PHOTOCHEMICAL CHARGE TRANSFER PHENOMENA - PICOSECOND LASER PHOTOLYSIS STUDIES

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Abstract – Fundamental aspects of the photoinduced charge transfer and charge separation processes have been discussed on the basis of the pico-second laser photolysis studies of some typical intra- and intermolecular exciplex systems, excited singlet state of EDA complexes and monophotonic electron ejection of some low ionization potential diamines in polar solvents. Picosecond laser studies have been extended to the biologically important porphyrin-quinone systems. Short-lived porphyrin-quinone exciplex can be observed in nonpolar solvent, but solvation-induced ultra-fast deactivation of the electron transfer state takes place in strongly polar solvents. It has been demonstrated that such ultrafast deactivaiton can be avoided by constructing intramolecular exciplex systems of por-phyrin and quinone combined by methylene chains and that more efficient charge separation can be acieved by two step electron transfer along the redox potential gradient in the systems with two kinds of quinones combined in series. Moreover, some related reaction processes such as hydrogen transfer due to the charge transfer followed by proton transfer, charge transfer interaction in the excited hydrogen bonding systems and coupling of the trans→cis photoisomerization with the intramolecular charge transfer have been investigated with picosecond laser spectroscopy.

INTRODUCTION

Photoinduced charge transfer (CT) or electron transfer (ET) phenomena are very important from various viewpoints including problems in chemistry and biology as well as solid state physics. For example, excitation trapping in some solids are fequently associated with CT interaction and quite many fundamental problems in the excited state chemistry are related with inter- and intramolecular photoinduced CT. Moreover, many important photobiological processes cannot be discussed without resorting to the photoinduced CT or ET. The most representive example is the photoinduced ET in the bacterial and green plant photosynthesis, although its mechanism is still not clear.

Since the elementary process of the photoinduced CT and related ones are very rapid in general, picosecond (ps) or subps laser photolysis methods are very effective for the eluci-dation of their microscopic and dynamical mechanisms. We are investigating photoinduced CT phenomena in solution by means of ps laser photolysis and transient absorption as well as fluorescence measurements and also ps laser induced photocurrent studies.

We have investigated, for example, the following problems by ps and ns laser photolysis method.
(1) Elementary processes of photochemical CT and charge separation (CS) processes in some exciplex systems and excited state of EDA (electron donor acceptor) complexes of such systems as aromatic hydrocarbon-amine or aromatic hydrocarbon-cyano-compounds as well as biologically important molecules like porphyrin-quinone or flavin-indole (2a,b,d,3-9, 10a,b,d,11,12,18c, 19,20).
(2) Direct observation and elucidation of the mechanisms of electron photoejection process from low ionization potential amine molecules such as TMPD (N,N,N',N'-tetramethyl-p-phenylene diamine) in polar solvents, and ps multiphoton ionization of pure liquids such as alcohols and benzene (13-16,26).
(3) Reaction processes coupled with the photoinduced CT such as formation of the triplet state of electron donor or acceptor from the CT state (9a,21,22), proton transfer coupled with photoinduced CT resulting in the hydrogen abstraction reaction (21), photocycloaddition reaction via exciplex state (27) and trans→cis photoisomerization reaction coupled with the intramolecular CT interaction in the singlet excited state (25).

In the following, some results of these investigations will be given and discussed.

I. PHOTOCHEMICAL ELECTRON TRANSFER AND CHARGE SEPARATION PROCESSES IN
SOME TYPICAL EXCIPLEX SYSTEMS AND EXCITED EDA COMPLEXES

Typical exciplex systems such as pyrene-N,N-dimethylaniline (DMA),pyrene-p-dicyanobenzene (DCNB) and anthracene-DMA as well as the excited state of weak EDA complexes such as 1,2,4,5-tetracyanobenzene(TCNB)-toluene system are very useful as model systems to investigate the mechanisms of photoinduced CT or ET processes (1). Their energy levels,electronic as well as geometical structures and dynamic behaviors seem to be profoundly affected by the interaction with polar solvents. The elucidation of the mechanisms of the solvent effect upon the photoinduced CT process and structures of produced CT state are of crucial importance for the understanding of the exciplex phenomena (2).

A. Photoinduced electron transfer and solvation in some exciplex systems.

The important role of solvation in the photoinduced ET can be demonstrated clearly by using intramolecular exciplex systems of the type $A-(CH_2)_n-D$ such as $p-(CH_3)_2N-(phenyl)-(CH_2)_n-$ (1-pyrenyl) (Pn) and $p-(CH_3)_2N-(phenyl)-(CH_2)_n-(9-anthryl)$ (An) (3). In the case of P_1 or A_1, fluorescence in nonpolar solvents is emitted from the LE state (excited singlet state localized in pyrene or anthracene part), $A^*-CH_2-D \rightarrow A-CH_2-D+h\nu_f$, while we can observe CT fluorescence in polar solvents, $(A^--CH_2-D^+)_S \rightarrow (A-CH_2-D)_S+h\nu_f'$. This fact demonstrates clearly the important role of the solvation in producing the photoinduced CT state.

The energy of the CT state as a function of the solvent dielectric constant when the solvent reorientation polarization is completed during the excited state lifetime is given by,

$$E_{CT} = Const. - (1/2) \cdot (\mu_e^{eq2}/a^3) \cdot f_\varepsilon \tag{1}$$

where $f_\varepsilon = 2(\varepsilon-1)/(2\varepsilon+1)$, $\vec{\mu}_e^{eq2}$ is the dipolemoment of the equilibrium (eq) CT state and a is the cavity radius in the reaction field theory. In the case of P_1 and A_1, CT state is higher than the LE state in nonpolar solvent and level inversion occurs with increase of the solvent polarity. At the inversion point, there arises solvent orientational destabilization energy δE_g^{FC} in the Franck-Condon (FC) ground state.

$$\delta E_g^{FC} = (1/2) \cdot (\mu_e^{eq2}/a^3) \cdot (f_\varepsilon - f_n) \tag{2}$$

where $f_n = 2(n^2-1)/(2n^2+1)$. Therefore the energy of the exciplex fluorescence is given by,

$$h\nu_e = (E_{CT} - \delta E_g^{FC}) = Const. - (\mu_e^{eq2}/a^3) \cdot \{f_\varepsilon - (1/2) \cdot f_n\} \tag{3}$$

and at the inversion point, the red shift of the CT fluorescence should be especially large owing to the effect of δE_g^{FC}, which is actually observed in the case of P_1 and A_1 (3). This result for P_1 or A_1 is a direct proof for the existence of the ground state destabilization energy due to the reorientation of the polar solvent molecules in the photoinduced CT or ET state. Although this destabilization energy is for the F.C. ground state of the radiative transition, its important implication in the non-radiative deactivation of the CT or ET state as indicated in Fig. 1 will be discussed later in the case of such biologically important
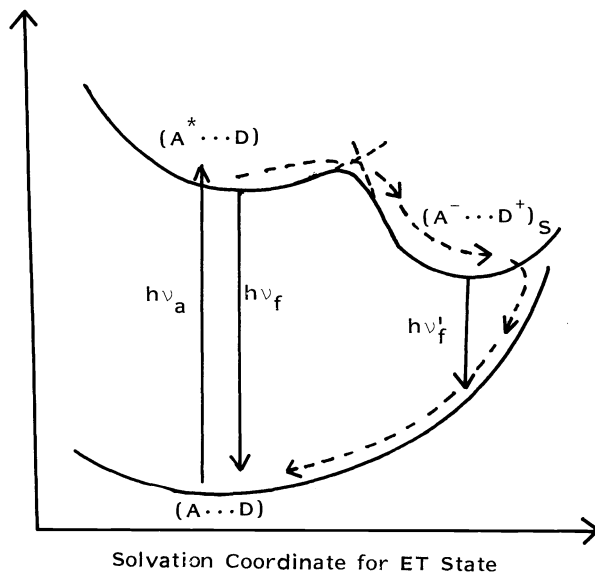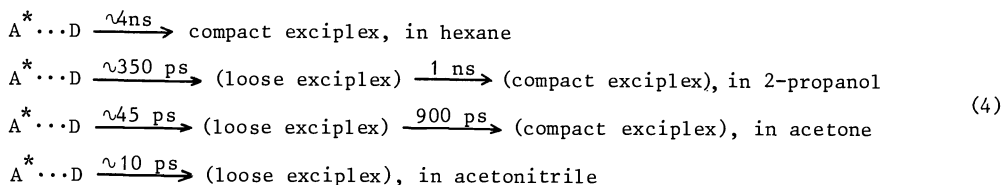

Fig. 1. A conceptual diagram of the stabilization of the ET state and destabilization of the ground state due to solvation in the ET state, and non-radiative process between the two states.

