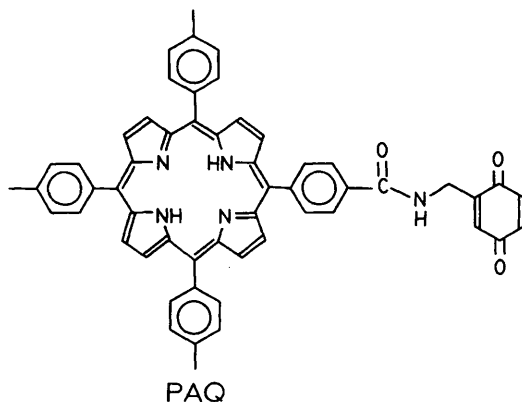
Mary D. Archer* and Victor P. Y. Gadzekpo

*Department of Physical Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EP*

The compound PAQ, which consists of a tetra-arylporphyrin attached to methyl-*p*-benzoquinone *via* a single amide linkage, exhibits light-induced intramolecular electron transfer from the porphyrin excited-singlet state to the quinone at a rate which is strongly solvent-dependent. The rate constants are found to correlate well with the semiclassical Marcus theory of electron transfer, provided that the solvent effect on both the Gibbs energy change, ΔG° , for the electron-transfer reaction ${}^1\text{P}^*\text{AQ} \rightarrow \text{P}^+\text{AQ}^-$ and the Marcus reorganisation energy, λ , are considered. The ΔG° values are obtained from direct measurement of redox potentials in each solvent with various work-term corrections for Coulombic interaction in P^+AQ^- , and λ is calculated from the optical and dielectric properties of each solvent. For fourteen solvents, reasonable agreement with Marcus theory is found using this approach on uncorrected ΔG° values and those corrected with a solvent-dependent work term; a solvent-independent correction is not successful. For two solvent mixtures (acetonitrile–benzonitrile and acetonitrile–chloroform), excellent agreement with Marcus theory is found using uncorrected ΔG° values and those corrected with a solvent-dependent work term. We have found that Weller's method for calculating ΔG° in various solvents from a single measurement in a reference solvent gives a poor correlation with Marcus theory, primarily because of a poor prediction of the solvent dependence of ΔG° .

Covalently linked porphyrin–quinone molecules are important as models of photosynthetic electron-transfer reactions. Increasingly complex synthetic strategies have been devised^{1–5} to mimic the molecular architecture of photosynthetic reaction centres, which has recently been revealed by X-ray crystal-structure determinations.^{6, 7}

We have studied the relatively simple porphyrin–quinone compound PAQ⁸



in which a free-base tetra-arylporphine is linked *via* a single amide group to methyl-*p*-benzoquinone. In an earlier communication⁹ we reported that the porphyrin excited singlet state of PAQ is quenched by electron transfer to the attached quinone group:



and that the rate constant k_{et} is strongly solvent-dependent. We showed a qualitative correlation between $\log k_{\text{et}}$ and the difference in solvation energy between the thermally equilibrated non-polar precursor state ${}^1\text{P}^*\text{AQ}$ and the corresponding high-dipole-moment Franck–Condon successor state $\text{P}^{+\cdot}\text{AQ}^{\cdot-}$. In a subsequent paper¹⁰ we compared this analysis with the semiclassical Marcus theory but with a constant, solvent-independent Gibbs energy change ΔG° for reaction (1); this gave a very poor correlation. However, in a recent preliminary report¹¹ we showed that when ΔG° is estimated from electrochemical measurements in each solvent, the agreement with Marcus theory improves dramatically. A complete characterisation of the photophysics of PAQ in benzonitrile solutions has recently been reported.¹²

In this paper we report a further analysis of the solvent effect on reaction (1). When the solvent dependence of ΔG° , and especially the reorganisation energy λ , are considered, the electron-transfer rate constants in fourteen solvents correlate reasonably well with semiclassical Marcus theory.^{13–15} Good agreement is obtained when the solvent properties are varied by using different compositions of binary solvent mixtures (acetonitrile–benzonitrile and acetonitrile–chloroform).

We analyse our results in terms of the high-temperature limit of semiclassical Marcus theory, which gives the electron-transfer rate constant k_{et} as^{14,15}

$$k_{\text{et}} = \frac{2\pi}{\hbar} \frac{H_{\text{ps}}^2}{(4\pi\lambda k_{\text{B}} T)^{\frac{1}{2}}} \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_{\text{B}} T}\right) \quad (2)$$

where H_{ps} is the electronic coupling between the precursor (${}^1\text{P}^*\text{AQ}$) and successor ($\text{P}^{+\cdot}\text{AQ}^{\cdot-}$), λ is the reorganisation energy and ΔG° is the Gibbs energy change for the electron transfer.†

We shall use eqn (2) in a logarithmic form

$$\log(k_{\text{et}} \lambda^{\frac{1}{2}}) = \log\left(\frac{2\pi}{\hbar} \frac{H_{\text{ps}}^2}{(4\pi k_{\text{B}} T)^{\frac{1}{2}}}\right) - \frac{(\Delta G^\circ + \lambda)^2}{(2.303) 4\lambda k_{\text{B}} T} \quad (3a)$$

$$\text{or} \quad Y = C - X \quad (3b)$$

$$\text{where} \quad Y = \log(k_{\text{et}} \lambda^{\frac{1}{2}})$$

$$C = \log\left(\frac{2\pi}{\hbar} \frac{H_{\text{ps}}^2}{(4\pi k_{\text{B}} T)^{\frac{1}{2}}}\right) \quad \text{and} \quad X = \frac{(\Delta G^\circ + \lambda)^2}{(2.303) 4\lambda k_{\text{B}} T} \quad (3c)$$

The reorganisation energy λ has two components, an inner term λ_{i} , arising from internal reorganisation (primarily bond-length changes) within the reacting molecule(s), and an outer term, λ_{o} , arising from changes in the surrounding medium:

$$\lambda = \lambda_{\text{i}} + \lambda_{\text{o}} \quad (4)$$

† As long as $\lambda > |\Delta G^\circ|$ (this is the case for almost all our data), then the more complex semiclassical equations,¹⁵ which do not require the high-temperature approximation, reduce to eqn (2).

In semiclassical Marcus theory the solvent is assumed to behave as a dielectric continuum and λ_0 is given by¹³

$$\lambda_0 = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{2a_P} + \frac{1}{2a_Q} - \frac{1}{a_{PQ}} \right) \quad (5a)$$

$$= B \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (5b)$$

where e is the electronic charge, ϵ_0 is the permittivity of free space, and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent: ϵ_{op} is given by the square of the refractive index.¹⁶ In eqn (5a) it is assumed that the donor (P) and acceptor (Q) are spheres of radii a_P and a_Q separated by a centre-to-centre distance $a_{PQ} \gg (a_P + a_Q)$; this model is hardly appropriate for PAQ, but a more realistic ellipsoidal model also yields an equation which closely approximates to the form of eqn (5b), and B turns out to be fairly model-insensitive.¹⁷

The use of eqn (2) and (5) implies that the precursor ${}^1P^*AQ$ is sufficiently long-lived to equilibrate both internally and with the surrounding solvent. The minimum observed lifetime was *ca.* 1 ns, sufficient for this condition to be fulfilled.

