# Photoinduced Electron Transfer in the *p*-Phenylenediamine–Paraguat Molecular Complex

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Flash photolysis of the charge-transfer band of the p-phenylenediamine-paraquat complex yields the paraquat radical cation ( $\lambda_{max} = 610$  nm) and the *p*-phenylenediamine radical cation ( $\lambda_{max} = 475$  nm). Since the photoreaction is energetically uphill, back-electron transfer from the paraquat radical to the p-phenylenediamine radical occurs spontaneously, with a rate constant (25 °C) of  $1.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The excited state from which electron transfer occurs is shown not to be  $S_1$  of paraquat ( $E_{S_0-S_1} = 92 \text{ kcal/mol}$ ),  $T_1$  of paraquat ( $E_{S_0-T_1} = 71.5 \text{ kcal/mol}$ ),  $S_1$  of *p*-phenylenediamine ( $E_{S_0-S_1} = 87 \text{ kcal/mol}$ ), or  $T_1$  of *p*-phenylenediamine ( $E_{S_0-T_1} > 44 \text{ kcal/mol}$ ). Failure of a cyanine dye ( $E_{S_0-T_1} = 39.2 \text{ kcal/mol}$ ) and oxygen ( $E_{3_2-1_2} = 22.5 \text{ kcal/mol}$ ) to decrease the radical yield implies that, if the reaction involves a triplet state, it lies lower than 22.5 kcal/mol; otherwise electron transfer originates from a charge-transfer singlet state.

# Introduction

Photolytic excitation of ground-state, charge-transfer complexes can result in electron transfer<sup>1-26</sup>

1.

$$\mathbf{D} \cdots \mathbf{A} \xrightarrow{n\nu} \mathbf{D}^+ \cdot + \mathbf{A}^- \cdot \tag{1}$$

where D = a donor molecule and A = an acceptor molecule. Frequently, the absorption bands of uncomplexed D or A overlap the charge-transfer (CT) band; consequently, much experimental effort is devoted to establish whether or not the photoactive state is a CT state. Few studies<sup>12,15,18,22,26</sup> have gone beyond this point and characterized the electronic structure of the excited state from which electron transfer occurs. This is nontrivial since there can be a variety of excited states populated after light absorption within the spectroscopic CT band. It is convenient to conceptually subdivide these states into five categories: (1)

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CT states which represent electron transfer from the donor HOMO to the acceptor LUMO or electron transfer from other donor orbitals to unoccupied acceptor orbitals,<sup>27</sup> (2) CT states which represent electron transfer from occupied acceptor orbitals to unoccupied donor orbitals, (3) localized excited states of the donor molecule (such as the donor triplet state) somewhat perturbed by complexation to the acceptor, (4) localized excited states of the acceptor molecule perturbed by complexation to the donor, and (5) states arising from different geometric structures of the ground state.

In a more practical vein, the discovery of new, reversible, photoinduced electron-transfer reactions holds the promise of use in photovoltaic or photogalvanic cells.<sup>28,29</sup> Most of the examples of reversible photoinduced electron transfers in fluid solution involve the bimolecular collision of an excited-state molecule with an electron-donating or electron-accepting quencher. The activity of visible-light-absorbing (400-700 nm), ground-state complexes has been largely ignored.

The electron acceptor 1,1'-dimethyl-4,4'-dipyridinium dichloride (paraguat) has been shown by White<sup>30</sup> to form CT complexes in the ground state with amines, phenols, hydroquinones, and sulfides. We are investigating the sepctroscopy and photoinduced transient changes in these paraquat CT complexes, beginning with the *p*-phenylenediamine complex. The study of paraquat complexes should be fruitful for several reasons. First, since excitation into the CT band can be achieved with visible light, the production of high-energy intermediates from such a process might have application in solar energy storage systems. Second, complexation between a neutral organic molecule and an organic dication is rare.<sup>31</sup> (Most CT complexes are formed from two neutral molecules or from oppositely charged ions.) Spectroscopic studies of such complexes may shed more light on the nature of bonding in the ground and excited states. We also thought that these systems would possess especially high quantum yields for photoinduced electron transfer. This follows because the CT first excited singlet (Frank-Condon) state,

