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Conference Note (Invited)

## The Influence of the Surrounding Medium on Electron Transfer Reactions in Linked Donor-Acceptor Molecules\*

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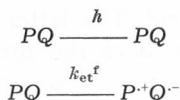
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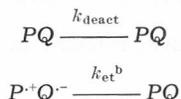
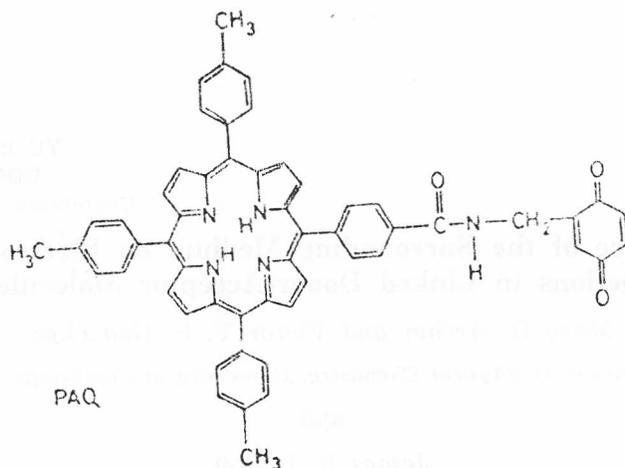
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Several theorists have considered the structural and kinetic factors which control electron transfer processes across interfaces and within defined molecular structures. Considerable insights have been achieved, particularly as to the influence of »inner sphere« geometric parameters on a related set of reactions occurring in a common (usually aqueous) medium. Rather less work has been performed on the effect of the medium itself on a given electron transfer reaction. In this paper, we discuss the effect of the solvent and supporting electrolyte on the kinetics and thermodynamics of intramolecular photochemical electron transfer reactions between the porphyrin (P) and quinone (Q) moieties in a set of covalently linked PQ molecules of restricted geometry, particularly the amide-linked compound PAQ shown below. Photochemical electron transfer reactions in these structures are of particular interest in that they resemble the primary energy-conversion step in photosynthesis.

Fluorescence quenching studies<sup>1</sup> and EPR spectra<sup>2</sup> provide strong evidence that visible-light excitation of molecules such as PAQ is followed by intramolecular electron transfer from the first excited singlet state *P* of the porphyrin to the quinone:



\* Based on an invited lecture presented by M.D.A. at the 7th »Ruder Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces, Red Island — Rovinj, Croatia, Yugoslavia, June 25—July 3, 1986.



The energy of the charge-separated  $P^+Q^-$  state with respect to  $PQ$ , obtained from the electrochemically measured difference in the standard redox potentials of the  $P^+/P$  and  $Q/Q^-$  couples in the linked molecules, is  $\sim 1.37$  eV in both dichloromethane and acetonitrile<sup>3</sup>. The 0—0 singlet excitation energy of  $P^*$  is 1.89 eV whereas the triplet energy is  $\sim 1.45$  eV. Thus formation of  $P^+Q^-$  from the triplet state would be only slightly exergonic, whereas its formation from the singlet  $P^*Q$  state is substantially exergonic, and possibly in the Marcus inverted region. The relevant potential energy surfaces are shown in Figure 1.

Our measured values of  $k_{\text{et}}^f$  for PAQ in 22 solvents of widely differing static ( $D_s$ ) and optical ( $D_{\text{op}}$ ) dielectric constants vary by more than two orders of magnitude<sup>4</sup>. We have considered this pronounced variation in the context of theories which predict the solvent dependence of electron transfer rates. All such theories predict a dependence of  $k_{\text{et}}^f$  on both  $D_s$  and  $D_{\text{op}}$ . Since PAQ is soluble in solvents of widely differing  $D_s$  and  $D_{\text{op}}$ , the solvent dependence of  $k_{\text{et}}^f$  can be tested more exactly than is possible for the redox reactions of inorganic complex ions, which can be examined only in aqueous solution or in solvents of high  $D_s$ . We have examined our data for conformity with various electron transfer theories, including classical Marcus theory<sup>5</sup> and Onsager reaction field theory<sup>6</sup>. The latter gives a better correlation with the observed rate constant than does the former, suggesting that electronic polarization is an important factor in determining the value of  $k_{\text{et}}^f$ . The failure of Marcus theory may imply that the PAQ molecule should be treated as a dipole surrounded by a dielectric continuum rather than as two separately solvated molecules or ions.