Evaluation of eqn (2) requires values of both λ and ΔG° for reaction (1) in each solvent. It is not uncommon in work of this type either to ignore any solvent dependence in ΔG° , or to calculate ΔG° in different solvents from the value in a single reference solvent using Weller's equation.¹⁸ We consider these procedures to be unsatisfactory, for the reasons adduced in the Discussion section. Therefore we have measured ΔG° from the difference $\Delta E^\circ = E_P^\circ - E_Q^\circ$ between the experimental redox potentials for the reactions $P^{+}AQ + e^- \rightarrow PAQ$ and $PAQ + e^- \rightarrow PAQ^{\cdot-}$ in each solvent and the energy U_{S_1} of the equilibrated porphyrin excited singlet state relative to the ground state.¹⁹ This quantity we denote ΔG_0° :

$$\Delta G_0^\circ = e(E_P^\circ - E_Q^\circ) - U_{S_1} \quad (6a)$$

This expression is not unexceptionable. It implies no work term, *i.e.* no Coulombic interaction or difference in interaction, in $P^{+}AQ^{\cdot-}$, $P^{+}AQ$ and $PAQ^{\cdot-}$. However, there is likely to be some Coulombic stabilisation of the ion pair $P^{+}AQ^{\cdot-}$ relative to the ions $P^{+}AQ$ and $PAQ^{\cdot-}$ produced separately in the electrochemical measurements, albeit in the presence of supporting electrolyte ions which afford some stabilisation. Therefore we have examined the effect of two methods of 'correcting' ΔG_0° . Our second estimate ΔG_1° assumes a Coulombic interaction through the solvent, exhibiting its bulk dielectric constant ϵ_s , between two point charges at the centre-to-centre distance a_{PQ} :

$$\Delta G_1^\circ = \Delta G_0^\circ - \frac{e^2}{4\pi\epsilon_0\epsilon_s a_{PQ}} \quad (6b)$$

Coulombic interaction in $P^{+}AQ^{\cdot-}$ must occur, at least in part, through the molecule itself rather than through the solvent. Moreover, insofar as this occurs through the solvent, local dielectric saturation may lower the effective static dielectric constant. As Suppan²⁰ has pointed out, a solvent-independent correction term w would then be appropriate, and our third estimate is

$$\Delta G_2^\circ = \Delta G_0^\circ - w \quad (6c)$$

where w was taken to be 0.1–0.4 eV; $w = 0.4$ eV is equivalent to assuming Coulombic interaction between two point charges a distance $a_{PQ} = 14$ Å apart separated by a medium of $\epsilon_s \approx 2.5$.

Finally, we have used our ΔG_0° measurement for one reference (ref) solvent (acetonitrile) to estimate ΔG° in other solvents from Weller's equation¹⁸

$$\Delta G_3^\circ = e(E_P^\circ - E_Q^\circ)_{\text{ref}} + \frac{e^2}{4\pi\epsilon_0\epsilon_s} \left(\frac{1}{a} - \frac{1}{a_{\text{PQ}}} \right) - \frac{e^2}{4\pi\epsilon_0\epsilon_s^{\text{ref}} a} - U_{S_1} \quad (6d)$$

where a_{PQ} is again the porphyrin–quinone centre-to-centre separation and a is the average of the radii of P^+ and Q^- . Use of eqn (6d) implies that the Born equation for individual ion solvation is applicable and that the work term correction of eqn (6b) is valid.

Experimental

The synthesis and characterisation of PAQ have been described,^{8,9} as have the procedures for determining the redox potentials of PAQ by differential pulse voltammetry in each solvent system in a mini-cell under vacuum.^{11,21} Experiment showed that the influence of i.r. drop on peak positions is negligible, so i.r. compensation was not used. All redox potentials were measured *vs.* ferrocene (Fc), added in small concentrations as an internal reference. Tetrabutylammonium hexafluorophosphate (TBAH) at a concentration of 0.1 mol dm⁻³, if soluble in the solvent, was used as the supporting electrolyte because the large size of its ions should minimise ion association with P^+AQ or PAQ^- .

Electron-transfer rate constants k_{et} were determined as previously described^{8,9,22} from the relation

$$k_{\text{et}} = 1/\tau_1 - 1/\tau_2 \quad (7)$$

where τ_1 and τ_2 are the fluorescence lifetimes of PAQ and the corresponding hydroquinone compound PAQH₂. It is assumed that the shorter lifetime of PAQ relative to that of PAQH₂ is entirely a consequence of reaction (1), and that all other decay pathways (fluorescence, internal conversion and intersystem crossing) have the same rate constants in PAQ and in PAQH₂. This assumption has been verified by picosecond absorption studies of PAQ in benzonitrile.¹²

All solvents were dried and distilled prior to use. Binary solvent mixtures were prepared by mixing appropriate volumes of each solvent. The percentage composition on a molar basis was calculated using densities of 1.4832, 1.0102 and 0.7857 g cm⁻³ for chloroform, benzonitrile and acetonitrile, respectively.²³ Refractive indices for solvent mixtures were measured at 20 °C with a Bausch and Lomb refractometer.

Static dielectric constants for solvent mixtures were measured using a General Radio model 1689 a.c. capacitance bridge, operated at 100 kHz.⁸

Results

Fluorescence Measurements

The fluorescence lifetimes of PAQ in 22 solvents have been reported previously:⁹ the relevant ones are repeated in table 1 in more detail. In some solvents, single exponential decays were observed, but in others, particularly for PAQ, the data could be fitted only with two exponential decays, as indicated in table 1. This we attribute to the simultaneous presence of both PAQ (shorter-lifetime component) and PAQH₂ (longer-lifetime component) in solvents in which complete reduction or oxidation was not achieved. In a few solvents τ_1 and τ_2 were rather close. To check the integrity of the compound in these cases, the solvent was evaporated after the lifetime measurements had been made and the precipitate was taken up in CH₂Cl₂. In all cases the fluorescence lifetimes observed for this recovered solution were those expected for PAQ in CH₂Cl₂.

Table 1. Analysis of fluorescence lifetimes for PAQ and PAQH₂

solvent	compound	τ_1/ns^a	τ_2/ns^b	χ^2^c	$k_{\text{et}}/10^8 \text{ s}^{-1}^d$
CH ₃ CN	PAQ	7.6	—	0.97	0.48
	PAQH ₂	—	12.0	1.10	
C ₃ H ₇ CN	PAQ	7.2	—	1.25	0.56
	PAQH ₂	—	12.0	1.25	
C ₆ H ₅ CN	PAQ	2.1	11.5 (2.2%)	1.06	3.9
	PAQH ₂	—	11.5	1.31	
acetone	PAQ	8.9	—	1.30	0.29
	PAQH ₂	—	12.0	1.16	
Bu ⁿ OH	PAQ	3.1	12.0 (4.1%)	1.20	2.4
	PAQH ₂	—	12.0	1.15	
1,2-DCE ^e	PAQ	1.5	—	1.16	5.6
	PAQH ₂	—	9.6	1.15	
CH ₂ Cl ₂	PAQ	1.1	8.8 (1.6%)	1.00	8.0
	PAQH ₂	—	9.1	1.14	
2-MTHF ^f	PAQ	9.4	—	1.18	0.23
	PAQH ₂	—	12.0	1.18	
1,1,1-TCE ^g	PAQ	1.7	10.5 (6.1%)	1.04	4.9
	PAQH ₂	—	10.5	1.02	
1,2-DME ^h	PAQ	10.0	—	1.30	0.20
	PAQH ₂	—	12.5	1.38	
EtOAc ⁱ	PAQ	9.5	—	0.96	0.22
	PAQH ₂	—	12.0	1.17	
Cl-Bz ^j	PAQ	1.1	10.5 (1.2%)	1.24	8.2
	PAQH ₂	1.0	11.0 (89%)	1.02	
Cl-Naph ^k	PAQ	1.2	10.0 (29%)	1.23	7.4
	PAQH ₂	1.4	10.5 (91%)	1.20	
CHCl ₃	PAQ	0.42	7.6 (2.9%)	1.09	22.7
	PAQH ₂	—	9.1	1.14	
1,2-DBE ^l	PAQ	0.52	1.3 (4.6%)	1.17	12.6
	PAQH ₂	0.53	1.5 (84%)	1.01	
anisole	PAQ	2.4	11.0 (1.5%)	1.41	3.3
	PAQH ₂	2.5	12.0 (93%)	0.97	

