

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231401126>

# Intramolecular photochemical electron transfer. 6. Bridge and solvent dependence of electron transfer in covalently linked porphyrin-peptide- quinone compounds

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · SEPTEMBER 1991

Impact Factor: 2.78 · DOI: 10.1021/j100171a035

---

CITATIONS

24

---

READS

52

3 AUTHORS, INCLUDING:



James R Bolton

University of Alberta

314 PUBLICATIONS 9,440 CITATIONS

SEE PROFILE

experimental techniques have verified the importance of selective solvation of small ions.<sup>45</sup> The general approach in distinguishing specific solvation, in studies of nonaqueous ion solvation and more recent electron-transfer studies, is to correlate the change of some macroscopic property of the ion, such as its conductance or its electron-transfer rate, to the composition of binary solvent mixtures. The ecl studies described herein suggests that the specific solvation of ions is not a perquisite of heterogeneous solvent mixtures but may be prominent in homogeneous solutions as well.

(44) Strehlow, H.; Koepp, H.-M. *Z. Elektrochem.* 1958, 62, 373-378.

(45) Burger, K. *Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents*; Elsevier: Amsterdam, 1983.

Our observation that ion-solvent interactions are reflected in the observed ecl efficiencies underscores the significance of a localized solvent microstructure in governing the rates of energetic bimolecular electron-transfer reactions.

**Acknowledgment.** We thank Robert I. Cukier for his useful comments on ion-dipole interactions and James Jackson and Claudia Turro for computational assistance. Financial support from the National Science Foundation (CHE-8705871) is acknowledged. D.G.N. also gratefully acknowledges a Presidential Young Investigator Award administered by the National Science Foundation and the financial assistance provided by the Center for Fundamental Material Research and Dow Chemical Co.

## Intramolecular Photochemical Electron Transfer. 6. Bridge and Solvent Dependence of Electron Transfer in Covalently Linked Porphyrin-Peptide-Quinone Compounds<sup>1</sup>

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

*Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7 (Received: September 21, 1990; In Final Form: April 11, 1991)*

Intramolecular electron transfer (ET) rate constants  $k_{ET}$  for three covalently linked porphyrin-peptide-quinone compounds have been measured in several solvents. The results show that not only "through-bridge", but also "through-solvent" interactions play important roles in the intramolecular ET process. This latter effect is deduced from the observation that aromatic groups, as both side groups in the bridge and in the solvent, appear to induce a significant increase in the ET rate.

### I. Introduction

Covalently linked porphyrin-quinone compounds have proven to be excellent models in which to examine the various factors that influence photoinduced electron transfer (PET) processes.<sup>2,3</sup> There has been considerable debate concerning the role of the bridging group(s) in the electron-transfer (ET) process;<sup>2</sup> however, it is now generally accepted that a superexchange mechanism<sup>4</sup> mediates ET between the donor and the acceptor. In this paper we examine the effect of changing the nature of the bridge and the solvent in a series of linked porphyrin-peptide-quinone molecules (structures are given in Chart I).

Since 1984, when Miller et al.<sup>5</sup> first showed that intramolecular ET rates can be predicted by the Marcus theory, particularly in the inverted region,<sup>6,7</sup> the study of intramolecular ET processes has gained increasing interest.

For nonadiabatic ET the rate constant can be simply expressed as<sup>8,9</sup>

$$k_{ET} = \frac{2\pi}{\hbar} \frac{H_{rp}^2}{(4\pi\lambda k_B T)^{1/2}} \exp\left[-\frac{\Delta G^*}{k_B T}\right] \quad (1)$$

(1) Contribution No. 436, Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

(2) Connolly, J. S.; Bolton, J. R. Intramolecular electron transfer: history and some implications for artificial photosynthesis. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1989; Vol. 4, pp 303-393.

(3) Paper 5. Schmidt, J. A.; Liu, J. Y.; Bolton, J. R.; Archer, M. D.; Gadzekpo, V. P. Y. *J. Chem. Soc., Faraday Trans. 1* 1989, 85, 1027.

(4) Miller, J. R. *Nouv. J. Chim.* 1987, 11, 83.