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applying the valence bond theory of CT complexes proposed by Mulliken,<sup>32</sup> can be qualitatively considered to be a paraquat radical cation and donor radical cation in the same geometry as the ground state of the complex. These species should have a high probability of dissociation into the bulk solvent due to electrostatic repulsion. (There is some evidence, e.g., ref 20, that, when oppositely charged radicals are produced in a solvent cage, attraction plays a role in reducing the yield of solvated radicals.) Third, this class of complexes can easily be excited without the complication of simultaneously exciting the equilibrium mixture of uncomplexed components. The CT bands are widely red shifted from the electronic absorption bands of paraquat (hereafter denoted  $PQ^{2+}$ ) and from the absorptions of many donors, including *p*-phenylenediamine (hereafter denoted PD), thiourea, catechol, and pyrene; and the spectrum of the one-electron reduced form of paraquat  $(PQ^+)$  has been described.<sup>33</sup> Fourth, this and related complexes are ideal for examining the possibility of photoinduced two-electron transfer (eq 2), since the

$$PQ^{2+} \cdots PD \xrightarrow{h\nu} PQ: + PD^{2+}$$
 (2)

doubly reduced form of paraquat (PD:) is stable,<sup>34</sup> and doubly oxidized phenylenediamines have been prepared.<sup>35,36</sup>

This paper describes the study of some ground-state and excited-state properties of  $PQ^{2+}\cdots PD$ . The following results are discussed: in acetonitrile-water the complex has a 1:1 stoichiometry; there is a significant blue shift in the CT bond energy,  $\nu_{CT}$ , with decreasing solvent polarity; one-electron transfer occurs on excitation into the CT band; an energy-level diagram for the lowest excited states of the complex and its component molecules can be constructed.

# **Experimental Section**

Reagents. Pure PD was obtained by dissolving pphenylenediamine hydrochloride in water and precipitating out free amine with NaOH. The filtered product was recrystallized several times from water containing NaHSO<sub>3</sub> to prevent oxidation. PD must be stored under a nitrogen atmosphere and freshly recrystallized before experimentation; otherwise, impurities will promote photochemical side reactions. PQ<sup>2+</sup> was obtained from Aldrich Chemical Co. and recrystallized from ethanol. Doubly reduced paraquat (PQ:) (1,1'-dimethyl-1,1'-dihydro-4,4'-bipyridyl) was prepared by Na<sub>2</sub>S<sub>2</sub>O<sub>6</sub> reduction of an aqueous solution of PQ<sup>2+</sup> at pH 9–10 in a nitrogen atmosphere.<sup>30</sup> The resulting PQ: was extracted with toluene, and the solution stored under a nitrogen atmosphere. The solvent system used for all experiments unless specified was a mixture of acetonitrile (Eastman Spectrograde) and singly distilled water in a volume/volume ratio of 6:19. Methanol (Mallinckrodt Reagent) was distilled from sodium methoxide under a nitrogen atmosphere. Toluene was Baker Reagent grade.

Spectroscopy. All ultraviolet-visible absorption spectra were taken on the Beckman Acta C III spectrophotometer using a cuvette which enabled samples to be prepared and analyzed under a nitrogen atmosphere. Low-temperature and room-temperature emission spectra were obtained on



**Figure 1.** (—) 1.0 × 10<sup>-4</sup> M *p*-phenylenediamine in CH<sub>3</sub>CN-H<sub>2</sub>O (12:38). (– – –) 1.5 × 10<sup>-4</sup> M paraquat in CH<sub>3</sub>CN-H<sub>2</sub>O (12:38). (×) Charge-transfer complex in CH<sub>3</sub>CN-H<sub>2</sub>O (12:38), extinction coefficients unknown.

a Perkin-Elmer Model 44-A spectrofluorometer. A chopper assembly was used to distinguish between phosphorescence and fluorescence.