^a Fluorescence lifetime; τ_1 is the lifetime of PAQ and τ_2 is the lifetime of PAQH₂; errors are ± 0.1 ns for τ_1 in PAQ and τ_2 in PAQH₂ and ± 0.5 ns for τ_2 in PAQ. ^b The figure in parenthesis, given only for a decay described by two exponential components rather than a single component, is the percentage of the component of lifetime τ_2 (*i.e.* PAQH₂). ^c Reduced χ^2 for the fit. ^d Calculated using eqn (7); error $\pm 5\%$. ^e 1,2-Dichloroethane. ^f 2-Methyltetrahydrofuran. ^g 1,1,1-Trichloroethane. ^h 1,2-Dimethoxyethane. ⁱ Ethyl acetate. ^j Chlorobenzene. ^k 1-Chloronaphthalene. ^l 1,2-Dibromoethane.

Electrochemical Measurements

The potentials R_1 and R_2 of the first and second reductions of the porphyrin ring of PAQ, Q_1 the first quinone reduction potential, and O_1 and O_2 , the first and second porphyrin ring oxidations, are given in table 2.

Table 2. Redox potentials of PAQ (V vs. Fc)

solvent ^a	electrolyte ^b	R ₂	R ₁	Q ₁	O ₁	O ₂	ΔE ^o ^c
CH ₃ CN	TBAH ^d	?	?	-0.985	0.425	?	1.41
C ₃ H ₇ CN	TBAH	?	-1.482	-0.830	0.582	?	1.41
C ₆ H ₅ CN	TBAH	-1.530	-1.290	-0.852	0.596	?	1.45
acetone	TBAH	?	?	-0.908	0.600	?	1.51
Bu ⁿ OH	TMAC ^e	?	-1.568	-0.920	0.496	?	1.42
1,2-DCE	TBAH	?	-1.512	-0.912	0.420	0.996	1.33
CH ₂ Cl ₂	TBAH	?	-1.526	-0.906	0.496	?	1.40
2-MTHF	TBAFB ^f	-1.536	-1.304	-0.948	0.468	0.636	1.42
1,1,1-TCE	TBAFB	?	-1.440	-0.816	0.648	0.888	1.46
1,2-DME	TBAH	?	-1.572	-0.936	0.636	?	1.57
EtOAc	TBAH ^g	?	-1.739	-1.175	0.364	?	1.54
Cl-Bz	TBAC ^h	-1.742	-1.542	-0.987	0.524	0.950	1.51
Cl-Naph	TBAC	-2.112	-1.536	-0.696	0.780	?	1.48
CHCl ₃	TBAH	?	?	-1.014	0.326	?	1.34
1,2-DBE	TBAFB	?	?	-0.940	0.480	0.980	1.42
anisole	TBAP ⁱ	-1.872	-1.386	-1.056	0.516	?	1.57

^a See footnotes to table 1 for definition of solvent symbols. ^b 0.1 mol dm⁻³ unless otherwise indicated. ^c ΔE^o/V = O₁ - Q₁ = E_p^o - E_q^o. The error in the difference between any pair of potentials = ±0.040 V; individual values vs. Fc are less precise than this because the potential of the quasi-reference electrode was time-dependent. ^d Tetrabutylammonium hexafluorophosphate. ^e Tetramethylammonium chloride. ^f Tetrabutylammonium fluoroborate; TBAH is insoluble in 2-MTHF, 1,1,1-TCE, anisole and 1,2-DBE. ^g Saturated solution (< 0.1 mol dm⁻³) TBAH in ethyl acetate. ^h Tetrabutylammonium chloride. ⁱ Tetrabutylammonium perchlorate.

Table 3. Effect of supporting electrolyte on electron-transfer rate constants for PAQ in three solvents

solvent	[TBAH]/ mol dm ⁻³	τ ₁ /ns	τ ₂ /ns	log(k _{et} /s ⁻¹)
CH ₃ CN	0	7.5 ± 0.1	14.7 ± 1.3	7.82 ± 0.05
	0.1	7.9 ± 0.1	13.6 ± 0.6	7.73 ± 0.04
C ₆ H ₅ CN	0	2.11 ± 0.02	11.95 ± 0.1	8.59 ± 0.01
	0.1	2.01 ± 0.03	11.67 ± 0.05	8.62 ± 0.01
2-MTHF	0	6.4 ± 0.3	11.8 ± 0.3	7.85 ± 0.06
	0.1	5.7 ± 0.5	11.8 ± 0.2	7.96 ± 0.08

Influence of the Supporting Electrolyte

Most of the fluorescence lifetimes and corresponding rate constants were determined using *ca.* 10⁻⁵ mol dm⁻³ PAQ solution without any other components present. On the other hand, most of the electrochemical measurements were carried out on *ca.* 10⁻⁴ mol dm⁻³ PAQ in the presence of *ca.* 0.1 mol dm⁻³ supporting electrolyte. Thus we were concerned as to whether the presence of supporting electrolyte would affect our photophysical measurements. The data collected in table 3 show that the effect of supporting electrolyte on k_{et} is small compared with the overall solvent effects. However, the effect of supporting electrolyte on the measured redox potentials may be more significant. Previously we showed¹¹ that varying the concentration of our favoured supporting electrolyte, TBAH, had little effect in the range