(5) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* 1984, 106, 3047.

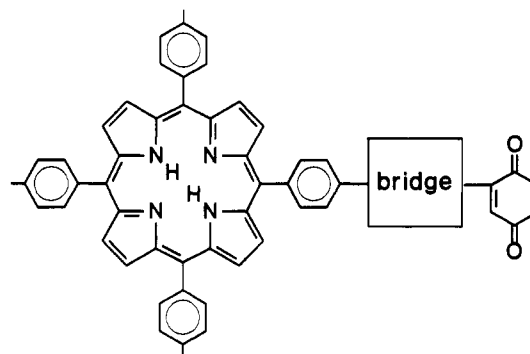
(6) Marcus, R. A. (a) *J. Chem. Phys.* 1956, 24, 966; (b) *Faraday Discuss., Chem. Soc.* 1960, 29, 21; (c) *Annu. Rev. Phys. Chem.* 1964, 15, 155; (d) *J. Chem. Phys.* 1965, 43, 679.

(7) For reviews, see: (a) Sutin, N.; Marcus, R. A. *Biochim. Biophys. Acta* 1985, 811, 265. (b) Bolton, J. R.; Archer, M. D. In *Electron Transfer in Inorganic, Organic and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G. L., Eds.; Advances in Chemistry 228; American Chemical Society: Washington, DC, 1991; Chapter 2, pp 7-23.

(8) Levich, V. G.; Dogonadze, R. R. *Collect. Czech. Chem. Commun.* 1961, 26, 193.

(9) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* 1974, 78, 2148.

CHART I: Molecular Structures of Porphyrin-Peptide-Quinone Molecules



bridge	symbol
	PAQ
	PGQ
	PPAQ

where  $\Delta G^* = [(\Delta G^\circ + \lambda)^2 / 4\lambda]$ , is the Marcus Gibbs activation energy,  $\lambda$  is the reorganization energy,  $k_B$  is the Boltzmann constant, and  $\Delta G^\circ$  is the Gibbs energy change (including Coulomb effects) for the ET reaction. The exponential part in eq 1 is called

the nuclear factor  $\kappa_n$ , and the preexponential part is called the electronic factor  $\kappa_{el}$ .

$H_{rp}$  is the electronic coupling matrix element for the precursor and successor complexes.  $H_{rp}$  is a function of the D-A distance and is usually expressed<sup>10-13</sup> as

$$H_{rp} = H_{rp}^0 \exp[-\beta(r - r_0)/2] \quad (2)$$

where  $r_0$  is the center-to-center distance between D and A when they are in van der Waals contact,  $r$  is the corresponding D-A distance in the molecule of concern,  $H_{rp}^0$  is the electronic coupling term when  $r = r_0$ , and  $\beta$  is a parameter that determines how quickly  $H_{rp}$  falls off with distance.

Two hypotheses have been proposed to explain rapid intramolecular ET reactions over a long distance: a through-bond interaction and a through-space interaction between the donor and the acceptor.<sup>10,11</sup> Since experiments show very small values of  $\beta$ ,<sup>12-15</sup> compared to those predicted by electron tunneling theory through space,<sup>16</sup> ET between D and A must be facilitated by the orbitals of the covalent bridge linking the two moieties, that is, a through-bond mechanism.<sup>4</sup> Many experiments<sup>17-20</sup> have supported the conclusion that through-bond interaction is much more important than through-space interaction.

The effect of solvent on the ET rates is a very complicated factor. The polarity of the solvent changes both the Coulomb stabilization energy for ET in solvents and the relative solvation energy of donor and acceptor; these in turn alter the Gibbs energy of the ET reaction. Also, the medium surrounding the donor and the acceptor can affect the Gibbs activation energy and the time for the reactant to reach the transition state. Finally, solvents may influence the conformation of flexible molecules, which may further change ET rates.