Flash Photolysis. The conventional flash photolysis apparatus was constructed at the University of California-Santa Cruz. The flash tube (Xenon Corp. N-108C) and a  $15 \times 1$  cm Pyrex sample cell were held at the focal points of an elliptical aluminum cavity by ebonite brackets. Up to 100 J of excitation energy (20- $\mu$ s duration) could be supplied by a Xenon Corp. Model 457A micropulser. The cavity design caused excitation radiation to pass through appropriate glass filters and then through the 1-cm width of the sample cell. Changes in transmittance of the solution at a single wavelength as a function of time were monitored by light from a 150-W quartziodine dc lamp passing through the 15-cm cell length into a 0.25-m monochromator (Oriel Model 7240, slit width = 5 nm) and then a 1 P28 photomultiplier tube. Oscilloscope scans of the photomultiplier output voltage were recorded on Type 47 Polaroid film. Unless specified, sample solutions were saturated with nitrogen.

#### Results

Nature of the Complex. When a molecule of relativity high electron affinity aggregates with a molecule of relatively low ionization potential such that there is transfer of electronic charge from the donor molecule to the acceptor but no bonds are broken in either component, the species is called a CT complex. The appearance of a new electronic transition upon mixing the components, without strong perturbation of the original spectroscopic transitions of the components, is often taken as evidence for the existence of a CT complex.

Upon mixing paraquat and PD in an acetonitrile-water mixture (6:19 volume ratio), there appears a new electronic absorption band ( $\lambda_{max} = 475$  nm) which is not present in the isolated components (Figure 1). We attribute this new absorption to formation of a 1:1 PQ<sup>2+</sup>...PD CT complex for the following reasons. (1) The original absorption bands of PQ<sup>2+</sup> and PD are not shifted in frequency in the mixture. (2) A Job's plot<sup>37</sup> of absorbance at 475 nm vs. mole fraction of PD has a maximum at mole fraction = 0.5 (Figure 2), indicative of 1:1 complex stoichiometry. (3)  $\nu_{CT}$  is sensitive to solvent polarity as is often observed with CT complexes (see Table I, the Discussion, and footnotes 38 and 39). There is a good correlation with (D-1)/2D

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**Figure 2.** Job's plot of CT absorption band at constant total concentration of  $PQ^{2+}$  and PD, with a variation of mole fraction of PD.



Figure 3. Frequency of the CT band at maximum intensity vs. a dielectric constant function.

TABLE I: Charge-Transfer Band Frequency in Various Solvents and Solvent Mixtures

solvent	$\nu_{\rm CT}$ , cm <sup>-1</sup>	$D^a$	n <sup>b</sup>
CH <sub>3</sub> CN/H <sub>2</sub> O, 12/38 v/v CH <sub>3</sub> OH/H <sub>2</sub> O, 1.29/5 v/v	21 052 21 052	69 69	1.744
$CH_3CN/H_2O, 78/24 v/v$ $CH_3CN/H_2O, 4/1 v/v$ $CH_3OH, neat$ $C_2H_5OH, neat$	19 607 19 417 18 248 17 605	52 44.9 32.7 24	1.749 1.759 1.690 1.813

<sup>a</sup> D = dielectric constant, from ref 58. <sup>b</sup> n = refractive index, determined on a Bausch and Lomb refractometer.

+ 1) (Figure 3), but there is not smooth variation with refractive index. (4) The 475-nm absorption appears within time of mixing as monitored by conventional spectrophotometry (3 s). CT complexes are anticipated to form rapidly (with nearly diffusion-controlled rate constants) because little structural or electronic change in the components occurs on complexation. (5) The equilibrium constant of the complex was determined by



Figure 4. (-O-) Transient spectrum produced by flash photolysis of paraquat phenylenediamine. (---) Absorption spectrum of paraquat cation radical in CH<sub>3</sub>CN.<sup>29</sup>

