

## BEHAVIOR OF RADICAL ION PAIRS PRODUCED BY PHOTOINDUCED ELECTRON TRANSFER IN POLAR SOLUTIONS

### THEIR DYNAMICS IN PICOSECOND-HUNDRED NANOSECOND REGIME

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(Received in U.S.A. 9 October 1985)

**Abstract**—The dynamic behavior of radical ion pairs in polar solvents has been studied by directly observing time-resolved transient absorption spectra in the picosecond-hundred nanosecond regime and also by observing the picosecond laser induced photocurrent. Pyrene-*N,N*-dimethylaniline, pyrene-*p*-dicyanobenzene, pyrene-triethylamine exciplex systems and the excited state of pyrene-pyromellitic dihydride electron donor-acceptor complexes in polar solvents have been examined. It has been clearly demonstrated that the rate constant  $k_r$  of the charge recombination deactivation of radical ion pairs shows a strong dependence upon the energy gap  $\Delta G_{ip}$  (between the ion pair and the neutral ground state) and upon the molecular nature of individual electron donor or acceptor ions. The plot of  $k_r$  vs  $\Delta G_{ip}$  for the chemically similar  $\pi$ - $\pi$  exciplex systems as well as singlet excited electron donor-acceptor complex systems studied in this and some previous works showed clearly the characteristic features of the so-called Marcus inverted region.

#### INTRODUCTION

It is well known that charge transfer (CT) or electron transfer (ET) in the excited state in solution is affected strongly by the solvent polarity.<sup>1</sup> Not only the exciplex formation process but also the electronic and geometrical structures of exciplexes seem to be controlled by solvent polarity. In considerably or strongly polar solvents, formation of solvated ion radicals becomes important as a non-radiative deactivation path of some typical exciplexes as well as excited EDA (electron donor-acceptor) complexes in addition to intracomplex radiationless transitions to the ground state or local triplet state. Details of the behavior of the produced radical ion pairs are of crucial importance as a basis for the studies of a broad range of chemical and biological systems such as mechanistic organic photochemistry, electrochemistry and photosynthesis.<sup>1</sup>

In order to elucidate these problems, Q-switched ruby laser and  $N_2$  gas laser photolysis and transient absorption as well as transient photoconductivity measurements were made on the typical exciplex systems and weak EDA complexes in polar solvents, which gave some important results especially on the relation between the ionic dissociation yield and solvent polarity as well as the molecular nature of each donor and acceptor.<sup>2</sup> However, because of the low time resolution of those previous measurements, some of the conclusions were not correct. We need measurements with higher time resolution including the picosecond (ps) regime.

We are now investigating the mechanisms of photoinduced ET, charge separation (CS) and charge recombination (CR) processes in radical ion pairs by means of mode-locked  $Nd^{3+}$ : YAG (ps) and excimer (ns- $\mu$ s) laser photolysis, transient absorption as well

as fluorescence measurements and also ps laser induced photocurrent measurements.

Roughly speaking, the photoinduced CS processes in polar solvents occur by:

- (a) the exciplex type interaction, i.e. the encounter collision between excited and ground state molecule or
- (b) the excitation of the ground state EDA complexes.

Both (a) and (b) lead to the formation of solvated radical ion pairs, which undergo CR deactivation and dissociation into free ions.

In addition to the photoinduced ET and related processes in the above systems with definite electron donor and acceptor solute molecules, electron ejection from the excited solute molecule into the solvent is also a very important primary process in photochemistry. Ultraviolet multiphoton ionization of solute or neat liquid under pulsed laser photolysis is a rather familiar phenomenon, on the one hand.<sup>3</sup> On the other hand, we have confirmed that TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) and similar low ionization potential diamines in some polar solvents undergo ET reaction from the fluorescent state to the surrounding solvent cluster, by directly observing the formation of the amine cation-solvent anion or solvated electron radical pair with ps spectroscopy.<sup>4</sup> These radical ion pairs undergo further dissociation and deactivation.<sup>4</sup>

In the following, we will show some recent results of our ps and ns laser photolysis investigations on the elementary processes of photoinduced CS as well as CR mainly in systems of the exciplex type and excited EDA complexes in polar solvents and will discuss the relevant mechanisms on the basis of theoretical considerations.