Molecules in which a porphyrin and quinone are covalently connected provide a structure similar to that in the natural photosynthetic reaction center and are very suitable for studying the mechanism of rapid PET reactions. All the molecules of this type generally react by the following mechanism: after the porphyrin chromophore group is excited to its first excited singlet state, electron transfer occurs from the porphyrin to the quinone to form a radical ion pair. ET rate constants are usually obtained from fluorescence lifetimes by use of the equation<sup>21</sup>

$$k_{ET} = \frac{1}{\tau_1} - \frac{1}{\tau_2} \quad (3)$$

where  $\tau_1$  and  $\tau_2$  are the fluorescence lifetimes of the porphyrin respectively with and without ET quenching. Usually  $\tau_2$  is obtained from a molecule of very similar structure, but in which ET does not occur. For example,  $\tau_2$  could be the lifetime of the covalently linked porphyrin-hydroquinone compound.

TABLE I: Fluorescence Lifetimes for P-Q( $\tau_1$ ) and P-QH<sub>2</sub>( $\tau_2$ )

solvent	$\tau^a$ /ns					
	PAQH <sub>2</sub>	PAQ	PGQH <sub>2</sub>	PGQ	PPAQH <sub>2</sub>	PPAQ
EtOAc <sup>b</sup>	12.0	9.5	12.3	10.3	12.3	6.7
1,2-DME <sup>c</sup>	12.5	10.0	12.5	10.5	12.3	9.1
2-MTHF <sup>d</sup>	12.0	9.4	12.0	10.6	12.4	8.8
acetone	12.0	8.9	11.8	10.8	12.0	5.8
CH <sub>3</sub> CN	12.0	7.6	12.0	9.7	12.1	5.5
n-C <sub>3</sub> H <sub>7</sub> CN	12.0	7.2	12.0	9.9		
1-butanol	12.0	3.1	12.0	4.9		
anisole	12.0	2.4	14 ± 1	7.0	11.4	4.6
C <sub>6</sub> H <sub>5</sub> CN	11.5	2.1	11.5	4.8	12.0	5.0
CH <sub>2</sub> Cl <sub>2</sub>	9.1	1.1	9.1	3.1	8.7	2.4
CHCl <sub>3</sub>	9.1	0.4	9.1	2.0	8.7	2.0

<sup>a</sup> ± 0.1 ns unless otherwise indicated. <sup>b</sup> Ethyl acetate. <sup>c</sup> 1,2-Dimethoxyethane. <sup>d</sup> 2-Methyltetrahydrofuran.

Several linked porphyrin-quinone compounds have been synthesized in our laboratory.<sup>21-24</sup> We have chosen to examine various peptide bridges (structures shown in Chart I), since biological ET is thought to occur at least in part along peptide chains. The intramolecular ET rate constants of these molecules were measured in a series of solvents. Our results provide further insight into the ET dependence on the nature of the bridge and on the solvent.

## II. Experimental Section

The three porphyrin-peptide-quinone molecules PAQ, PGQ, and PPAQ examined in this paper have been synthesized by similar methods.<sup>22-24</sup>

The UV absorption spectra of solutions of each porphyrin-hydroquinone compound (P-QH<sub>2</sub>) and porphyrin-quinone compound (P-Q) were run first before the fluorescence lifetime measurements were carried out. For the P-QH<sub>2</sub> compounds, there is a broad peak at 300 nm in the absorption spectrum arising from the absorbance of the hydroquinone entity. After the hydroquinone is oxidized to the quinone entity by lead dioxide, the UV absorbance peak shifts to 246 nm, characteristic of the quinone. When  $A_{246} > 1.8A_{318}$ , we assume that over 80% of the P-QH<sub>2</sub> molecules in the sample have been oxidized.<sup>23</sup>

All the solvents were first distilled and stored over freshly dried molecular sieves for more than 24 h. The fluorescence of pure solvents under the experimental conditions was first checked and no extra emission was observed.

The fluorescence lifetimes of P-Q and P-QH<sub>2</sub> were measured by the time-correlated single-photon counting technique.<sup>25,26</sup> Both laser and flash lamp excitation were used. The excitation wavelength of the flash lamp was adjusted to 418 nm by a monochromator; a Corning 2-58 glass filter (cutoff wavelengths below 620 nm) was used to cut off the scattered light. The laser output was fixed at 570 nm. The laser system consisted of a mode-locked argon laser and a synchronously pumped rhodamine 6G coherent dye laser. The scattered light was cut off by both a Corning 2-58 filter and a 650-nm monochromator.