White<sup>30</sup> to be 15.4 M<sup>-1</sup> in methanol, and in acetonitrilewater (this work) it was determined to be 8.0 M<sup>-1</sup>. Constants less than 200 are invariably observed for organic CT complexes. (6)  $\nu_{\rm CT}$  for paraquat complexes with a variety of neutral donors, including PD, varies linearly with  $\nu_{CT}$ for benzoquinone with the same donors.<sup>30</sup> (Methanol is the solvent.) Such behavior is expected from the theo-retical equation  $h\nu_{\rm CT} = I^{\rm D} - E^{\rm A} - C.^{40,41}$   $I^{\rm D}$  is the donor ionization potential,  $E^{\rm A}$  is the acceptor electron affinity, and C is a sum which represents CT resonance energy and the difference in non-charge-transfer bonding energies (polarization, Coulombic forces) between ground and excited state.

It was necessary to maintain solutions of PD under an atmosphere of nitrogen, even when complexed with PQ<sup>2+</sup>. to prevent slow air oxidation. Solutions prepared under nitrogen show no evidence of paraguat radical<sup>33</sup> or oxidized PD.<sup>42</sup> Incidentally, both components are very soluble in the acetonitrile-water mixture. Methanol was found to be unsuitable as a solvent for photochemical studies.<sup>43</sup>

Flash Photolysis of the CT Band. Flash photolysis of  $2 \times 10^{-2}$  M PD and  $2 \times 10^{-2}$  M PQ<sup>2+</sup> in acetonitrile–water with excitation wavelengths greater than 360 nm results in transient absorption and decay. The absorption spectrum of the intermediate 100  $\mu$ s after the flash begins is shown in Figure 4. The reaction was completely reversible, and both the absorption magnitude and the decay kinetics were unaffected by 15 consecutive flashes. When a flash cell equipped with a side-arm cuvette was used, it was determined spectrophotometrically that photolysis did not cause any destruction of the CT complex. We assign the transient spectrum as a composite of the paraquat radical and the *p*-phenylenediamine radical (Figure 7) arising from reaction 3.

$$PQ^{2+} \cdots PD \xrightarrow{n\nu} PQ^{+} \cdot + PD^{+} \cdot$$
(3)

<sup>(38)</sup> There is no correlation between the solvent refractive index and  $\nu_{CT}$ ; a correlation is expected for nonpolar ground states (K. M. C. Davis in "Molecular Association", Vol. 1, R. Foster, Ed., Academic Press, London, 1975, pp 156-7).

<sup>(39)</sup> A slight discrepancy has been found between our results and those of B. G. White, ref 28. White reports  $\lambda_{max}$  of the complex as 555 nm in methanol while our result is 548 nm.

<sup>(40)</sup> R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, 1969, p 37.

<sup>1</sup> ress, ivew 10rK, 1969, p 37. (41) For a series of paraquat or benzoquinone (BEN) complexes with various electron donors, D,  $h_{VCT}(p_{2}^{\circ 2+}...p) = I^{D} - E^{PQ^{2+}} - C_1$  and  $h_{VCT}(r_{BEN}...p)$ =  $I^{D} - E^{BEN} - C_2$ . If  $E^{PQ^{2+}} + C_2 = E^{BEN} + C_1$ , then  $\nu_{CT}(p_{Q}^{\circ 2+}...p) = \nu_{CT}(BEN...p)$ . A plot of  $\nu_{CT}(p_{Q}^{\circ 2+}...p)$  vs.  $\nu_{CT}(BEN...p)$  should be linear with slope = 1

<sup>(42)</sup> F. Brady and M. S. Burns, J. Soc. Cosmet. Chem., 19, 361 (1968). (43) While the complex is thermally stable in methanol, flash photolysis resulted in irreversible photochemical change, possibly due to methanol acting as an electron donor. (The singlet state of PQ2+ has been shown by Ledwith et al., Chem. Commun., 494 (1970), to accept an electron from alcohols). In acetonitrile-water, only reversible photochemical reaction occurs.



Figure 5. Second-order kinetic plot of PQ<sup>2+</sup>···PD transient decay at 585 nm.