Solvation Coordinate for ET State

exciplex systems as porphyrin-quinone (4) and flavin-indole (5) as well as some strong EDA complexes in polar solvents (6).

The growing-in of the photoinduced CT state and the decay process of the LE state can be observed directly by means of the ps time-resolved transient absorption as well as fluorescence measurements (7,8) in relatively viscous polar solvents like 2-propanol. For example, the LE fluorescence decay and CT state absorbance rise time of P_1 in 2-propanol are ca. 65 ps. The CT state formation becomes much faster in a less viscous solvent such as acetone and acetonitrile, where it is realized within a few ps. In contrast to P_1 and A_1, formation of the photoinduced CT state is possible even in nonpolar solvents in the case of P_3 and A_3 where extensive conformation change during the excited state lifetime is possible to make plane parallel sandwich. In this configuration, the CT state seems to become lower than the LE state due to the strong interaction between A^- and D^+ even in nonpolar solvent. However, it takes a few ns in hexane for the conformation charge to the sandwich form. Since the energy of the CT state depends upon the solvent polarity as it is demonstrated in the case of P_1 and A_1, the CT state formation will be affected by solvent polarity also in P_3. The stabilization of the $A^-\cdots D^+$ state by solvation will make possible the ET without taking compact sandwich configuration, and formation of loose exciplex may be possible. The results of studies of P_3 in several solvents of different polarities and viscosities by means of ps time-resolved transient absorption spectral measurements and fluorescence rise and decay curve measurements can be summarized as follows.

$$A^*\cdots D \xrightarrow{\sim 4ns} \text{compact exciplex, in hexane}$$

$$A^*\cdots D \xrightarrow{\sim 350\ ps} (\text{loose exciplex}) \xrightarrow{1\ ns} (\text{compact exciplex}), \text{in 2-propanol}$$

$$A^*\cdots D \xrightarrow{\sim 45\ ps} (\text{loose exciplex}) \xrightarrow{900\ ps} (\text{compact exciplex}), \text{in acetone}$$

$$A^*\cdots D \xrightarrow{\sim 10\ ps} (\text{loose exciplex}), \text{in acetonitrile}$$
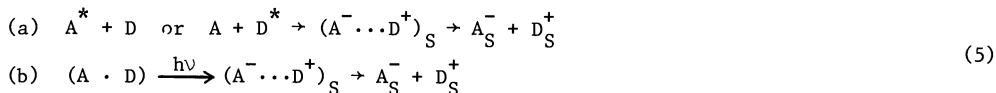
(4)

In 2-propanol and acetone, not only the solvent reorganization but also a slight approach to each other and reorientational motion of the two chromophores are necessary for the ET. In acetonitrile solution, the photoinduced ET can take place without such conformation change due to the rapid and strong solvation. If $\underline{E}_{CT}$ is already lower than $\underline{E}_{LE}$ even in nonpolar solvents, the photoinduced ET can take place by intramolecular electron tunnelling without the assistance of polar solvents as well as conformation change. The energetics of photochemical ET seem to be more favorable in porphyrin-quinone system than in pyrene-DMA or anthracene-DMA system as it is discussed later.

In relation to the above statement, it should be noted here that there are several possible cases of inter- and intramolecular relaxations associated with the photochemical ET reaction. Namely, (a) only the intra- and intermolecular vibrations of cation-anion pair is responsible, (b) both of such vibrational relaxation and solvent reorientation relaxation are involved, or (c) solvent relaxation alone may operate to stabilize the ion-pairs produced (1a). When solvation plays crucial role to make the photoinduced ET energetically possible the ET in a loose configuration without compact exciplex formation seems to become easier with increasing solvent polarity, as it is directly demonstrated in the case of P_3 (8). It is well-known that a systematic study of the fluorescence quenching in strongly polar solvents has revealed a relation between the bimolecular quenching rate constant $\underline{k}_q$ and the free energy difference $\Delta G°$ between the relaxed states in encounter before and after the ET, $A^*\cdots D$ or $A\cdots D^* \rightarrow A_s^-\cdots D_s^+$ (28). Namely, the results of measurements indicate that when $\Delta G°$ <-10 kcal/mol, the reaction is diffusion-controlled, and no "inverted region" is observed contrary to theoretical studies of ET probability (29). Although there are several explanations for this discrepancy, definite conclusion does not seem to be arrived at yet (3a). In the usual theoretical treatment of ET probability, the same shape of potential energy surface is assumed for the states before and after ET. Since A and D in the above described fluorescence quenching experiments in strongly polar solvents are neutral molecules and become charged after ET, the strong solvation seems to make the potential surface for $A_s^-\cdots D_s^+$ state much steeper than that for $A^*\cdots D$ or $A\cdots D^*$ state. In this case, the effect of the Franck-Condon restriction for the ET which is responsible for the appearance of the "inverted region" becomes much smaller. A theoretical formulation for the ET probability for such case (31) has been given recently, which shows hardly the decrease of the ET probability even at large energy gap.

B. Charge separation and deactivation processes from the photochemical electron transfer state.

Transient absorption spectral measurements with ps laser photolysis as well as ps laser

induced photocurrent measurements are most powerful methods for the elucidation of the
mechanisms of photoinduced ET and CS processes of exciplex and excited EDA systems in polar
solvents (9). These processes can be summarized as follows.

$$(a) \quad A^* + D \quad or \quad A + D^* \rightarrow (A^-\cdots D^+)_S \rightarrow A_S^- + D_S^+$$

$$(b) \quad (A \cdot D) \xrightarrow{h\nu} (A^-\cdots D^+)_S \rightarrow A_S^- + D_S^+ \tag{5}$$

where $(A^-\cdots D^+)_S$ is the ET state relaxed with respect to intracomplex configurations and
solvation (contact ion-pair or solvent-shared ion-pair), and A_S^- as well as D_S^+ represent
solvated free ion radicals escaped from the influence of gegen ion. Usually, free ions are
formed via the geminate ion-pair, $(A_S^-\cdots D_S^+)$, loosely combined by coulomb attraction.