Table 4. Rate constants, reorganisation energies and Gibbs energies for electron transfer in PAQ

solvent ^a	log k_{et}^b	ϵ_{op}^c	ϵ_s^d	λ^e	$-\Delta G_0^{of}$	$-\Delta G_1^{og}$	$-\Delta G_2^{oh}$	$-\Delta G_3^{oi}$
CH ₃ CN	7.71	1.800	35.94	1.15	0.49	0.52	0.69	0.52
C ₃ H ₇ CN	7.72	1.910	24.83	1.07	0.49	0.54	0.69	0.48
C ₆ H ₅ CN	8.60	2.328	25.20	0.90	0.45	0.49	0.65	0.50
acetone	7.47	1.839	20.56	1.09	0.39	0.44	0.59	0.48
Bu ⁿ OH	8.37	1.953	17.51	1.02	0.48	0.54	0.68	0.46
1,2-DCE	8.73	2.080	10.37	0.89	0.57	0.67	0.77	0.40
CH ₂ Cl ₂	8.91	2.020	8.93	0.89	0.50	0.61	0.70	0.38
2-MTHF	7.31	1.974	7.60	0.87	0.48	0.62	0.68	0.34
1,1,1-TCE	8.70	2.062	7.25	0.83	0.44	0.57	0.64	0.33
1,2-DME	7.28	1.899	7.20	0.90	0.33	0.47	0.53	0.32
EtOAc	7.32	1.876	6.02	0.86	0.36	0.53	0.56	0.28
Cl-Bz	8.89	2.316	5.62	0.66	0.39	0.57	0.59	0.25
Cl-Naph	8.89	2.667	5.04	0.52	0.42	0.63	0.62	0.22
CHCl ₃	9.35	2.082	4.81	0.69	0.56	0.77	0.76	0.20
1,2-DBE	9.10	2.369	4.78	0.59	0.48	0.70	0.68	0.20
anisole	8.51	2.293	4.33	0.57	0.33	0.57	0.53	0.16

^a See footnotes to table 1 for definition of solvent symbols. ^b log ($k_{\text{et}}/\text{s}^{-1}$) calculated from eqn (7) (values from ref 9); error in log $k_{\text{et}} \pm 0.04$. ^c Optical dielectric constant (square of the refractive index). Static dielectric constants and refractive indices were taken from J. A. Riddick, W. B. Bunger and T. K. Sakano, *Techniques of Chemistry II, Organic Solvents* (Wiley, New York, 4th edn, 1986). ^d Static dielectric constant. ^e Reorganisation energy in eV calculated from eqn (4) and (5b), with $B = 1.80$ eV and $\lambda_i = 0.2$ eV. ^f Calculated in eV from eqn (6a) using ΔE° from table 2 and $U_{\text{S}_1} = 1.90$ eV as obtained from the overlap of the absorption and fluorescence spectra;²⁹ this value is not solvent-sensitive to more than ± 0.02 eV.⁸ Error in $\Delta G_0^\circ \pm 0.04$ eV. ^g Calculated in eV from eqn (6b); error ± 0.04 eV. ^h Calculated in eV from eqn (6c) taking $w = 0.2$ eV; error ± 0.04 eV. ⁱ Calculated in eV from eqn (6d) using electrochemical data for PAQ in CH₃CN as the reference solvent; $a = 5.2$ Å; $a_{\text{PQ}} = 14$ Å.

0.05–0.3 mol dm⁻³, but that varying the electrolyte itself had a perceptible effect. Some ion pairing of P⁺AQ and PAQ⁻ with the ions of the supporting electrolyte is inevitable for solvents of lower ϵ_s . We found, for example, that tetrabutylammonium fluoroborate (TBAFB) lowered ΔE° values by ca. 0.15 V in dichloromethane.¹¹

Marcus Analysis of Results for Different Solvents

The rate constants k_{et} for reaction (1) were calculated from eqn (7) and are given in table 1. To estimate λ_0 [eqn (5a)] we took $a_{\text{P}} = 7$ Å and $a_{\text{Q}} = 4$ Å. Computer modelling of extreme conformations of PAQ¹² showed a_{PQ} to lie in the range 12.7–14.3 Å and we have taken $a_{\text{PQ}} = 14$ Å. Using these values, B in eqn (5b) was calculated to be 1.80 eV. For each of the 16 solvents for which we have electrochemical measurements, calculated values of λ are given in table 4. Measurement errors in ϵ_s and ϵ_{op} result in an uncertainty in λ_0 of ± 0.01 eV, small compared with the uncertainty in λ_i , which we assumed to lie in the range 0–0.2 eV because bond-length differences between the precursor state ¹P*AQ and the successor state P⁺AQ⁻ are thought to be small.^{24, 25} Brunschwig *et al.*¹⁷ used $\lambda_i = 0.1$ eV for a series of transition-metal complexes. If λ_i is in this range, then the values of λ listed in table 4 are reasonably consistent with other estimates of $\lambda \approx 0.7$ eV²⁶ and $\lambda \approx 0.9$ eV²⁷ for similar porphyrin–quinone molecules. Closs *et al.*²⁸ estimate $\lambda = 0.75$ eV in methyltetrahydrofuran for a biphenyl anion linked to an acceptor *via* a steroid bridge.

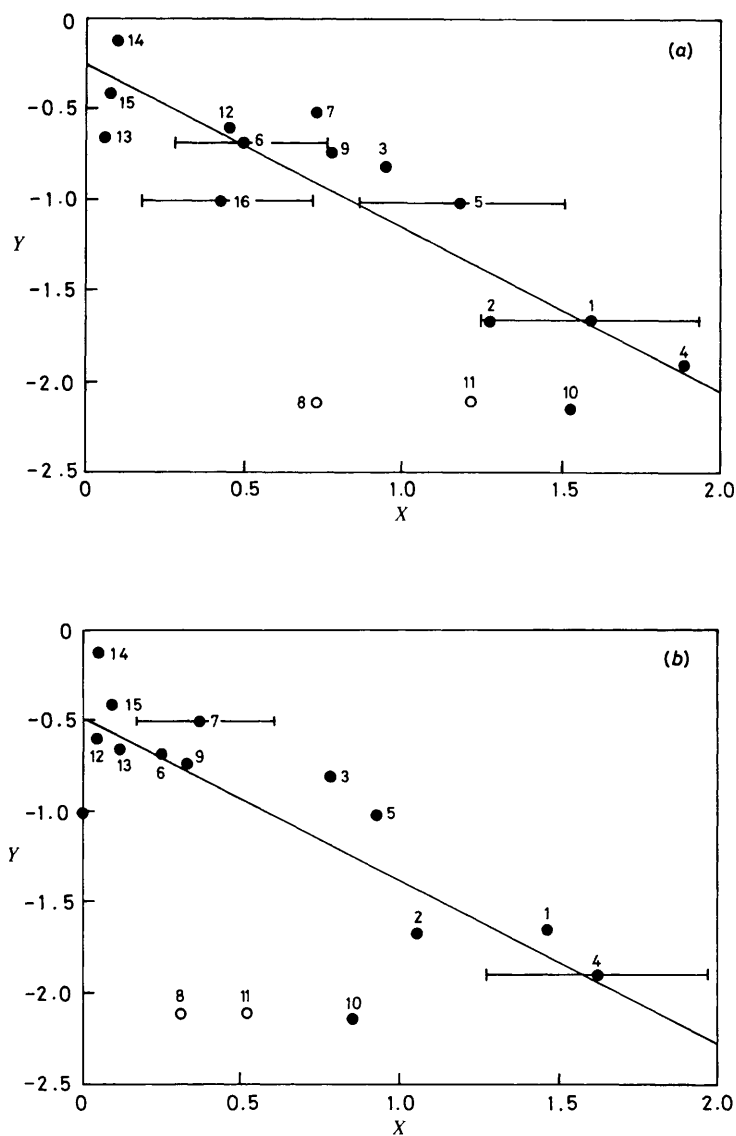


Fig. 1. For legend see opposite.

Also given in table 4 are the kinetic and solvent data and four representative sets of ΔG° values calculated from eqn (6a)–(6d).