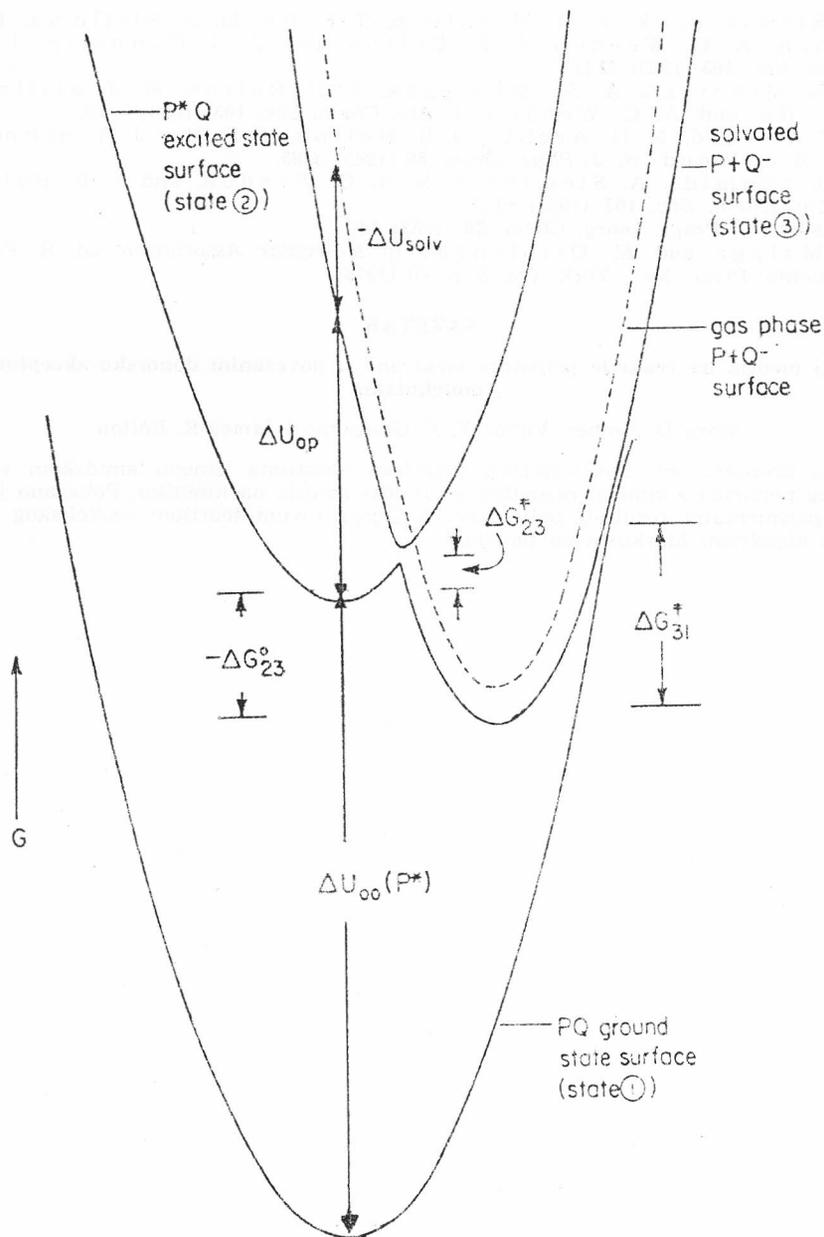


Figure 1. Gibbs energy diagram showing the surfaces for the  $PQ$  ground state (1), the  $PQ$  excited state (2) and the charge-separated  $P^+Q^-$  state (3) as a function of the reaction coordinate.  $U$  is the singlet excitation energy of the porphyrin;  $U_{solv}$  is the solvation energy of the  $P^+Q^-$  state. The gas phase  $P^+Q^-$  curve is not drawn to scale.

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## SAŽETAK

**Utjecaj medija na reakcije prijenosa elektrona u povezanim donorsko-akceptorskim molekulama**

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Na primjeru intramolekularnog prijenosa elektrona između amidskom vezom vezanog porfirina i kinona, razmatra se utjecaj medija na kinetiku. Pokazano je, da se eksperimentalni rezultati bolje slažu s Onsagerovom teorijom reakcijskog polja nego s klasičnom Markusovom teorijom.