EDA complexes of TCNB in polar solvents   We have made detailed ps laser photolysis investiga-
tions on the mechanisms of ET and CS processes of excited EDA complex in the case of TCNB-
toluene system and also some investigations on other TCNB complexes (9a,c). The TCNB-toluene
complex shows broad CT fluorescence with a very large Stokes shift in less polar fluid solu-
tions (2d), which is due to the stabilization of CT state by solvent reorientation and con-
formational change associated with an increase of CT degree from about 50% to approximately
100% in the course of relaxation from the FC to the eq excited state (10a,b,c). In strongly
polar solvents, the CT fluorescence is quenched and dissociated ion radicals are produced
(10d,11c,11d). We have observed directly the dissociation process by means of ps laser
photolysis and transient absorption spectral measurements (9a,c). Fig. 2 shows transient
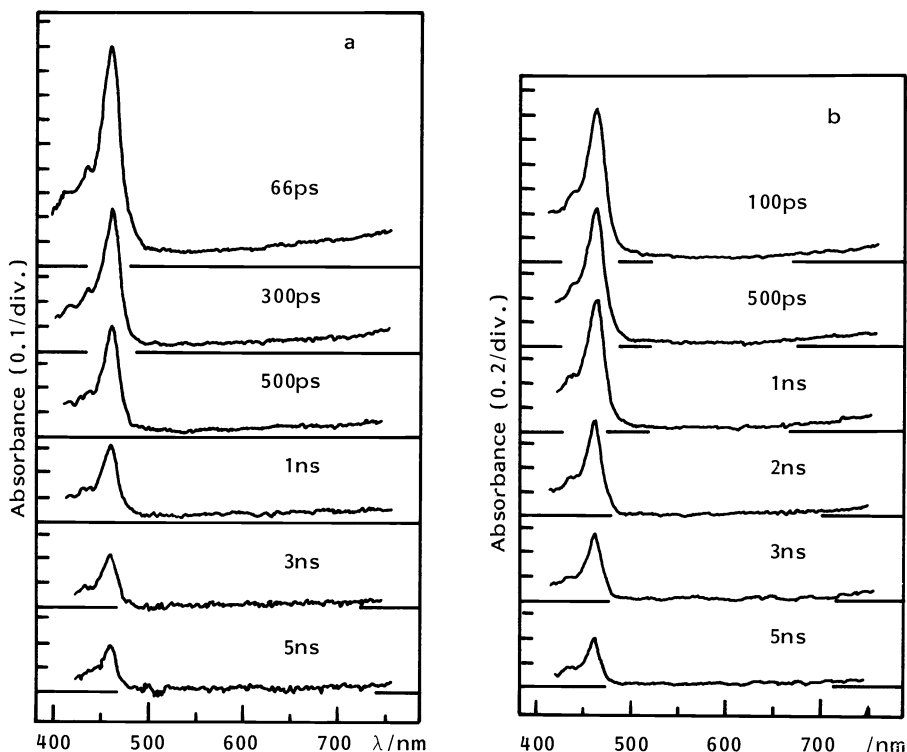absorbance spectra of TCNB-toluene system in aceton and 1,2-dichloroethane.

Fig. 2. Time-resolved transient absorption spectra of TCNB-toluene
complex in acetone (a) and 1,2-dichloroethane (b), excited with third
harmonic of ps ND^{3+}:YAG laser. Delay times from the exciting single
pulse are indicated in the figure.

The rise of the ion-like absorption is completed within the exciting pulse, reflecting the
ultrafast relaxation from the excited FC state. On the other hand, the absorbance shows
considerable decay over several hundreds ps $\sim$ 1 ns regime and converges to a constant value,
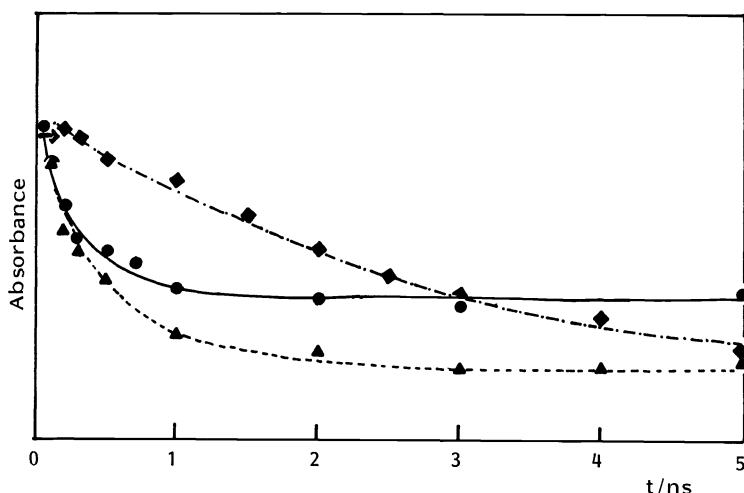as shown in Fig. 3.

Fig. 3. Time-dependence of the absorbance of excited TCNB-toluene system in several solvents of different polarity. Solvents, ●: acetonitrile, ▲: acetone, ◆: 1,2-dichloroethane.

This behavior of the TCNB complex can be explained by assuming the following reaction scheme, from which the time-dependence

$$(A \cdots D) \underset{k_n}{\longleftarrow} (A^- \cdots D^+)_S \xrightarrow{k_d} A^-_S + D^+_S \tag{6}$$

of the absorbance is given by Eq. 7.

$$OD(t) = C + D \cdot \exp\{-(\underline{k}_d + \underline{k}_n)t\} \tag{7}$$

From the observed values of quantum yield of dissociation, $\phi_{ion} = \underline{k}_d/(\underline{k}_d + \underline{k}_n)$, and lifetime τ of $(A^- \cdots D^+)_S$, absolute values of $\underline{k}_d$ and $\underline{k}_n$ are obtained as shown in Table I. As it is discussed in the later part of this paper concerning the ionic dissociation process of some typical exciplex systems, a direct confirmation of the dissociation process $(\underline{k}_d)$ in Eq. 6 is provided by the measurements of ps laser-induced photocurrent. Rapid rise of photocurrent corresponding to the decay of dissociating state has been confirmed in the case of TCNB-toluene system in nitrile solutions (9c).

TABLE I. Quantum yield of dissociation, lifetime of dissociating state, and $\underline{k}_d$ and $\underline{k}_n$ values of TCNB-toluene system in various polar solvents.

Solvent	ε_{mix}^a	$\phi_{ion}(\%)$	$\tau(ps)$	$\underline{k}_d(s^{-1})$	$\underline{k}_n(s^{-1})$
Acetonitrile	30.48	45	300	1.5×10^9	1.8×10^9
Acetone	17.04	25	450	5.6×10^8	1.7×10^9
2-Butanone	15.28	20	600	3.3×10^8	1.3×10^9
Hexanenitrile	14.28	19	650	2.9×10^8	1.2×10^9
Octanenitrile	11.60	10	1100	9.1×10^7	8.2×10^8
1,2-Dichloroethane	8.76	<1	3800	$<2.6 \times 10^6$	2.6×10^8

a. dielectric constant of solvent containing 20 vol.% toluene

The results in Table I show clearly that not only $\underline{k}_d$ but also $\underline{k}_n$ increases with increase of solvent dielectric constant, which suggests strongly that the solvation plays important role not only in dissociation process but also in the nonradiative deactivation from the ET state, as indicated in Fig. 1. It has been confirmed that the peak wavelength of the absortpion band of the dissociating state of the TCNB-toluene system in acetonitrile solution is the same as that of the dissociated ion radical in the same solvent. Similar results have been obtained also in the case of hexanenitrile solution. In both cases, the peak wavelength is blue-shifted a few nm compared with that of the TCNB-toluene two-component system. However, the peak wavelength in 1,2-dichloroethane is the same as that of the TCNB-toluene two-
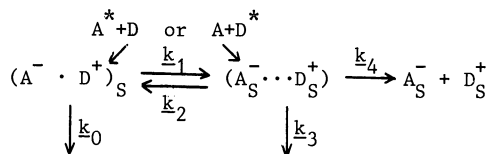
component system. Moreover, it has been confirmed that the CT fluorescence is observed in 1,2-dichloroethane while it is completely quenched in other polar solvents indicated in Table I. These results suggest strongly that the dissociating state in 1,2-dichloroethane is the weakly fluorescent contact ion-pair state while it is solvent-shared ion-pair or pair of solvated radical ions $(A_S^- \cdots D_S^+)$ in more polar solvents. In accordance with this arguments, $\log k_d$ and $\log k_n$ are approximately proportional to $(-1/\varepsilon_{mix})$ in solvents given in Table I except 1,2-dichloroethane where $\underline{k}_d$ as well as $\underline{k}_n$ value deviate strongly from the linear relation. These results can be understood easily by assuming the proportionality of the activation free energy for dissociation to the free energy difference between the solvent shared ion-pair state $(A_S^- \cdots D_S^+)$ and dissociated state $(A_S^- \cdots D_S^+)$, and also by assuming the exponential dependence of the non-radiative deactivation rate upon the energy gap between $(A_S^- \cdots D_S^+)$ and $(A_S \cdots D_S)$ states (9c). In addition to the above results, detailed ps laser photolysis and transient absorption spectral measurements over entire visible region have revealed that the main ionic species responsible for the dissociation process in 20% toluene solution are TCNB anion and toluene dimer cation formed immediately after excitation (9c). Namely, 1:1 complex seems to be further loosely bound with toluene molecules already in the ground state.