Fig. 1(a)–(d) show plots of Y vs. X [eqn (3b)] for the four alternative sets of ΔG° values and representative values of w and λ_1 . On each plot is given the least-squares slope for a linear fit to the data for 14 solvents and the correlation coefficient r for that fit. The data for two solvents, 2-MTHF and EtOAc, were excluded from all fits in fig. 1: EtOAc because cyclic voltammetry showed it to be attacked by $\text{PAQ}^{\cdot-}$, and 2-MTHF because TBAFB had to be used as supporting electrolyte.

Both ΔG_0° and ΔG_1° (which differ little at higher ϵ_s) yield reasonable agreement with Marcus theory. In particular, it is satisfactory that the least-squares slopes are very close

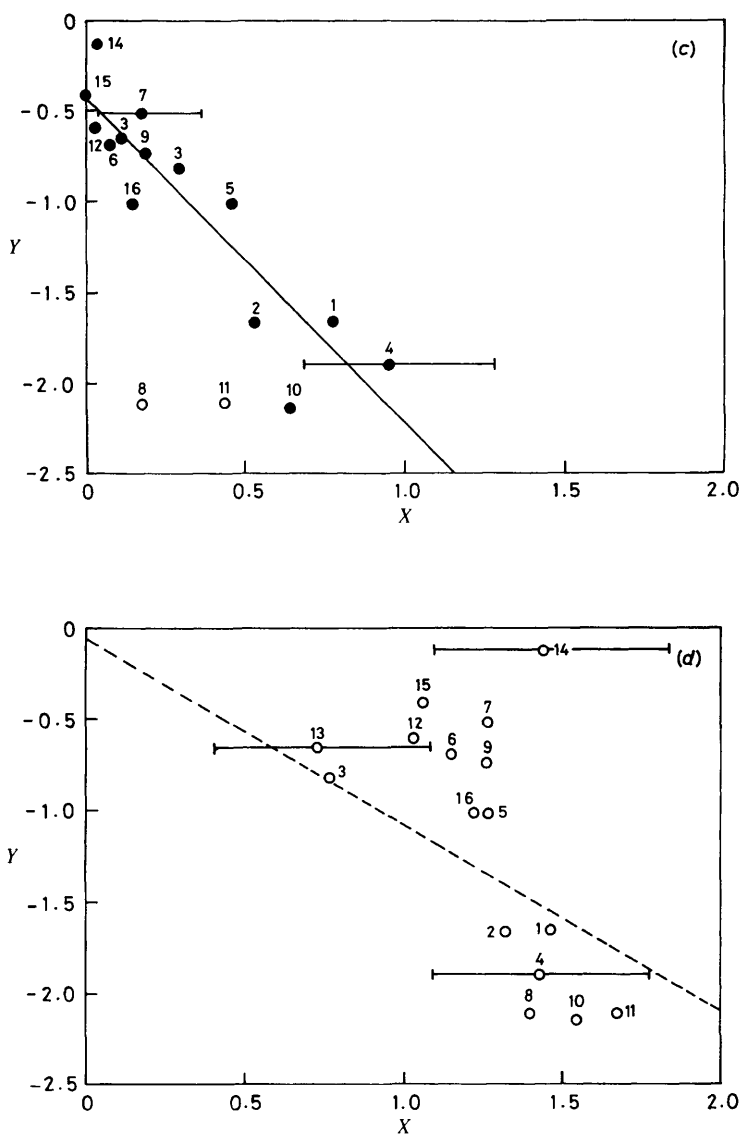


Fig. 1. (a)–(d) Plots of $Y = \log(k_{\text{et}} \lambda^{1/2} / J^{1/2} \text{s}^{-1})$ vs. $X = (\Delta G_n^\circ + \lambda)^2 / (2.303) 4\lambda k_B T$ [see eqn (3)] using the ΔG_n° and λ_0 data of table 4, $\lambda_1 = 0.2$ eV and $w = 0.2$ eV in eqn (6c), where (a) $n = 0$ [eqn (6a)], (b) $n = 1$ [eqn (6b)], (c) $n = 2$ [eqn (6c)] and (d) $n = 3$ [eqn (6d)]. The solid lines in fig. 1(a)–(c) are least-squares fits to the solid points: (a) slope = -0.90 , $r = 0.893$; (b) slope = -0.89 ; $r = 0.817$; (c) slope = -1.80 , $r = 0.911$. The open points have been excluded for the reasons stated in the text. The dotted line in fig. 1(d) is a line with the expected slope of -1 for comparison. The error bars show the effect of changing λ by ± 0.1 eV. The number code for the solvents is: (1) CH_3CN , (2) $\text{C}_3\text{H}_7\text{CN}$, (3) $\text{C}_6\text{H}_5\text{CN}$, (4) acetone, (5) n-butanol, (6) 1,2-dichloroethane, (7) CH_2Cl_2 , (8) 2-methyltetrahydrofuran, (9) 1,1,1-trichloroethane, (10) dimethoxyethane, (11) ethyl acetate, (12) chlorobenzene, (13) 1-chloronaphthalene, (14) CHCl_3 , (15) 1,2-dibromoethane, (16) anisole.

to the expected value of -1 . Also, the high rate constant observed in chloroform can be explained by the approximate equality of the calculated λ and predicted $-\Delta G^\circ$ values. Moreover, the rate constants for solvents with widely different properties and functional groups correlate satisfactorily with Marcus theory. There is little to choose between ΔG_0° and ΔG_1° in terms of fit.

We have explored the sensitivity of the correlation in fig. 1(a) to holding either ΔG_0° or λ constant. When ΔG_0° is held constant at -0.48 eV (the value for acetonitrile) the slope is -0.78 but the correlation coefficient drops from 0.893 to 0.690. When λ is held constant at 0.80 eV, the slope is -1.03 but r drops to 0.477. Clearly the best correlation is found when the solvent dependence of both ΔG° and λ are taken into account.

The uncertainty in λ dominates the errors in X and Y , and the representative X error bars in the figures show the effect of changing λ by ± 0.1 eV; the error in Y produced by this variation in λ is negligible. As the X error bars indicate, a change in the chosen value of λ_i changes the absolute value of X and hence the intercept, but we found that the correlations of fig. 1(a) and (b) were little affected in the chosen range $\lambda_i = 0-0.2$ eV, although higher λ_i values increase the range of λ and reduce the best-fit slope.

Both the constant work-term expression ΔG_2° and Weller's ΔG_3° are markedly less successful in correlating the data in different solvents [fig. 1(c) and (d)]. In fig. 1(c) (in which w was taken as 0.2 eV), the correlation is good but the slope (-1.80) is too large in magnitude. For $w = 0.1$ eV, the slope is -1.33 , while $w = 0.4$ eV brings the predicted rate constants largely into the inverted region and produces poor correlation.

As fig. 1(d) shows, Weller's equation [eqn (6d)] is not successful in correlating the data in different solvents. The trends in ΔG_3° and λ_o with increasing ϵ_s partly cancel in the calculation of X [eqn (3c)], leading to the small range of X evident in fig. 1(d). Moreover, examination of table 4 shows that Weller's equation does not predict the experimental values ΔG_0° well in low dielectric solvents, in which $-\Delta G_3^\circ$ is small in magnitude because of the predicted low Born solvation energies of ions in such solvents. Furthermore, the predicted trend in ΔG_3° cannot explain the observed trend in k_{et} . Any reasonable variant of transition-state theory, whether a linear or a quadratic free-energy relationship is employed, predicts that $\log k_{et}$ would increase as ΔG_3° becomes more negative, but the actual trend is opposite to that predicted by Weller's ΔG_3° .