In the reduced (P-QH<sub>2</sub>) sample no intramolecular ET can occur and usually only one fluorescence lifetime ( $\tau_2$ ) is observed.<sup>27</sup> After the P-QH<sub>2</sub> is oxidized to P-Q, intramolecular ET can occur from the excited singlet state of the porphyrin to the quinone entity. Now the molecule exhibits two fluorescence lifetimes, one

(10) (a) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

(11) Redi, M.; Hopfield, J. J. *J. Chem. Phys.* **1980**, *72*, 6651.

(12) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

(13) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

(14) Guarr, T.; McGuire, M. E.; McLendon, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 5104.

(15) McLendon, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 7811.

(16) Hale, P. D.; Ratner, M. A. *Int. J. Quantum. Chem., Quantum Chem. Symp.* **1984**, *18*, 195.

(17) Pasman, P.; Verhoeven, J. W.; De Boer, J. Th. *Chem. Phys. Lett.* **1978**, *59*, 381.

(18) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127.

(19) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061.

(20) Therien, M. J.; Bowler, B. E.; Selman, M. A.; Gray, H. B.; Chang, I.-J.; Winkler, J. R. In *Electron Transfer In Inorganic, Organic and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G. L., Eds.; Advances in Chemistry 228; American Chemical Society: Washington, DC, 1991; Chapter 12, pp 191-213.

(21) Paper 2. Siemiarz, A.; McIntosh, A. R.; Ho, T. F.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.

(22) Paper 3. Schmidt, J. A.; Siemiarz, A.; Weedon, A. C.; Bolton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6112.

(23) Paper 4. Schmidt, J. A.; McIntosh, A. R.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S.; Hurley, J. K.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1988**, *110*, 1733.

(24) Schmidt, J. A. Ph.D. Thesis, The University of Western Ontario, London, Ontario, Canada, 1986.

(25) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: New York, 1984.

(26) Siemiarz, A.; Wagner, B. D.; Ware, W. R. *J. Phys. Chem.* **1990**, *94*, 1661.

(27) In some solvents, such as anisole, P-QH<sub>2</sub> is partially oxidized by the solvent and there are two fluorescence lifetimes in the P-QH<sub>2</sub> sample. After P-QH<sub>2</sub> was oxidized to P-Q, the amplitude of the short lifetime component was greatly increased.

TABLE II: Electron-Transfer Rate Constants

solvent	$\epsilon_s^b$	$\epsilon_{op}^b$	$\Delta G^\circ(\text{PAQ})^c/\text{eV}$	$\Delta G^\circ(\text{PGQ})^c/\text{eV}$	$k_{ET}^e/(10^8 \text{ s}^{-1})$		
					PAQ	PGQ	PPAQ
EtOAc	6.02	1.876	-0.53	-0.50	0.22	0.16	0.68
1,2-DME	7.20	1.899	-0.47	-0.44	0.20	0.15	0.29
2-MTHF	7.60	1.974	-0.62	-0.60	0.23	0.11	0.33
acetone	20.90	1.839	-0.44	-0.43	0.29	0.078	0.89
CH <sub>3</sub> CN	35.94	1.800	-0.52	-0.51	0.48	0.20	0.99
<i>n</i> -C <sub>3</sub> H <sub>7</sub> CN	24.83	1.910	-0.54	-0.53	0.56	0.18	
1-butanol	17.51	1.953	-0.54	-0.53	2.39	1.2	
anisole	4.33	2.293	-0.57	-0.53	3.3	0.71 $\pm$ 7%	1.3
C <sub>6</sub> H <sub>5</sub> CN	25.20	2.328	-0.49	-0.48	3.9	1.2	1.2
CH <sub>2</sub> Cl <sub>2</sub>	8.93	2.020	-0.61	-0.59	8.0	2.1	3.0
CHCl <sub>3</sub>	4.81	2.082	-0.77	-0.73	24.	3.9	3.9