Concerning the nonradiative deactivation from the ET state, we have examined the effect of the strength of donor or acceptor. For example, pyromellitic dianhydride-pyrene EDA system is a strong complex showing CT absorption band around 500 nm. The excitation at this absorption band produces directly the ET state. In acetonitrile solution, although the absorption band due to the transition, $(A^- \cdots D^+)_S \xrightarrow{h\nu} (A^{-*} \cdots D^+)_S$, can be observed around 670 nm, the lifetime of the ET state is shorter than 10 ps. In ethylacetate solution, the lifetime becomes a little longer (60 ps). However, in both of these solutions, the dissociation into free solvated ions cannot compete with the non-radiative deactivation to the ground state (6). In benzene solution, the lifetime of the transient absorbance is ca. 400 ps which agrees with the decay time of CT fluorescence (6). These results are clear demonstration of the solvation induced very rapid non-radiative deactivation as indicated in Fig. 1. In view of the above results, a previously proposed model, in which the dissociation from the state non-relaxed with respect to solvation was assumed (11), does not seem to be correct.

Pyrene-DMA and pyrene-DCNB exciplex systems. Usually it is rather difficult to discriminate between contact ion-pair, solvent-shared or geminate ion-pair and dissociated ions by measuring only the transient absorption spectra, since all these species show very similar spectra. For example, the spectra of the dissociating state and the dissociated ions of TCNB-toluene system in moderately or strongly polar solvents are the same as discussed above. On the other hand, the ionic dissociation process can be detected directly by the ps or ns laser induced transient photocurrent measurements.

Direct observation of the dissociation process from the geminate ion-pair of such typical exciplex systems as pyrene-DMA and pyrene-DCNB in polar solvents has been made recently by means of ps laser induced photocurrent studies (9b). Although the CT fluorescence of these exciplexes are largely quenched in solvents of high polarity due to the formation of non-fluorescent geminate or solvent-shared ion-pairs, we can still observe very weak exciplex fluorescence even in acetone or acetonitrile solution. The rise time of the photocurrent, τ_r^{ion}, which corresponds to the dissociation process from the geminate ion-pair, does not agree with the exciplex fluorescence decay time τ_f^{ex} in the same solvent, in general (9b). For example, $\tau_r^{ion} \lesssim 2$ ns, $\tau_f^{ex} \sim 2.3$ ns in acetonitrile, $\tau_r^{ion} \sim 7.0 \pm 0.5$ ns, $\tau_f^{ex} \sim 7.7 \pm 0.2$ ms in acetone and $\tau_r^{ion} \sim 23.8 \pm 1.4$ ns, $\tau_f^{ex} \sim 33.2 \pm 0.5$ ns in pyridine in the case of pyrene-DMA system. In the case of pyrene-DCNB system, exciplex fluorescence cannot be observed while τ_r^{ion} is shorter than a few ns, in acetonitrile and acetone solution. However, $\tau_r^{ion} \sim 16.4 \pm 0.8$ ns, $\tau_f^{ex} \sim 19.3 \pm 0.2$ ns in pyridine solution (9b).
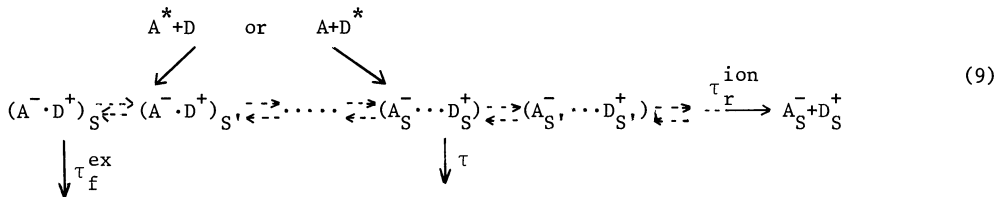
If we assume the "two states" model,

$$(A^- \cdot D^+)_S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (A_S^- \cdots D_S^+) \xrightarrow{k_4} A_S^- + D_S^+$$

with A^*+D or $A+D^*$ entering via k_1, $\downarrow k_0$ from $(A^- \cdot D^+)_S$ and $\downarrow k_3$ from $(A_S^- \cdots D_S^+)$,

where $(A^-D^+)_S$ is the fluorescent exciplex, $(A_S^- \cdots D_S^+)$ the geminate ion-pair, and $A_S^- + D_S^+$ the dissociated ion radicals. From this scheme, the photocurrent rise curve $i(t)$ and the exciplex fluorescence decay curve $\underline{I}_f^{ex}(t)$ are given by,

$$\underline{I}_f^{ex}(t) = \underline{A}_1 \exp(-\lambda_1 \cdot t) + \underline{A}_2 \exp(-\lambda_2 \cdot t)$$

$$\underline{i}(t) = \underline{A}_1'\{1-\exp(-\lambda_1 \cdot t)\} + \underline{A}_2'\{1-\exp(-\lambda_2 \cdot t)\}$$

(8)

According to Eq. 8, the exciplex fluorescence decay must correspond exactly to the photocurrent rise contrary to the observed results. Observed $\underline{I}_f^{ex}(t)$ and $\underline{i}(t)$ can be reproduced approximately by $\underline{I}_f^{ex}(t){\sim}\exp(-t/\tau_f^{ex})$ and $\underline{i}(t){\sim}\{1-\exp(-t/\tau_r^{ion})\}$, respectively and τ_f^{ex} is not equal to τ_r^{ion}. These results lead to the "multiple states" model which assume the existence of various kinds of exciplexes and geminate ion-pairs which undergo partial interconversions between each other, as indicated in Eq. 9 (9b).

$$A^*+D \quad \text{or} \quad A+D^* \tag{9}$$

$$(A^- \cdot D^+)_S \xleftrightarrow{} (A^- \cdot D^+)_{S'} \xleftrightarrow{} \cdots \cdots \xrightarrow{} (A_S^- \cdots D_S^+) \xleftrightarrow{} (A_{S'}^-, \cdots D_{S'}^+) \xleftrightarrow{} \xrightarrow[\text{r}]{\tau^{ion}} A_S^- + D_S^+$$

$$\downarrow \tau_f^{ex} \qquad\qquad\qquad \downarrow \tau$$

This reaction scheme gives Eq. 10 for $\underline{I}_f^{ex}(t)$ and $\underline{i}(t)$,

$$\underline{I}_f^{ex}(t) = \sum_i \underline{A}_i \exp(-\lambda_i \cdot t)$$

$$\underline{i}(t) = \sum_i \underline{A}_i'\{1-\exp(-\lambda_i \cdot t)\}$$
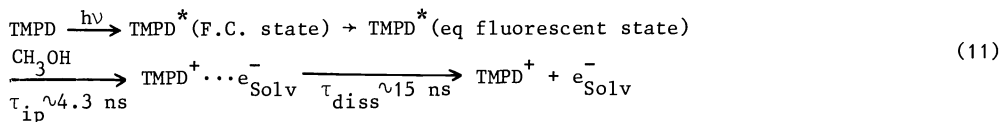
(10)

The ion-pairs which undergo mainly dissociation into free ions may not be directly combined with the exciplexes which show CT fluorescence but there may be intervening exciplexes and ion-pairs (9b).