Marcus Analysis of Results for Mixed Solvents

The use of binary solvent mixtures minimises abrupt changes in short-range solvent properties, while still providing a wide range of calculated λ values. We chose two binary mixtures for study: the acetonitrile–chloroform system because these two solvents span a wide range of experimental rate constants, and the acetonitrile–benzonitrile system because these two solvents have the same functional group but also exhibit quite different rate constants. We chose acetonitrile as the common component to minimise the extrapolation required to calculate ΔG_3° [eqn (6d)].

Table 5 gives the measured dielectric properties of these solvent mixtures, the fluorescence lifetimes and electron-transfer rate constants and four representative sets of ΔG° values calculated from eqn (6). Electrochemical measurements on some of these mixed solvents indicated that, within experimental error, $\Delta E^\circ (= E_p^\circ - E_Q^\circ)$ varied smoothly between the values for the two pure solvents. We therefore assumed a linear dependence of ΔE° on mole fraction to effect both interpolations. The ΔE° values do not span a wide range in either mixture, so the interpolation is not expected to introduce significant error into the analysis.

In order to emphasise the overall correlation we have plotted the data for the two solvent mixtures together in fig. 2 for the four alternative ΔG° values. For the acetonitrile–benzonitrile solvent mixture, the agreement of experiment with Marcus theory is very good when either ΔG_0° or ΔG_1° [fig. 2(a or b)] is selected. ΔG_3° also gives a good correlation [fig. 2(d)]. This lack of discrimination results from the small range and

Table 5. Rate constants, reorganisation energies and Gibbs energies for acetonitrile–benzonitrile and acetonitrile–chloroform mixtures

$v:v^a$	x^b	τ_1/ns^c	τ_2/ns^c	$\log k_{et}^d$	ϵ_s^e	ϵ_{op}^f	λ^g	$-\Delta G_0^\circ{}^h$	$-\Delta G_1^\circ$	$-\Delta G_2^\circ{}^i$	$-\Delta G_3^\circ$
acetonitrile–benzonitrile											
0:1	0.000	2.06	11.74	8.60	25.20	2.328	0.90	0.45	0.49	0.65	0.50
1:8	0.196	2.21	11.82	8.57	26.70	2.275	0.92	0.46	0.50	0.66	0.50
1:4	0.328	2.44	11.82	8.51	27.74	2.238	0.94	0.46	0.50	0.66	0.50
1:2	0.494	2.77	11.82	8.44	29.41	2.167	0.97	0.47	0.51	0.67	0.51
1:1	0.661	3.38	11.97	8.33	31.60	2.085	1.01	0.48	0.51	0.68	0.51
2:1	0.796	4.16	11.99	8.20	33.61	1.986	1.05	0.48	0.51	0.68	0.51
4:1	0.887	4.96	11.99	8.07	35.26	1.907	1.09	0.49	0.52	0.69	0.52
8:1	0.940	5.68	12.00	7.97	36.23	1.863	1.12	0.49	0.52	0.69	0.52
1:0	1.000	7.44	11.95	7.71	35.94	1.800	1.15	0.49	0.52	0.69	0.52
acetonitrile–chloroform											
0:1	0.000	0.42	9.05	9.36	4.81	2.082	0.69	0.56	0.77	0.76	0.20
1:8	0.161	1.05	9.37	8.93	10.10	2.047	0.90	0.55	0.64	0.75	0.39
1:4	0.278	1.41	9.25	8.78	12.40	2.029	0.94	0.54	0.60	0.74	0.42
1:2	0.435	2.01	9.83	8.60	17.00	1.989	1.00	0.53	0.57	0.74	0.46
1:1	0.606	3.36	9.80	8.29	22.50	1.937	1.05	0.52	0.55	0.72	0.49
2:1	0.755	4.45	10.66	8.12	27.10	1.888	1.09	0.51	0.53	0.71	0.50
4:1	0.860	5.40	11.15	7.98	31.00	1.850	1.12	0.50	0.53	0.70	0.51
8:1	0.925	5.90	10.37	7.86	33.00	1.833	1.13	0.50	0.52	0.70	0.51
1:0	1.000	7.44	11.95	7.71	35.94	1.800	1.15	0.49	0.52	0.69	0.52

^a Volume ratio CH₃CN:C₆H₅CN or CH₃CN:CHCl₃. ^b Mole fraction of CH₃CN. ^c $\pm 5\%$.

^d Calculated from τ_1 and τ_2 using eqn (7); error in $\log k_{et} \pm 0.04$. ^e ± 0.05 . ^f ± 0.005 .

^g Reorganisation energy in eV calculated from eqn (4) and (5b) with $B = 1.80$ eV and $\lambda_i = 0.2$ eV.

^h All ΔG° in eV. ⁱ Calculated from eqn (6c) with $w = 0.2$ eV.

close similarity of the three ΔG_n° sets, which in turn derives from the similar ΔE° values in the two pure solvents and the relatively large static dielectric constants of the whole range of mixtures. The solvent reorganisation energy λ_0 is high, and the fit and the slope are rather insensitive to the choice of λ_i in the range 0–0.2 eV. It is evident that the measured dielectric properties account very well for the effect of solvent on k_{et} in these mixtures.

For acetonitrile–chloroform mixtures, good correlation with Marcus theory is obtained using either ΔG_0° or ΔG_1° [fig. 2(a) and (b)], although here the ranges of λ and ΔG_1° are larger and the best-fit slope is more sensitive to the choice of λ_i , changing from -1.04 for $\lambda_i = 0.2$ eV to -1.17 for $\lambda_i = 0.1$ eV and -1.58 for $\lambda_i = 0$.

For both solvent mixtures in the case of ΔG_2° calculated with $w = 0.2$ eV, the correlation is linear but the slope is too large (-1.78) in magnitude. It is reduced to ca. -1.0 by the choice of $w = 0.1$ eV. However, this would require a choice of $\epsilon_s \approx 10$ for the dielectrically saturated linkage, a value which we feel is unreasonable.

For the acetonitrile–chloroform mixtures, the use of Weller's ΔG_3° values yields a small range of X due to partial cancellation of trends in ΔG_3° and λ_0 with increasing ϵ_s , and hence no correlation with Marcus theory [fig. 2(d)]. Again, this can be ascribed to the low ion solvation energies predicted by the Born equation. It is notable that the correlation is reasonable for those mixtures in which $\epsilon_s \geq 15$.