The radicals decayed by second-order kinetics (Figure 5), which indicates that the radical products have separated into the bulk solvent. When the PQ<sup>+</sup> extinction coefficient of  $1.06 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> at 610 nm<sup>33</sup> is used, a second-order rate constant of  $1.01 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> is calculated. The transient absorbance at 610 nm (where only PQ<sup>+</sup> absorbs) is 0.45. From this value, an extinction coefficient of  $2.35 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> is obtained for PD<sup>+</sup> at 475 nm.<sup>44</sup>

In order to examine the likelihood of detecting reaction 2 if it were to occur, we determined the extinction coefficient of PQ: for its 400-nm band. A toluene solution PQ: of known absorbance was added to an aqueous solution containing a large excess of  $PQ^{2+}$  under nitrogen. The disproportionation reaction 4 occurred,<sup>45</sup> and the concen-

$$PQ: + PQ^{2+} \to 2PQ^{+}$$
 (4)

tration of the resulting PQ<sup>+</sup> was determined spectrophotometrically. An extinction coefficient for PQ: of  $4.9 \times 10^3$  $M^{-1}$  cm<sup>-1</sup> at 400 nm is calculated. In a typical flash photolysis experiment  $2 \times 10^{-6}$  M PQ<sup>+</sup> is produced. Since we did not observe absorbance in the region of 400 nm resembling that for PQ:, an upper limit on the concentration produced yet undetected in flash photolysis is  $1.4 \times 10^{-7}$ M.

Photoreaction 3 can occur when only the CT band is irradiated and no exciting light is absorbed by localized  $PQ^{2+}$  and PD: chromophores. Flash excitation at wavelengths greater than 410 nm produces a substantial concentration of radicals even though the absorbance of uncomplexed  $2 \times 10^{-2}$  M PD: or  $2 \times 10^{-2}$  M PQ<sup>2+</sup> is identically zero in this region. Also, flash photolysis of  $2 \times 10^{-2}$ M PD: using the same 410-nm cutoff filter showed no PD<sup>+</sup> absorption, even though PD: excitation with ultraviolet light leads to PD<sup>+</sup> formation with high efficiency (see below). Finally, at constant PD concentration the



**Figure 6.** (---) Translent produced by flashing PD with NaHSO<sub>3</sub> in  $CH_3CN-H_2O$  (12:38) and using no filters. (---) translent produced by flashing PD in  $CH_3CN-H_2O$  (12:38) without NaHSO<sub>3</sub> or filters.



**Figure 7.** Transient spectrum produced by photolysis of  $5.54 \times 10^{-3}$  M PD and  $1.12 \times 10^{-2}$  M NaHSO<sub>3</sub>.

radical yield on flash photolysis increases symbatically with  $PQ^{2+}$  concentration, and at constant  $PQ^{2+}$  concentration the radical yield increases with PD concentration; this is consistent with  $PQ^{2+}\cdots PD$  complexation prior to electron transfer.

Flash Photolysis of PD. Flash photolysis of  $5 \times 10^{-3}$  M PD: in acetonitrile-water with ultraviolet light between 280 and 380 nm under a nitrogen atmosphere gives absorption changes in the region of 400–550 nm. A possible reaction sequence is

$$PD \xrightarrow{h_{\nu}} PD^+ + e_s^-$$
 (5)

 $e_s^-$  + solvent, residual O<sub>2</sub>, impurities  $\rightarrow$ 

radical products (6)

radical products + 
$$PD^+ \rightarrow PD$$
 (7)



The initial increase in absorbance and partial relaxation is assigned to reactions  $5^{46}$  and 7. The irreversible increase in absorbance is assigned to reaction 8, the absorption spectrum of the irreversible photolysis product matches

<sup>(44)</sup> Two reviewers were suspicious of the similarity of  $\lambda_{max}$  for the species assigned as PD<sup>+</sup> and  $\lambda_{max}$  of the CT complex. However, we believe that the difference in bandwidth (72 nm = width at half-maximum absorbance for the species assigned to PQ<sup>+</sup>.; for PQ<sup>2+</sup>...PD the width at half-maximum is greater than 200 nm) establishes that they are different species.