In order to elucidate further this problem, we have made detailed measurements of the rise and decay of transient absorbance due to ion-pairs and exciplexes over the delay times of several 10 ps to µs (12). Results of these measurements confirm the above assumption of the existence of various geminate ion-pairs and exciplexes. Namely, almost all pyrene-DMA geminate ion-pairs formed in acetonitrile solution dissociate without deactivation. However, in acetone and pyridine solution, considerable amount of the geminate ion-pairs are deactivated with lifetimes much longer than τ^{ion} or τ_f^{ex} ($\tau{\sim}30$ ns in acetone, $\tau{\sim}50$ ns in pyridine). Moreover, a large amount of geminate ion-pairs of pyrene-DCNB system show such decay not only in acetone and pyridine solutions but also in acetonitrile solution ($\tau{\sim}30$ ns in all of these solutions). Therefore, although the free energy of the ion-pair state estimated from the oxidation potential of donor and reduction potential of acceptor is the same in pyrene-DMA and pyrene-DCNB systems, the behaviors of geminate ion-pairs as well as exciplex are quite different. Above results seem to reflect directly the complex and dynamical micro-structures of polar solutions of charged species, which has been revealed only with these time-resolved transient absorption and conductivity studies in ps${\sim}$100 ns regime.

II. ELECTRON PHOTOEJECTION FROM SOLUTE TO POLAR SOLVENT MOLECULES AND CHARGE SEPARATION PROCESSES - SIMILARITY TO EXCIPLEX SYSTEMS.

In addition to the photoinduced ET and CS processes in the systems of electron donor and acceptor solute molecules as described above, electron ejection from excited solute molecule into polar solvent is also an important primary process in photochemistry and photobiology. We discuss here briefly very important role of solute-solvent interaction in the monophotonic electron ejection from some aromatic diamine molecules with low ionization potential in polar solvents. For example, mechanisms of the photoionization of some low ionization potential amine like TMPD have been investigated quite intensively since the time of G. N. Lewis. Nevertheless, the true mechanism of its photoionization in polar solvents has never been made clear by those previous studies. For the elucidation of this problem, ps laser photolysis and measurements of transient absorption spectra as well as transient photocurrent are powerful means.

According to our measurements with ps laser, the photoionization of TMPD in methanol occurs from the relaxed fluorescent state and the reaction mechanism can be written as follows (13).

$$\text{TMPD} \xrightarrow{h\nu} \text{TMPD}^*(\text{F.C. state}) \to \text{TMPD}^*(\text{eq fluorescent state})$$

$$\xrightarrow[\tau_{ip}{\sim}4.3 \text{ ns}]{CH_3OH} \text{TMPD}^+\cdots e_{Solv}^- \xrightarrow[\tau_{diss}{\sim}15 \text{ ns}]{} \text{TMPD}^+ + e_{Solv}^-$$

(11)

The ionization results in the formation of TMPD cation – solvated electron geminate pair which dissociate within ca. 15 ns. Although τ_{ip} as well as τ_{diss} become longer in higher alcohols, very similar mechanism of electron ejection seems to be prevailing. Electron photoejection from the eq fluorescent state similar to the TMPD-methanol system has been observed directly by means of ps laser photolysis method in the case of TMPD (14), BDATP (bis(dimethylamino)-4,5,9,10-tetrahydropyrene) (15) and TMB(N,N,N',N'-tetramethylbenzidine) (16) in some nitrile solutions. For example, in the case of TMPD-acetonitrile solution, electron ejection leads to the formation of TMPD$^+$ and acetonitrile dimer anion geminate pair with τ_{ip}=1.2 ns. Quite similar result has been obtained also in the case of BDATP-aceto-nitrile system where the BDATP$^+\cdots$(ACN)$_2^-$ geminate pair formation occurs with τ_{ip}=2.3 ns and this geminate pair dissociate with τ_{diss}=9 ns. The acetonitrile dimer anion changes to higher aggregate anion in the course of time. TMPD$^+$ and acetonitrile polymer anion geminate pair has in general very long lifetime because of slow recombination.

Above results show very clearly that the so-called electron photoejection of these diamines in polar solvents is not a mere "ejection" into solvent continuum but a more specific exciplex type interaction between excited solute molecule in the fluorescent state and solvent molecules play crucial role for the ionization.

III.   PHOTOCHEMICAL ELECTRON TRANSFER AND CHARGE SEPARATION PROCESSES IN PORPHYRIN-QUINONE SYSTEMS.

In relation to the mechanisms of photoinduced CT or ET and CS processes in biological as well as biomimetic photosynthetic systems, investigations on porphyrin-electron acceptor model systems have been made quite extensively (4,17,18). However, in contrast to the typical exciplex systems and weak EDA complexes discussed in I, solvated radical ions or ion-pairs produced from S_1 state have never been detected even by means of ps laser spectroscopy in the case of porphyrin-quinone intermolecular exciplex systems in considerably or strongly polar solvents. It seems to be very important to elucidate the mechanisms underlying the quite different behaviors of porphyrin-quinone systems from those of typical exciplexes and excited singlet state of weak EDA complexes in polar solvents in order to design any biomimetic photosynthetic systems. Presumably, such a rapid non-radiative deactivation process which shows strong dependence upon solvent polarity as observed in the strong EDA complex of PMDA-pyrene (6), is prevailing also in the porphyrin-quinone systems. In order to elucidate this problem, we have made a detailed ps laser photolysis studies of solvent effects upon these systems.

A. Solvation-induced ultrafast nonradiative deactivation of porphyrin-quinone intermolecular exciplexes.

Detailed ps laser photolysis studies have been made for ethyletioporphyrin(EEP)-toluquinone (TQ) intermolecular exciplex system (4,19). For example, the ps transient absorption spectra of EEP-TQ system in acetone, where the fluorescence of EEP is completely quenched, are very similar to the $S_n \leftarrow S_1$ absorption spectrum of EEP itself. This result indicates that the singlet ET or ion-pair state of EEP-TQ system in acetone is deactivated to the original ground state very rapidly without producing dissociated ions and we are observing only the S_1 state of EEP before deactivation by collisional interaction with TQ. The decay time of this transient absorbance was $\tau_{obs} \sim$70 ps which was in an approximate agreement with the value estimated from the relation, $\tau_{calc}=\tau_0/(1+k_q\tau_0[TQ])$ ($\tau_{calc}\sim$80 ps), where τ_0 is the lifetime of the S_1 state of EEP and k_q is the bimolecular rate constant of the quenching by TQ. Moreover, examinations of the ground state absorption spectra and fluorescence yield vs. [TQ] relations have revealed that ground state loose complexes are formed at high concentrations of TQ under which the transient absorption measurements are performed and the reaction scheme of the fluorescence quenching is given by,

$$P^* + Q \xrightarrow{k_q} (P^+\cdots Q^-)_S$$
$$\uparrow\downarrow\tau_0^{-1} \qquad K_g \qquad \uparrow\downarrow(\underline{k}_f'+\underline{k}_i') \qquad\qquad (12)$$
$$P + Q \rightleftharpoons (P\cdots Q)$$

where $(P^+\cdots Q^-)_S$ is the solvated ET state (exciplex or solvent-shared ion-pair) and the non-radiative rate constant $\underline{k}_i'$ is much larger than the fluorescence rate constant $\underline{k}_f'$ in view of the non-fluorescent character of the exciplex. In acetone solution, about 60% of EEP forms ground state loose complex. In view of the results of ps transient absorption studies, this loose complex also seems to undergo ultrafast deactivation via the solvated ET states immediately after excitation within a few ps.