The intercepts in fig. 1(a) and 2(a) each give $C \approx 0$ [eqn 3(c)]. From eqn (3a) we can thus estimate that the electronic coupling term $H_{ps} \approx 4 \times 10^{-4}$ eV at 300 K; this low value is consistent with a non-adiabatic electron-transfer process.¹⁵

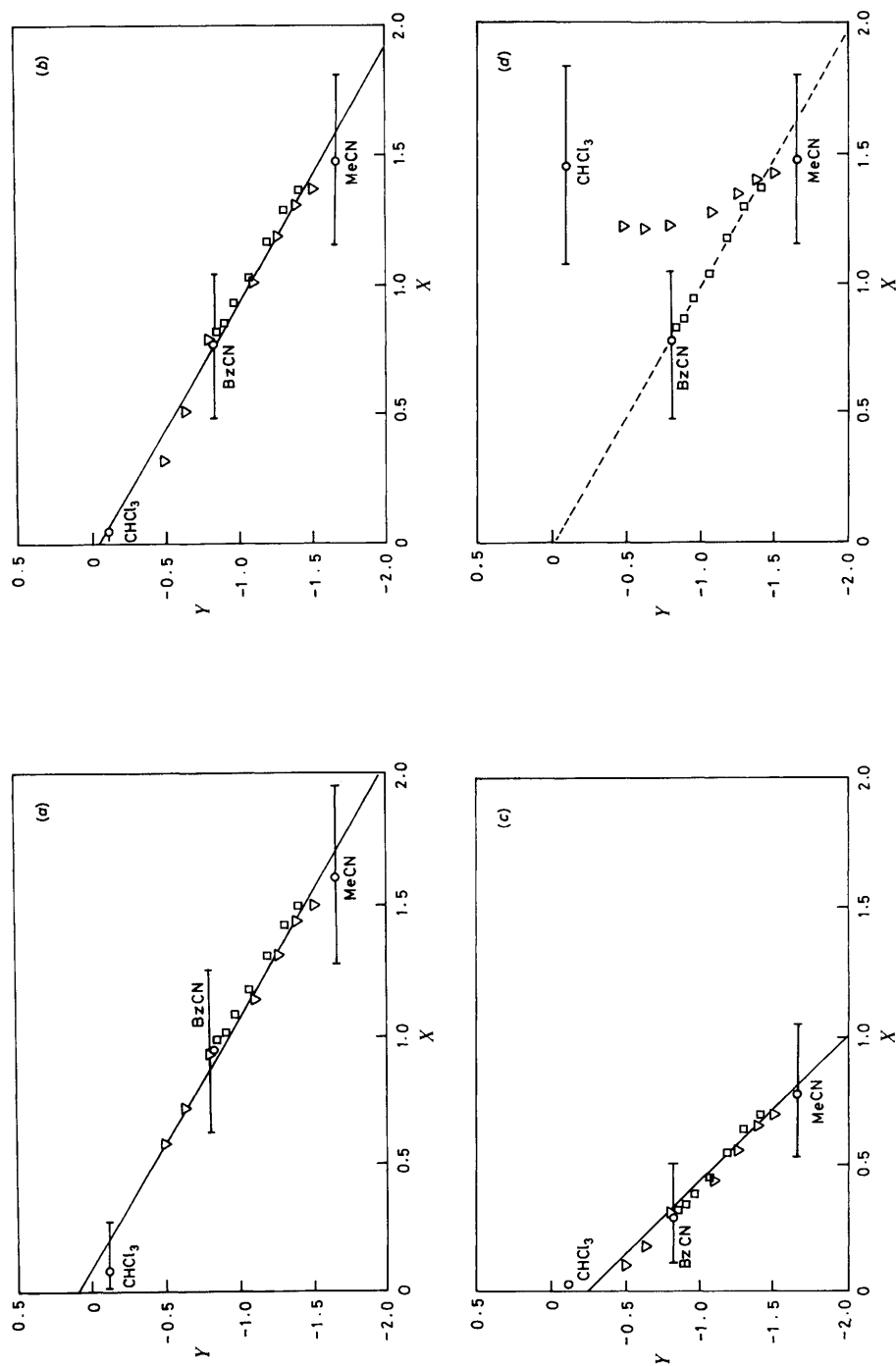


Fig. 2. Same as for fig. 1 except for the solvent mixtures acetonitrile-benzonitrile and acetonitrile-chloroform. The points were calculated from the data in table 5. The open circles refer to the pure solvents; the open triangles to the acetonitrile-chloroform mixtures and the open squares to the acetonitrile-benzonitrile mixtures. (a) Slope = -1.04 , $r = 0.988$; (b) slope = -1.02 , $r = 0.989$; (c) slope = -1.78 ; $r = 0.988$.

Discussion

Our results show that the semiclassical Marcus theory provides a satisfactory explanation of the large solvent effects on the rates of intramolecular electron transfer observed in PAQ, provided that the solvent dependence of the Gibbs energy change and, more importantly, the reorganisation energy, are considered. The data for most of the 16 solvents studied correlate well with the predictions of Marcus theory. The correlation is even better when the bulk solvent dielectric properties are manipulated by varying the composition of binary mixtures.

We have looked at four methods of estimating ΔG° for the electron-transfer reaction from the excited singlet state. The first three (ΔG_0° , ΔG_1° and ΔG_2°) utilise redox potentials measured in each of the solvents with, respectively, no work correction, a solvent-dependent work correction and a constant solvent-independent work correction. The fourth estimate (ΔG_3°) utilises Weller's equation for estimating ΔG_0° in solvents for which electrochemical measurements are not available. We have found that both ΔG_0° and ΔG_1° give a good correlation with Marcus theory, and in particular yield a slope, in plots based on eqn (3b), very close to the predicted value of -1 . ΔG_2° yields a good linear correlation but generates incorrect slopes for $w = 0.1$ – 0.4 eV.

The use of Weller's equation to estimate ΔG° in various solvents does not provide a good correlation of our data with the Marcus theory, primarily because the predicted ΔG° values do not agree well with our experimental values. We therefore consider the use of the Weller equation, as for example by Irvine *et al.*²⁶ and Wasielewski *et al.*,^{5, 27} to be a risky procedure.

It is clear from the data of table 4 that the experimental ΔG_0° values vary less, and less systematically, with solvent ϵ_s than do Weller's ΔG_3° values. Moreover, the range of λ_0 is greater than the range of ΔG_0° , particularly for the solvent mixtures, so λ_0 is the major determinant of X in eqn (3b). We have placed considerable faith in eqn (5a) as a method of calculating λ_0 while we have been critical of Weller's equation, eqn (6d). Since the expressions for λ_0 and ΔG_3° both derive from Coulomb's law and the behaviour of charges in dielectric media, a comment as to why we think eqn (5b) to be more acceptable than eqn (6d) is appropriate.

The solvent reorganisation energy λ_0 is linearly related to the energy that would be required to effect a Franck–Condon transition from the almost non-polar precursor ${}^1\text{P}^*\text{AQ}$ in its equilibrium solvation state to P^+AQ^- surrounded by solvent which retains the pre-existing nuclear coordinates (*i.e.* orientation polarisation) but which has adjusted its electronic polarisation in response to the transfer of the electron. Hence λ_0 is more sensitive to ϵ_{op} and the solvent polarisability than to ϵ_s and the solvent polarity. Indeed, if $\epsilon_s \gg \epsilon_{\text{op}}$, λ_0 is insensitive to ϵ_s [eqn (5b)]. The higher ϵ_{op} , the lower λ_0 because the transferring electron is stabilised by simultaneous adjustment in the electronic polarisation of the medium, which is well described by the continuum property ϵ_{op} .