<sup>(45)</sup> From the data in ref 30, reaction 4 is calculated to have a standard free-energy charge of -8.28 kcal.

<sup>(46)</sup> Solvated electron ejection by the first excited singlet state of the N,N,N',N'-tetramethyl-substituted form of *p*-phenylenediamine has been documented. See N. Yamamoto, Y. Nakato, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **39**, 2603 (1966).



Figure 8. Uncorrected emission and excitation spectra: (---) fluorescence excitation spectrum of PD ( $\lambda_{em}$  = 477 nm); (---) emission spectrum of PD ( $\lambda_{ex}$  = 312 nm, fluorescence and phosphorescence); (X) phosphoresence emission spectrum of PD ( $\lambda_{ex}$  = 312 nm, chopper on). All spectra taken at 77 K in a cracked glass of CH<sub>3</sub>OH/glycerol (1:2).

that of a solution of PD: oxidized by  $H_2O_2$  at pH 9-10. This chemical product has been identified by Brady and Burns.42

When  $2.5 \times 10^{-2}$  M sulfite anion is added to the PD: solution before photolysis, the absorption change becomes totally reversible (Figure 6). The transient absorption spectrum immediately after the pulse is shown in Figure 7 and is seen to be identical with the difference between the paraquat radical spectrum and the transient absorption spectrum obtained from exciting the CT complex (Figure 4). We assign the transient in the presence of sulfite ion as due to reactions 5, 7, and 9. Reaction 9 acts to rapidly  $2PD^+ + HSO_3^- + H_2O \rightarrow 2PD: + HSO_4^- + 2H^+$ (9)

consume PD<sup>+</sup>, thus preventing polymerization (reaction 8).

Reaction 5 most likely originates from the PD: singlet state since both  $O_2$  (2 × 10<sup>-4</sup> M) and 3,3'-diethylthiacarbocyanine iodide  $(1 \times 10^{-4} \text{ M})$  have no effect on the PD<sup>+</sup>· yield. O<sub>2</sub> is a generally good scavenger of aromatic triplet states.<sup>47,48</sup> Since the T<sub>1</sub>–S<sub>0</sub> energies of both the cyanine dye (39.2 kcal/mol<sup>49</sup>) and molecular oxygen (37.5 kcal/mol for  ${}^{3}\Sigma_{g} \rightarrow {}^{1}\Sigma_{g}$  and 22.5 kcal/mol for  ${}^{3}\Sigma_{g} \rightarrow {}^{1}\Delta)^{50}$ are lower than that of PD (esimated below as 44 kcal/mol), they are capable of deactivating PD triplets by energy transfer. Failure to affect the PD<sup>+</sup> yield is thus evidence that reaction 5 is not a triplet-state reaction.

Effect of O<sub>2</sub> and 3,3'-Diethylthiacarbocyanine Iodide on Reaction 3. Flash photolysis of  $2 \times 10^{-2}$  M PD and 2  $\times 10^{-2}$  M PQ<sup>2+</sup> in acetonitrile–water gives the same radical yield whether performed under a nitrogen atmosphere or air, although the rate of radical decay is increased by the presence of air, presumably because of reaction 10. The

$$PD^+ \cdot + O_2 \rightarrow PQ^{2+} + O_{2-} \tag{10}$$

presence of  $1 \times 10^{-5}$  M 3,3'-diethylthiacarbocyanine iodide does not alter the radical yield or affect the radical decay kinetics.