Contrary to the above results, the ps transient absorption spectra of EEP-TQ system in benzene are quite different from the $S_n \leftarrow S_1$ spectra of EEP and are very similar to that of

EEP cation radical. In benzene solution used for the transient absorption measurements ($[TQ]$=0.62M, K_g=12.4), about 90% of EEP forms loose complex. Accordingly, the transient absorption spectra in benzene solution can be assigned to the exciplex state (EEP$^+\cdot$TQ$^-$) formed by the excitation of the ground state loose complex and its decay time was determined to be 40 ps. Above results provide direct connection between the porphyrin-quinone systems and usual exciplex systems as well as excited singlet state of weak EDA complexes. Although it is short-lived, porphyrin-quinone exciplex can be observed in relatively nonpolar solvent, while the ET state undergoes solvation-induced ultrafast deactivation to the ground state in polar solvents. As indicated in Fig. 1, solvation in the ET state lowers its energy but lifts up the energy of the neutral ground state compared to that relaxed with respect to solvation, which results in a very small energy gap between two states leading to the ultra-fast deactivation in the porphyrin-quinone system. The dissociation into solvated ion radicals cannot compete with this ultrafast deactivation. Quite similar circumstance seems to be prevailing also in the flavin-indole exciplex system (5). A rough estimation of the energies of solvated ion-pair and solvated neutral pair in the case of porphyrin-quinone system shows that they are almost equal in acetone solution (19). However, similar estima-tion shows that the energy gap is still considerably large even in acetonitrile solution in the case of pyrene DMA and -DCNB systems (19).

A way to avoid the ultrafast deactivation of the porphyrin-quinone ET state seems to const-ruct the intramolecular exciplex type compounds where porphyrin and quinone are combined by some insulating chains of various lengths in order to make weaker the interaction between the chromophores and also to prevent the strong solvation by intervening chains. In the follow-ing, some results of ps laser photolysis studies upon (octaethylporphyrin)-(CH$_2$)$_n$-(benzo-quinone) (PnQ, n=2,4,6), (etioporphyrin)-(CH$_2$)$_4$-(benzoquinone) (EP4Q) and (etioporphyrin)-(CH$_2$)$_n$-(benzoquinone)-(CH$_2$)$_m$-(trichlorobenzoquinone) (PnQmQ', n=m=4) (20) are discussed briefly.

B. Porphyrin-quinone intramolecular exciplex systems.

Some examples of ps time-resolved transient absorption spectra of PnQ (n=2,4,6) are indicated in Fig. 4. P2Q shows absorption band characteristic to the ET state immediately after exci-tation, which means that the photoinduced intramolecular ET takes place within 10 ps. The transient spectra of P6Q immediately after excitation are very similar to the $S_n\leftarrow S_1$ spectra of porphyrin monomer indicating much slower ET compared with P2Q. The fluorescence decay time of P6Q determined with ps streak camera was 590 ps which represents approximately the time constant of photoinduced ET since the fluorescence lifetime of nonaethylporphyrin is about 10 ns. The transient absorption spectra of P4Q show features intermediate between
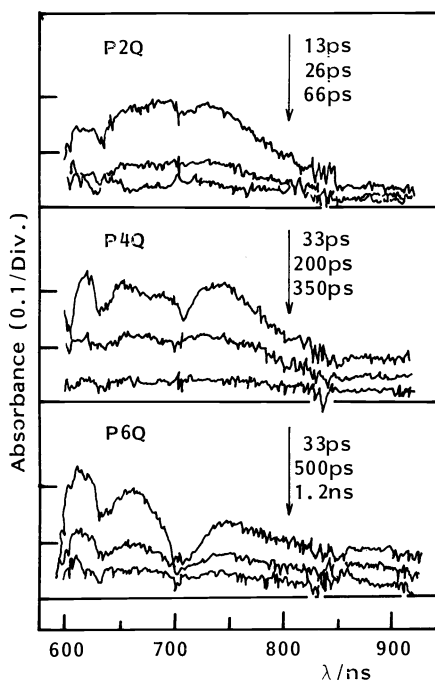

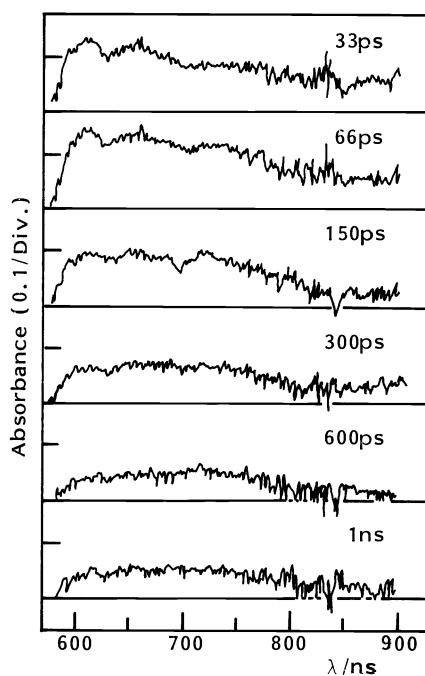Fig. 4. Picosecond time-resolved transient absorption spectra of PnQ in benzene.

Fig. 5. Picosecond time-resolved transient absorption spectra of P4Q4' in dioxane.

those of P2Q and P6Q. The fluorescence decay time of P4Q was determined to be 70 ps which represents also the time constant of ET. The transient abosrption spectra can be analyzed according to the reaction scheme of Eq. 13, by using Eqs. 14, 15 and 16 derived from it.

$$S_1(P^*nQ) \xrightarrow{\underline{k}} ET(P^+nQ^-) \tag{13}$$

$$\downarrow 1/\tau_0 \qquad \downarrow 1/\tau'$$

$$[S_1] = [S_1]_0 \exp(-t/\tau), \quad \tau = (\underline{k} + \tau_0^{-1})^{-1} \tag{14}$$

$$[ET] = \{\tau'[S_1]_0 / (\tau - \tau')\}[\exp(-t/\tau) - \exp(-t/\tau')] \tag{15}$$

$$\underline{A}^{\lambda}(t) = \varepsilon_{S_1}^{\lambda}[S_1] + \varepsilon_{ET}^{\lambda}[ET] \tag{16}$$

where $\varepsilon_{S_1}^{\lambda}$ and $\varepsilon_{ET}^{\lambda}$ are molar extinction coefficient of S_1 and ET state, respectively, at λ. From the analysis according to these equations with the τ values given above, τ' values have been estimated to be ∿10 ps, ∿130 ps and ∿600 ps for P2Q, P4Q and P6Q, respectively.

Above results of ps laser studies of PnQ clearly show the remarkable dependence of the rate of photoinduced ET as well as the rate of back ET upon the chain length. Namely, $1/\tau \gtrsim 10^{11}$ s^{-1}, ∿10^{10} s^{-1} and ∿10^9 s^{-1} for n=2,4 and 6, respectively. The dependence of $1/\tau'$ upon n is similar to that of $1/\tau$, as discussed above. This exponential dependence of the ET rate upon the chain length is indicative of the intramolecular electron tunneling mechanism. It is well-known that the probability of ET($\underline{k}_{ET}$) in the weak interaction limit is given by,