<sup>a</sup>Data calculated from use of eq 3; error in the rate constants is  $\pm 5\%$  unless otherwise indicated. <sup>b</sup>Static and optical dielectric constants were taken from ref 3. <sup>c</sup>Data calculated from  $\Delta G^\circ = \Delta G_0^\circ - e^2/(4\pi\epsilon_0\epsilon_{op}r_{DA})$ , where values of  $\Delta G_0^\circ(\text{PAQ})$  are from ref 3 (error  $\pm 0.04$  eV). The values of  $\Delta G^\circ$  for PGQ are assumed to be the same as those for PAQ, except for the change in the Coulomb correction term arising from the increased value of  $r_{DA}$  [ $r_{DA}(\text{PAQ}) = 14$  Å;  $r_{DA}(\text{PGQ}) = 17$  Å].

TABLE III: Comparison of the Effect of Donor and Acceptor Distance on the Nuclear and Electronic Factors

solvents	$k_{ET}(\text{PAQ})/k_{ET}(\text{PGQ})^a$	$\lambda(\text{PAQ})^b/\text{eV}$	$\lambda(\text{PGQ})^b/\text{eV}$	$\kappa_n(\text{PAQ})/\kappa_n(\text{PGQ})^c$	$[H_{TP}(\text{PAQ})]^2/[H_{TP}(\text{PGQ})]^2^d$	$\beta^e/\text{\AA}^{-1}$
EtOAc	1.38	0.86	0.93	2.01	0.69	-0.12
1,2-DME	1.33	0.90	0.97	2.26	0.59	-0.18
2-MTHF	2.09	0.88	0.94	1.56	1.34	0.10
acetone	3.72	1.09	1.18	2.37	1.57	0.15
CH <sub>3</sub> CN	2.40	1.15	1.25	2.46	0.98	-0.01
<i>n</i> -C <sub>3</sub> H <sub>7</sub> CN	3.11	1.07	1.16	2.18	1.43	0.12
1-butanol	1.99	1.02	1.10	1.96	1.02	0.01
anisole	4.65	0.57	0.61	1.11	4.19	0.48
C <sub>6</sub> H <sub>5</sub> CN	3.25	0.90	0.97	1.80	1.81	0.20
CH <sub>2</sub> Cl <sub>2</sub>	3.81	0.89	0.96	1.69	2.25	0.27
CHCl <sub>3</sub>	6.15	0.69	0.74	0.98	6.28	0.61

<sup>a</sup>ET rate constant ratio for PAQ and PGQ. <sup>b</sup> $\lambda$  calculated from eq 6.  $r_D = 7$  Å;  $r_A = 4$  Å;  $r_{DA} = 14$  (PAQ) and 17 Å (PGQ). <sup>c</sup>Nuclear factor ratio for PAQ and PGQ, calculated from eq 4. <sup>d</sup>Electronic factor ratio for PAQ and PGQ, calculated from eq 4. <sup>e</sup>Values calculated from eq 5.

(generally of high intensity) from the oxidized P-Q portion, the other (much weaker) from the residue of unoxidized P-QH<sub>2</sub>.

### III. Results and Discussion

The fluorescence lifetimes for all the compounds in the different solvents are given in Table I. The intramolecular ET rate constants were calculated from eq 3. The results are given in Table II.

The solvent dependence for all three peptide-linked porphyrin-quinone compounds is very similar (see Table II). Thus, we can conclude that the effect of the solvent parameters ( $\epsilon_{op}$ ,  $\epsilon_s$ ) and the Gibbs energy changes ( $-\Delta G^\circ$ ) are almost the same for the three compounds (the rate constants decrease by the factor 2–6 between PAQ and PGQ). A detailed study of the solvent dependence of  $k_{ET}$  for PAQ has already been reported.<sup>3</sup> If the ET rate constants for PGQ and PAQ are compared, it is seen that the relative change in  $k_{ET}$  with solvent is about the same for each compound. We thus conclude that the ET rate difference between these two molecules in a given solvent is caused primarily by an increase in the D-A distance, since there is one additional amino acid in the peptide linkage of the PGQ molecule.