The Born equation, and hence Weller's equation, reflect the difference in equilibrium orientation polarisation of the solvent. If the solvent is viewed as a continuum, this is sensitive only to ϵ_s . The Born equation is well known to be quantitatively unreliable even for spherical ions in water and the situation is worse for non-aqueous solvents. Strehlow³⁰ quotes extensive data 'to show conclusively that the free energy of transfer of electrolytes from one solvent to another is not simply proportional to the difference of the reciprocal dielectric constants.' In the case of water–methanol and water–dioxane mixtures, 'application of the Born equation could do no more than correctly predict the sign of the free energy of transfer'.³¹

Successful correlation of the thermodynamics of charge-transfer reactions with solvent properties commonly requires three or four parameters, not one.³² Although some dependence on ϵ_s is likely, there are also specific solvent effects. For example,

Q^- is probably stabilised by Lewis acidity in the solvent. On the other hand, the porphyrin moiety of PAQ is sufficiently large that the equivalent of the 'ferrocene assumption'³⁰ might well be made in respect of P^{+}/P , *i.e.* its redox potential might well be taken to be insensitive to the solvent rather than varying systematically with ϵ_s in the manner suggested by the Weller equation.

The acetonitrile–chloroform data provide further evidence of the failure of the Weller equation. The experimentally determined rate constant k_{et} decreases systematically as the solvent is varied from pure chloroform to pure acetonitrile, while the polarity (ϵ_s) rises and the polarisability (ϵ_{op}) falls over the same range. Weller's equation, responsive to ϵ_s , predicts ΔG_3° to become strongly more favourable (negative) over this range. The observed trend in k_{et} is thus inexplicable in terms of ΔG_3° and any linear or quadratic free energy relationship between $\log k_{et}$ and ΔG° in the non-inverted region. In our interpretation, the decrease in k_{et} is caused by the trend in λ_0 from lower to higher values as the solvent polarisability decreases.

Trends similar to those for acetonitrile–chloroform are observed for k_{et} , ϵ_s , ϵ_{op} and λ in the acetonitrile–benzonitrile mixtures. However, the ranges of both ΔG_0° and ΔG_3° are so small that λ_0 controls the range of the predicted rate constants, and the data do not discriminate between the various expressions for ΔG° .

Finally, we note that the electron-transfer rate constant and the position of equilibrium in a reaction such as eqn (1) are controlled by different parameters. Writing k_{et} as k_{et}^f for the forward electron transfer and k_{et}^b for the back electron transfer to ${}^1P^*AQ$

$$\ln\left(\frac{k_{et}^f}{k_{et}^b}\right) = -\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T} + \frac{(-\Delta G^\circ + \lambda)^2}{4\lambda k_B T} = -\frac{\Delta G^\circ}{k_B T} \quad (8)$$

Thus while λ may dominate the predicted range of k_{et}^f and k_{et}^b , it has of itself no influence on ΔG° . To conclude, we therefore think that, while eqn (5a) for λ_0 is reasonable, eqn (6d) is unreliable as a means of estimating ΔG° .

This work was supported by a Strategic Grant in Energy and an Operating Grant from the Canadian Natural Sciences and Engineering Research Council, by a NATO Research Grant to JRB and MDA for International Research Collaboration and by financial support of VPYG by LKB Biochrom Ltd and Trinity College, Cambridge. We are grateful to Dr John S. Connolly of the Solar Energy Research Institute, Golden, Colorado for helpful discussions regarding the data analysis and a critical review of the manuscript.

References

- 1 S. Gaspard, C. Giannotti, P. Maillard, C. Schaeffer and T-M. Trin-Thi, *J. Chem. Soc., Chem. Commun.*, 1986, 1239.
- 2 G. M. Dubowchik and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1986, 1391.
- 3 G. M. Sanders, M. van Dijk, A. van Veldhuizen and H. C. van der Plas, *J. Chem. Soc., Chem. Commun.*, 1986, 1311.
- 4 P. Seta, E. Bienvenue, A. L. Moore, P. Mathis, R. V. Bensasson, P. Liddell, P. J. Pessiki, A. Joy, T. A. Moore and D. Gust, *Nature (London)*, 1985, **316**, 653.
- 5 M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 5562.
- 6 J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, *J. Mol. Biol.*, 1984, **80**, 385.
- 7 C. H. Chang, D. Tiede, J. Tang, U. Smith, J. R. Norris and M. Schiffer, *FEBS Lett.*, 1986, **205**, 82.
- 8 J. A. Schmidt, *Ph.D. Thesis* (The University of Western Ontario, London, Canada, 1986).
- 9 Part 3: J. A. Schmidt, A. Siemiarzuc, A. C. Weedon and J. R. Bolton, *J. Am. Chem. Soc.*, 1985, **107**, 6112.
- 10 J. R. Bolton, J. A. Schmidt, A. Siemiarzuc, M. D. Archer and J. H. Wilford, in *Homogeneous and Heterogeneous Photocatalysis*, ed. E. Pelizzetti and N. Serpone, NATO Advanced Study Institute (Reidel, Dordrecht, 1986); ser. C, vol. 174, pp. 175–187.

- 11 M. D. Archer, V. P. Y. Gadzekpo, J. R. Bolton, J. A. Schmidt and A. C. Weedon, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 2305.
- 12 Part 4: J. A. Schmidt, A. R. McIntosh, A. C. Weedon, J. R. Bolton, J. S. Connolly, J. K. Hurley and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1988, **110**, 1733.
- 13 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
- 14 P. Siders and R. A. Marcus, *J. Am. Chem. Soc.*, 1981, **103**, 748.
- 15 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.
- 16 M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, London, 1975); pp. 10–13.
- 17 B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.*, 1986, **90**, 3657.
- 18 A. Weller, *Z. Phys. Chem.*, 1982, **133**, 93.
- 19 D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834.
- 20 P. Suppan, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 509.
- 21 J. H. Wilford, M. D. Archer, J. R. Bolton, T-F. Ho, J. A. Schmidt and A. C. Weedon, *J. Phys. Chem.*, 1985, **89**, 5395.
- 22 Part 2: A. Siemiarczuk, A. R. McIntosh, T-F. Ho, M. J. Stillman, K. J. Roach, A. C. Weedon, J. R. Bolton and J. S. Connolly, *J. Am. Chem. Soc.*, 1983, **105**, 7224.
- 23 *The Handbook of Chemistry and Physics*, ed. R. C. Weast, (CRC Press, Cleveland, 1985) pp. C52, C136 and C350.
- 24 D. Huppert, H. Kanety and E. M. Kosower, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 161.
- 25 M. Bixon and J. Jortner, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 17.
- 26 M. P. Irvine, R. J. Harrison, G. S. Beddard, P. Leighton and J. K. M. Sanders, *Chem. Phys.*, 1986, **104**, 315.
- 27 M. R. Wasielewski, M. P. Niemczyk, W. A. Svec and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080.
- 28 G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield and J. R. Miller, *J. Phys. Chem.*, 1986, **90**, 3673.
- 29 D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, 1976, **97**, 5111.
- 30 H. Strehlow, in *The Chemistry of Non-aqueous Solvents*, ed. J. Lagowski, (Academic Press, New York, 1966); vol. 1, pp. 129–171.
- 31 J. I. Padova, in *Modern Aspects of Electrochemistry*, ed. B. E. Conway and J. O'M. Bockris (Butterworths, London, 1972); no. 7, chap. 1.
- 32 J. Shorter, *Correlation Analysis of Organic Reactivity, with Particular Reference to Multiple Regression* (Research Studies Press, Chichester, 1982).

Paper 8/01345D; Received 6th April, 1988