Scheme I

$$PQ^{2+} \cdots PD \xrightarrow{n_{\nu}} PQ^{+} + PD^{+}$$

$$catolyst \\ H^{+}$$

$$PQ^{2+} + \frac{1}{2}H_2 PD + M^{(n+1)+}$$

 $M^{n+}$  = transition metal catalyst

These results demonstrate that the excited-state origin of reaction 3 is not a localized triplet state of  $PQ^{2+}$  ( $E_{S_0-T_1} = 71 \text{ kcal/mol}^{51}$ ) or PD ( $E_{S_0-T_1} > 44 \text{ kcal/mol}$ ) since the triplet energy of both reagents would have been quenched by the dye or oxygen. In addition, we can conclude that, if reaction 3 occurs from a triplet exciplex, it must lie lower in energy than 22.5 kcal/mol.

Emission Spectra. In a glycerin-MeOH (2:1 v/v)cracked glass at 77 K, PD exhibits a fluorescence emission maximum at 366 nm and a phosphorescence emission maximum at 446 nm (Figure 8). From the onset of phosphorescence at 648 nm we estimate<sup>52</sup>  $E_{S_0-T_1}$  as > 44 kcal/mol. The energy midpoint between the lowest-energy PD absorption band and the PD fluorescence band is 87 kcal/mol, an estimate of  $E_{S_0-S_1}$ . Irradiation of the PQ<sup>2+</sup>...PD CT band does not result in any emission in the region 400-900 nm.

### Discussion

These studies confirmed our expectation that excitation into the CT band of the PQ<sup>2+</sup>...PD complex would lead to one-electron transfer and formation of solvated radicals. This phenomenon was first demonstrated by Kosower<sup>4</sup> for a complex of oppositely charged ground-state components, N-ethyl-4-carbomethoxypyridinium iodide; other workers<sup>12,15,18</sup> demonstrated the phenomena for complexes of neutral ground-state components. This is probably the first report of photoinduced electron transfer for the charge type (+2,0).

Several properties of the photoreaction give it potential for solar energy storage. (1) Energy is stored momentarily in the form of radicals. This is on the order of 20 kcal/mol, an estimation made by using the reversible redox potentials of N,N'-dimethyl-p-phenylenediamine<sup>36</sup> (the PD redox potential is not reversible)<sup>36</sup> and  $PQ^{2+,34}$  (2) The reaction is quantitatively reversible. (3) Light can be absorbed by the complex in the region of maximum solar intensity, 500-750 nm. (4) The complex is soluble in polar solvents, including water, allowing the system to be tested for photogalvanic response. A drawback to effective energy storage is the rapidity of back-electron transfer. This might be retarded by addition of micelles<sup>53</sup> or other changes in the reaction medium. Alternatively, the radicals could be used to create other, more long-lived, high-energy species, as in Scheme I. Catalysis of electron transfer from  $PQ^+$  to  $H^+$  with Pt asbestos has been demonstrated.<sup>54</sup> We have tried using  $Fe^{2+}$  to reduce  $PD^+$ , but the metal ion quenches the photoreaction.

One objective of this study was to determine the nature of the excited state from which electron transfer occurs. Figure 9 is a qualitative energy diagram for the lowestenergy, excited-state transitions. A CT singlet state is the most likely precursor of electron transfer, based upon Figure 9 and failure of  $O_2$  and cyanine dye to quench the photoreaction. A very low-lying CT triplet state, however,

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<sup>(48)</sup> O. L. J. Gijzeman, P. Anderson, F. Anderson, F. Anderson, J. G. (1973).
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<sup>(52)</sup> N. J. Turro, "Modern Molecular Photochemistry", Benjamin/ Cummings, Menlo Park, 1978, p 114.

<sup>(53)</sup> D. Meyerstein, J. Rabini, M. S. Matheson, and D. Meisel, J. Phys. Chem., 82, 1879 (1978).

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Figure 9. Energy diagram for processes relevant to PQ2+...PD excited-state behavior.



Figure 10. A possible symmetrical structure for the PQ<sup>2+</sup>...PD complex. The components are drawn to scale by using the bond distances for PQ2+ cited in ref 59 and using the N-C and C-C bond distances for TMPD cited in ref 60.

cannot be ruled out. It is reassuring to find that electron transfer occurs upon light excitation in a polar solvent and furthermore that no CT emission is observed; this is common singlet exciplex behavior. (We were unable to look for emission in nonpolar solvents because of the low solubility of paraquat.)