Isied and co-workers<sup>28–30</sup> have studied ground-state ET in a series of Ru-Co binuclear complexes, in which the two metal centers are linked via amino acids, involving three atoms in the linkage, or by peptide groups with two or more linked amino acids. They found that  $k_{ET}$  drops by a factor of  $\sim 10^2$  for each additional proline in the peptide bridge. For a three-atom increase in the linkage length, this is a considerably larger factor than was found in our case.

In contrast, Schanze and Sauer,<sup>31</sup> in a study of PET in a series of polypyridyl-Ru(II) complexes linked to *p*-benzoquinone by proline peptide bridges ( $n = 0–4$ ), found that each additional

proline decreased the rate constant by  $\sim 10$ . Cabana and Schanze<sup>32</sup> found similar results in a study of PET in a series of polypyridyl-Re(I) complexes linked to 4-(*N,N*-dimethylamino)-benzoate by proline peptide bridges ( $n = 0–2$ ). The results of these latter two studies are closer to our findings.

It is interesting to examine the variation of  $k_{ET}$  values for the first five solvents of Table III; the rate constants for PPAQ are 1–4 times those in PGQ, and 1–3 times those in PAQ. The PPAQ and PGQ molecules have the same peptide backbone between the porphyrin and quinone entities; the only difference is that PPAQ has a phenyl group in the peptide chain, which can insert between the porphyrin and the quinone entities. Concerning the PPAQ and PAQ molecules, the former has three more bonds between the donor and the acceptor, so the D-A distance in PPAQ is larger than in PAQ. One should thus expect that the ET rate in PPAQ would be smaller than in PAQ; however, the experiments show the contrary result. Clearly the phenyl side group in PPAQ has enhanced the ET rate constant. The overlap of three  $\pi$ -electron systems (donor, acceptor, and bridge) appears to have increased the electronic coupling by a factor necessary to compensate for the increase in the D-A distance.

Of the last four solvents, anisole and benzonitrile are solvents with aromatic rings that may promote orbital overlap of the donor and acceptor. Here the shorter D-A distance in PAQ is probably the determining factor that gives it the larger ET rate, whereas PGQ and PPAQ have almost the same  $k_{ET}$  values. In PPAQ the phenyl side group probably replaces an aromatic solvent molecule, and so  $k_{ET}$  remains about the same, instead of decreasing as is the case in aliphatic solvents.

Methylene chloride and chloroform are both solvents with heavy atoms. The fluorescence lifetimes of both reduced and oxidized molecules are reduced by a heavy-atom effect, but the  $k_{ET}$  calculated from eq 3 is increased as well. It is not known why  $k_{ET}$  is increased in chlorinated solvents. A possible explanation is that

(28) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1726, 1732.

(29) Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443.

(30) Isied, S. S. *Adv. Chem. Ser.* **1990**, No. 226, 91.

(31) Schanze, K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180.

(32) Cabana, L. A.; Schanze, K. S. *Adv. Chem. Ser.* **1990**, No. 226, 101.

chlorine could increase the electronic coupling term  $H_{rp}$  between donor and acceptor, but in temperature-dependent experiments<sup>33</sup> we found that the  $H_{rp}$  values in these solvents are not larger than those in the polar solvents. The experimental data show that the fast ET rates in these solvents are caused by small  $\Delta G^*$  values. Another explanation is that a heavy-atom effect may increase electron spin correlation and thus may increase the transition probability from the singlet excited state to the triplet radical-ion-pair state.<sup>33</sup>

Recently Sutin<sup>34</sup> has pointed out that a variation of the distance between the donor and the acceptor changes not only the electronic factor in  $k_{ET}$ , but also the nuclear factor. In PAQ the center-to-center D-A distance is  $\sim 14$  Å;<sup>3,23</sup> in PGQ it is estimated to be  $\sim 17$  Å.<sup>24</sup> If we take the ratio of  $k_{ET}$  in these two molecules as (see eq 1)