$$\underline{k}_{ET} \sim (2\pi/\hbar) \cdot \beta^2 \cdot (F.C.) \tag{17}$$

where β^2 is the electronic interaction term which is usually assumed to be $\exp(-Const \cdot \underline{r}_{PQ})$ in the simplified treatment of electron tunneling or electron exchange and (F.C.) is the Franck-Condon term. Since (F.C.) may be the same for the series of PnQ, the observed result seems to reflect the $\underline{r}_{PQ}$ dependence of β^2. In the case of Pn or An, intramolecular photoinduced ET shows a considerable dependence upon the solvent polarity as discussed in I (ET becomes more feasible with increase of solvent polarity). However, increase of solvent polarity does not so much affect the rate of photoinduced ET in the case of PnQ, which may be ascribed to the more favorable ET energetics in porphyrin-quinone pair than in pyrene or anthracene-DMA pair.
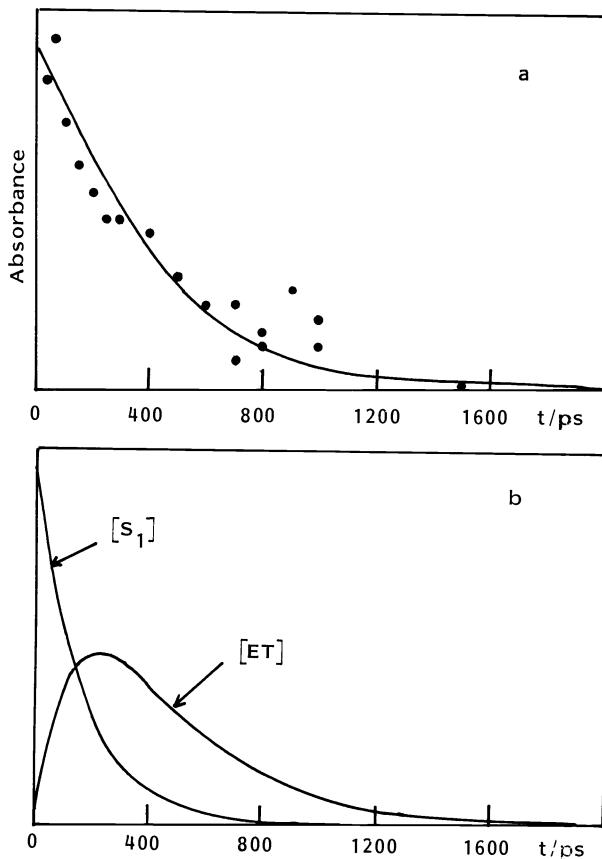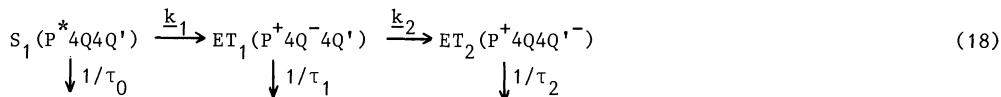

Fig. 6. Analysis of the results in Figure 5 according to the scheme of Eq. 15.
a. ●: observed values at 750 nm.
—: decay curve calculated by Eq. 16.
b. relative concentrations of S_1 and ET states calculated by Eqs. 14 and 15, respectively.

Transient absorption spectra of PnQ in polar solvents can be analyzed also by using the scheme of Eq. 13. For example, the observed result of P4Q in dioxane can be reproduced satisfactorily with τ=140 ps and τ'=100 ps. Therefore, even in dioxane which can solvate the ET state rather strongly, the lifetime of the ET state of P4Q is much longer than that ($\sim$40 ps) of the EEP-TQ intermolecular exciplex in benzene. Fig. 5 shows the transient absorption spectra of P4Q4' in dioxane. The band shape at small delay times indicates a considerable contribution from the S_1 state, but the spectra at the delay times of several hundreds ps are characteristic to ET state. The lifetime of photoinduced ET state of this system is much longer compared with that of P4Q in dioxane probably due to the more extensive CS as indicated in Eq. 18, where $\underline{k}_2$ should be larger than $1/\tau_1$.

$$S_1(P^*4Q4') \xrightarrow{\underline{k}_1} ET_1(P^+4Q^-4') \xrightarrow{\underline{k}_2} ET_2(P^+4Q4'^-) \qquad (18)$$
$$\downarrow 1/\tau_0 \qquad\qquad \downarrow 1/\tau_1 \qquad\qquad\quad \downarrow 1/\tau_2$$

If $\underline{k}_2$ is much larger than $\underline{k}_1$ and $1/\tau_1$, equation for $[ET_2]$ reduces to Eq. 15. The observed results of P4Q4' in dioxane can be reproduced satisfactorily with Eqs. 14-16 as indicated in Fig. 6. From this analysis, τ' has been estimated to be 300 ps. Similar results in tetrahydrofurane solution give τ' value of 400 ps.
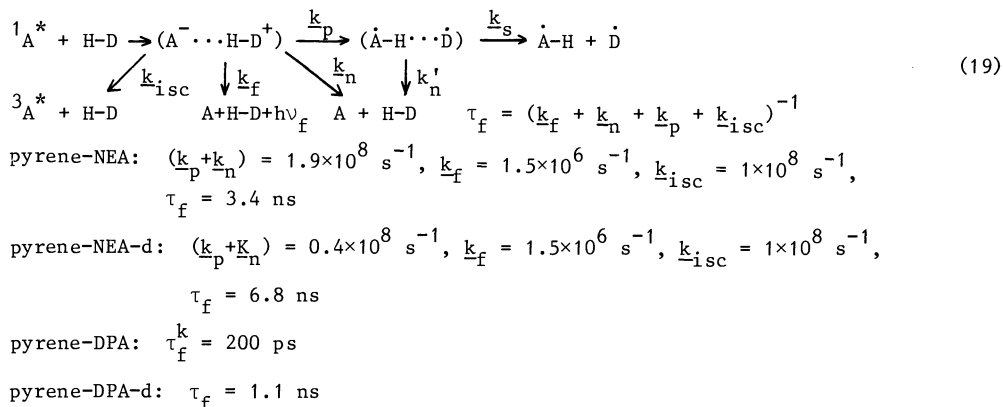
The lifetime of the photoinduced ET state in the intramolecular exciplex systems of porphyrin-quinone is much longer compared with that of the intermolecular exciplex, and it increases with increase of the chain length. However, if the chain becomes too long, the photoinduced CS becomes inefficient because not only the back ET deactivation but also the forward ET becomes very slow. In this respect, it is evident that the two step ET as demonstrated above is of crucial importance for the realization of rapid and extensive CS. These results are extremely important for designing any biomimetic photosynthetic systems.

IV. SOME CHEMICAL REACTION PROCESSES COUPLED WITH PHOTOINDUCED CT.

Many photochemical processes such as enhancement of intersystem crossing in encounter collision, hydrogen abstraction, cycloaddition and some trans/cis isomerization reaction are believed to occur via the inter- or intramolecular CT state. However, direct experimental evidence for it is scarce. Here, some examples of proton transfer or proton shift coupled with photoinduced CT resulting in the hydrogen atom transfer or deactivation to the ground state as well as the trans/cis isomerization accelerated by the photoinduced intramolecular CT are discussed.

A. Proton transfer and proton shift in photoinduced CT state of hydrogen bonding systems.

It has been proposed frequently that the photochemical hydrogen abstraction takes place by the mechanism of ET followed by proton transfer: $A^*\cdots H\text{-}D$ or $A\cdots H\text{-}D^*{\rightarrow}(A^-\cdots H\text{-}\dot{D}^+){\rightarrow}\dot{A}\text{-}H{+}\dot{D}$. The first direct experiment demonstration of this process has been given for the pyrene-secondary aromatic amine exciplex system in nonpolar solvent with ps laser photolysis method (7a,7b,21). The results obtained for pyrene-N-ethylaniline(NEA) and pyrene-diphenylamine (DPA) systems can be summarized as follows assuming the reacton scheme of Eq. 19.