An interesting feature of the visible spectrum of the complex is the moderately large hypsochromic shift of the CT band with increasing solvent polarity (Table I). To our knowledge, there are only two other studies of the effect of solvent on  $v_{CT}$  for a complex containing a neutral donor molecule and a cationic acceptor. White<sup>30</sup> noticed that for  $PQ^{2+}$ ...hydroquinone,  $\nu_{CT}$  changed from 22880 to 24510 cm<sup>-1</sup> on changing the solvent from methanol (D =32.7) to water (D = 78.5). Complexes of tropylium cation with neutral donors such as pyrene and phenothiazine, on the other hand, are insensitive to solvent polarity.<sup>55</sup>

Hypsochromic shifts are usually observed for CT complexes which are ion pairs in the ground state (gs) and which are neutral in the excited state (es). That is

$$\Psi_{gs} = a\Psi_{D^+A^-} + b\Psi_{D\cdot A}, \qquad a \gg b \tag{11a}$$

$$\Psi_{\rm es} = a^* \Psi_{\rm D^+A^-} + b^* \Psi_{\rm D\cdot A}, \qquad b^* \gg a^* \qquad (11b)$$

(55) (a) T. G. Beaumont and K. M. C. Davis, J. Chem. Soc. B, 1010 (1968); (b) M. Feldman and B. G. Graves, J. Phys. Chem., 70, 955 (1966). The energy of the ground state is said to be lowered by interaction between the dipole of the complex and solvent dipoles. As D increases,  $\nu_{\rm CT}$  should also increase. However, for  $PQ^{2+}\cdots PD$ , the ground state probably only possesses a small ion-induced dipole within the complex, perpendicular to the molecular planes of the components (see Figure 10 and footnote 56), caused by polarization of the system or nitrogen lone pair toward  $PQ^{2+}$ . This dipole should be absent in the excited state since  $PQ^{2+}$  is not expected to be a strong electron acceptor (the one-electron reduction of PQ<sup>+</sup> occurs at -1.04 V vs. SCE<sup>34</sup>). A fairly good correlation of  $v_{\rm CT}$  with (D-1)/(2D+1), expected for this model,<sup>57</sup> is in fact observed (Figure 3).

Another contribution to absorbance shift may come from the difference in ion solvation energy in the ground vs. excited state. In the ground state, the complex will be surrounded by solvent molecules with the negative end of their dipoles pointing toward the positive field. This will be especially strong near quaternary nitrogen. (A region of high solvent dipole alignment was termed the cybotactic region by Kosower.<sup>4</sup>) In the excited state, positive charge moves away from PQ<sup>2+</sup> toward PD and thus away from the region of high alignment. Since nuclear motion such as solvent reorganization does not occur within the time of a Frank-Condon transition, the cybotactic region, which is oriented toward minimum energy for the ground-state electronic distribution, will actually cause destabilization of the excited state. Destabilization will be greatest for most strongly oriented solvent (highest D).

One final contribution to the solvent shift may be the lowering of the energy of free PD ground state (an increase in its ionization potential and therefore an increase in  $\nu_{\rm CT}$ according to the equation  $h\nu_{\rm CT} = I_{\rm D} - E_{\rm A} - C^{40,41}$ ) by the solvent. Evidence for this is found in the shift of the 315and 243-nm bands of PD in cyclohexane to 303 and 238 nm in water.

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<sup>(56)</sup> The proposed structure in Figure 10 is reasonable since the LUMO of PQ<sup>2+</sup> is a  $\pi^*$  orbital, which can interact with the  $\pi$  HOMO of PD. Also, the tetramethyl derivative of PD (TMPD) generally acts as a  $\pi$  donor. (Z. G. Soos and D. J. Klein in "Molecular Association", R. Foster, Ed., Academic Press, London, 1975; ref 32, Chapter 8; C. K. Prout and B. Kamenov, Mol. Complexes, 1 (1973).

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