$$\frac{k_{ET}(\text{PAQ})}{k_{ET}(\text{PGQ})} = \frac{[H_{rp}(\text{PAQ})]^2 \lambda(\text{PGQ})^{1/2}}{[H_{rp}(\text{PGQ})]^2 \lambda(\text{PAQ})^{1/2}} \frac{\exp\left[-\frac{[\lambda(\text{PAQ}) + \Delta G^*(\text{PAQ})]^2}{4\lambda(\text{PAQ})kT}\right]}{\exp\left[-\frac{[\lambda(\text{PGQ}) + \Delta G^*(\text{PGQ})]^2}{4\lambda(\text{PGQ})kT}\right]} \quad (4)$$

$$\frac{[H_{rp}(\text{PAQ})]^2}{[H_{rp}(\text{PGQ})]^2} = \frac{\exp[-\beta(r_1 - r_0)]}{\exp[-\beta(r_2 - r_0)]} = \exp[\beta\Delta r] \quad (5)$$

where  $\Delta r = r_2 - r_1$ .

In eq 4 we have assumed that, in a given solvent,  $\Delta G^*$  is slightly reduced in magnitude in PGQ due to the smaller Coulomb correction in that molecule compared to that in PAQ (see Table II).

The reorganization energy  $\lambda$  is usually divided into an inner-sphere term  $\lambda_{in}$  involving vibrational energy changes between the reactant and product states and an outer-sphere term  $\lambda_{out}$  involving the solvent molecule orientation and polarization, so that

$$\lambda = \lambda_{in} + \lambda_{out} \quad (6a)$$

$\lambda_{out}$  can be calculated within the dielectric continuum model by<sup>7</sup>

$$\lambda_{out} = \frac{e^2}{4\pi\epsilon_0} \left[ \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right] \left[ \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right] \quad (6b)$$

where  $r_D$  and  $r_A$  are the radii of the porphyrin and the quinone entities. We estimate  $r_D = 7$  Å and  $r_A = 4$  Å.  $\lambda_{in}$  is fixed at 0.2 eV for both molecules from our previous study.<sup>3</sup> We take  $r_{DA}$  as 14 Å in PAQ and 17 Å in PGQ, since these are the respective average values between the most compact and most extended conformations and thus approximate the most probable molecular conformations.

The calculations in Table III indicate that both the electronic and the nuclear factors depend on the donor-acceptor distance. The ratio of the electronic factors  $\kappa_{el}(\text{PAQ})/\kappa_{el}(\text{PGQ})$  varies strongly with solvent, whereas the ratio of the nuclear factors  $\kappa_n(\text{PAQ})/\kappa_n(\text{PGQ})$  has a small variation with solvent. It is important to note that the contributions from  $\kappa_{el}$  and  $\kappa_n$  to the changes in  $k_{ET}$  are comparable, and in some solvents the nuclear factor dominates. The net result is that we get small (even negative) values for  $\beta$  in most solvents. We note that PAQ and PGQ are flexible molecules, and so the difference in  $r_{DA}$  between them may be smaller than  $\sim 3$  Å. Thus, we probably have overestimated the distance changes in the nuclear factors, but we see that the distance dependence of the nuclear factor cannot be ignored. Our values of  $\beta$  are very much smaller than those obtained in other systems<sup>2</sup> where  $\beta \approx 1.0$  Å<sup>-1</sup>; however, there the distance dependence of  $\kappa_n$  was not considered.

#### IV. Conclusions

Our experimental results indicate again that through-bond interactions are more important than through-space interactions in mediating ET between a linked donor and acceptor. The results also indicate that  $\pi$  electrons play an important role in the ET process. This effect can be manifested either through aromatic groups in the bridge or in the solvent. Both can be explained well by superexchange theory, i.e., a model consisting of supramolecular orbitals of either a donor-bridge-acceptor or donor-solvent-acceptor combination, or more likely a combination of these routes. Also the calculations show that a consideration of the  $\pi$ -electron effect is important in assessing the distance dependence of ET in these types of molecules.

(33) Liu, J. Y.; Bolton, J. R., unpublished work.

(34) Sutin, N. In *Electron Transfer in Inorganic, Organic and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G. L., Eds.; Advances in Chemistry 228; American Chemical Society: Washington, DC, 1991; Chapter 3, pp 25-43.