$$^1A^* + H\text{-}D \rightarrow (A^-\cdots H\text{-}D^+) \xrightarrow{\underline{k}_p} (\dot{A}\text{-}H\cdots\dot{D}) \xrightarrow{\underline{k}_s} \dot{A}\text{-}H + \dot{D}$$

$$\nearrow \underline{k}_{isc} \quad \downarrow \underline{k}_f \quad \searrow \underline{k}_n \quad \downarrow k_n' \qquad\qquad\qquad\qquad (19)$$

$$^3A^* + H\text{-}D \qquad A{+}H\text{-}D{+}h\nu_f \quad A + H\text{-}D \quad \tau_f = (\underline{k}_f + \underline{k}_n + \underline{k}_p + \underline{k}_{isc})^{-1}$$

pyrene-NEA: $(\underline{k}_p+\underline{k}_n) = 1.9\times10^8 \text{ s}^{-1}$, $\underline{k}_f = 1.5\times10^6 \text{ s}^{-1}$, $\underline{k}_{isc} = 1\times10^8 \text{ s}^{-1}$,
$\tau_f = 3.4$ ns

pyrene-NEA-d: $(\underline{k}_p+\underline{K}_n) = 0.4\times10^8 \text{ s}^{-1}$, $\underline{k}_f = 1.5\times10^6 \text{ s}^{-1}$, $\underline{k}_{isc} = 1\times10^8 \text{ s}^{-1}$,
$\tau_f = 6.8$ ns

pyrene-DPA: $\tau_f^k = 200$ ps

pyrene-DPA-d: $\tau_f = 1.1$ ns

The value of $(\underline{k}_p+\underline{k}_n)$ for pyrene-NEA is affected remarkably by deuteration of amino group, which is most probably due to the change of $\underline{k}_p$. The much smaller τ_f value of pyrene-DPA system compared with the pyrene-NEA system can be ascribed to the much faster proton transfer in the CT state of the former due to the larger acidity of the N-H proton in DPA. For the proton transfer in the CT state, an oblique configuration of the exciplex, where the N-H bond is almost perpendicular to the pyrene plane at C_1 position and hydrogen (H) bond is formed between 2pπAO at C_1 of pyrene anion and N-H of amine cation, may be favorable. This oblique

configuration is favorable also for the much larger $\underline{k}_{isc}$ of pyrene-NEA system than that of the pyrene-DMA exciplex ($\sim 10^6$ s^{-1}), because of the enhancement of the spin-orbit interaction matrix element between the singlet CT state and the pyrene local triplet states in this configuration (9a,21b,22). This interpretation is supported by the fact that we have already demonstrated a quite remarkable example of fast ISC from the singlet CT state of the system with non-parallel conformation, (1-pyrenyl)-CH$_2$-N(CH$_3$)-(phenyl), where $\underline{k}_{isc} \geq 10^{10}$ s^{-1} (22).

In the course of proton transfer, the N-H bond of the amine cation is stretched, which causes destabilization of the ground state facilitating the back CT deactivation as indicated in Fig. 7a. This circumstance is very similar to the case of solvation of ET state depicted in Fig. 1. In spite of these processes of proton transfer and back CT deactivation, we can
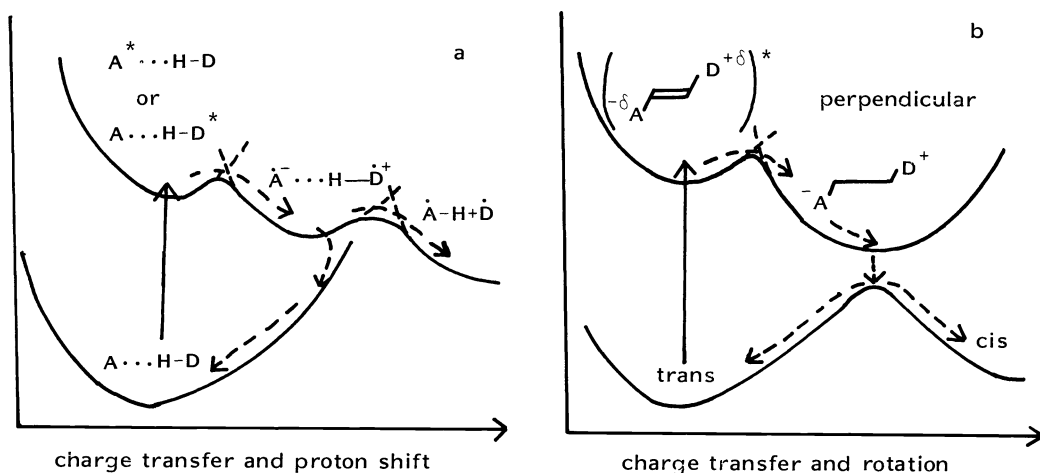

Fig. 7. Proton shift or proton transfer (a) and trans/cis isomerization (b) coupled with photoinduced CT.

still observe weak CT fluorescence in these systems because of the considerable π-electronic overlap between the donor cation and acceptor anion in the exciplex. There is another type of more usual hydrogen bonding interaction in the excited state, which causes the quenching of the fluorescence of proton donor or acceptor. In this case, both proton donor and acceptor are conjugate π-electron systems and directly connected by hydrogen bond. For example, when naphthylamine is hydrogen bonded with pyridine, the fluorescence of former is quenched and no new fluorescence such as exciplex emission can be observed. As a possible mechanism, photoinduced CT from proton donor to acceptor resulting in the formation of a kind of nonfluorescent exciplex was proposed (23). We have made systematic ps laser photolysis studies of this problem and have confirmed the formation of the CT state for the systems of 2-naphthylamine-pyridine (24a), 13H- and 7H-dibenzocarbazole-pyridine (24b) and 1-aminopyrene-pyridine systems (24c). The nonfluorescent character of the CT state in this type of hydrogen bonding systems compared with the weakly emitting aromatic hydrocarbon-secondary amine exciplexes may be ascribed to the much weaker overlap between π-electron systems of donor and acceptor in the former systems leading to very small radiative transition probability. This very small radiative transition probability cannot compete with the nonradiative deactivation caused by the proton shift in the CT state as indicated in Fig. 7a.

B. Trans/cis photoisomerization coupled with intramolecular photoinduced CT.

There are various problems of conformation change coupled with photoinduced CT. Some problems in the case of intramolecular exciplex systems of the type: A-(CH$_2$)$_n$-D, have been discussed already. Another important problem is the relation between the photoinduced intramolecular CT and rotation around ethylenic bond leading to trans/cis isomerization. However, clear-cut experimental example showing such relation was quite scarce. In view of the importance of this problem in photochemical and photobiological reactions, we have examined several systems of the type: A-CH=CH-D (25). In the following, results obtained for the compound, where A is pyrenyl and D is p-substituted phenyl group (4-substituted β-(1-pyrenyl)styrenes) with substituent groups methyl (I), methoxy (II) and dimethylamino (III), are discussed (25b).

These compounds show trans→cis photoisomerization exclusively from the S$_1$ state, and both of the isomerization yield and rate of isomerization determined by ps transient absorption measurement increase with increase of the substituent electron donating ability and the solvent polarity, in general. For example, the photoisomerization yield $\Phi_{t \to c}$ and isomerization rate constant $\underline{k}_{t \to c}$ of I, II, and III in ethylether are as follows; I: $\Phi_{t \to c}$=0.002,

$\underline{k}_{t\to c}=0.003\times10^8$ s^{-1}, II: $\Phi_{t\to c}=0.18$, $\underline{k}_{t\to c}=1.4\times10^8$ s^{-1}, III: $\Phi_{t\to c}=0.23$, $\underline{k}_{t\to c}=3.0\times10^8$ s^{-1}.
The effect of solvent polarity upon $\Phi_{t\to c}$, $\underline{k}_{t\to c}$, Φ_f (fluorescence yield) and τ_f (fluorescence lifetime) is indicated in Table II for compound II. One can recognize clearly that the trans →cis photoisomerization of these compounds becomes more feasible with increase of the extent

TABLE II. Solvent effect upon Φ_f, τ_f, $\Phi_{t\to c}$ and $\underline{k}_{t\to c}$ of methoxy compound (II).

Solvent	Φ_f	τ_f	$\Phi_{t\to c}$	$\underline{k}_{t\to c}/10^8$ s^{-1}
Hexane	0.74	3.2 ns	0.03	0.10
Ethylether	0.55	1.3 ns	0.18	1.4
Acetonitrile	0.28	650 ps	0.27	4.2

of intramolecular CT. These results can be well-comprehended on the basis of the mechanism indicated in Fig. 7b. The lowering of the energy of the perpendicular configuration with full charge transfer structure increases with increase of the substituent electron donating ability and also with increase of the solvent polarity. The extent of the energy lowering of the perpendicular state may be larger than that of the fluorescent state of trans form, which results in the lowering of the barrier between the fluorescent state and the perpendicular state.

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