## RESULTS AND DISCUSSIONS

## 1. Photoinduced electron transfer and behavior of transient radical ion pair in some typical exciplex systems

In the following, we discuss mainly the results obtained for the pyrene–DMA (N,N-dimethylaniline), pyrene–DCNB (*p*-dicyanobenzene) and pyrene–TEA (triethylamine) systems in polar solvents. We have made quantitative measurements of transient absorbance in the ps–hundred ns regime by using a mode-locked Nd<sup>3+</sup>:YAG laser photolysis system and an excimer laser photolysis system, and have also made measurements of ps laser induced transient photocurrents.

Although the CT fluorescence of those exciplexes are largely quenched in high polarity solvents due to non-fluorescent geminate ion pair formation, one can still observe very weak exciplex fluorescence even in acetone or acetonitrile solution in the case of the pyrene–DMA system. We have confirmed that the rise time of the photocurrent  $\tau_d$ , which corresponds to the dissociation from the geminate ion pair, does not agree with the exciplex fluorescence decay time  $\tau_f$  in the same solvent, in general.<sup>5</sup> For example,  $\tau_d < 2$  ns,  $\tau_f \sim 2.3$  ns in acetonitrile,  $\tau_d = 7.0 \pm 0.5$  ns,  $\tau_f = 7.7 \pm 0.2$  ns in acetone  $\tau_d = 12.7 \pm 0.9$  ns,  $\tau_f = 14.1 \pm 0.7$  ns in methylethylketone and  $\tau_d = 23.8 \pm 1.4$  ns,  $\tau_f = 33.2 \pm 0.5$  ns in pyridine.<sup>5</sup> These results indicate that the weakly fluorescent exciplex is not directly combined with the dissociating geminate ion pair although there is evidence that there is an interconversion between the exciplex and the geminate ion pair as revealed by the study of the magnetic field effect upon exciplex fluorescence.<sup>6</sup> It should be noted here that, although it was suggested on the basis of the previous low time resolution measurement of the photocurrent on the pyrene–DMA–pyridine system that the ionic dissociation takes place from the non-relaxed CT state before the relaxed fluorescent exciplex is formed, the dissociating state with  $\tau_d \sim 23.8$  ns cannot be such a non-relaxed state.<sup>2b</sup>

Summarizing the above results, it seems necessary to assume the existence of multiple exciplexes and geminate ion pairs under incomplete mutual interconversions for the pyrene–DMA system in polar solvents. In order to elucidate further this problem, we have made detailed transient absorption measurements on the same system in the ps–several hundred ns regime. In acetonitrile, acetone and pyridine solutions, transient absorbance due to ions does not show any decrease until 5–10 ns after their formation by diffusion-controlled encounter as well as excitation of the contact pair [(DMA) = 0.5 M]. This initial yield,  $\Phi_{ion}$ , however, is a little different depending on the nature of the solvents, and decreases a little with a decrease in solvent polarity (e.g.  $\Phi_{ion} \sim 1.0$  and  $\sim 0.9$  in acetonitrile and acetone, respectively).

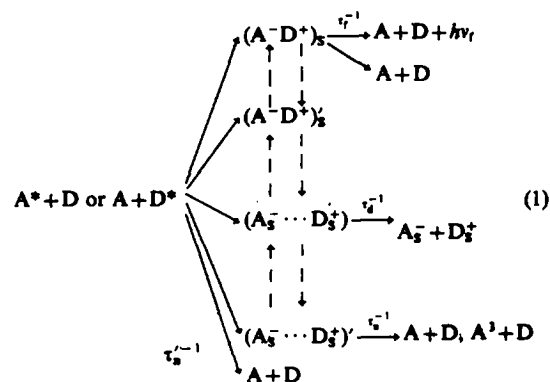
Since no decay of absorbance was observed in the 10–100 ns regime in acetonitrile solution, all ion pairs of pyrene–DMA formed with a quantum yield of unity dissociate without geminate recombination in this solvent. However, in acetone and pyridine solutions, a considerable amount of the geminate ion pairs are deactivated in the 10–100 ns regime although their lifetimes  $\tau_g$  are longer than  $\tau_d$  and  $\tau_f$  ( $\tau_g \sim 17$  and

$\sim 50$  ns in acetone and pyridine, respectively). This result strongly suggests the existence of different kinds of geminate ion pairs as discussed above.

On the other hand, no exciplex fluorescence can be detected while  $\tau_d < 2$  ns in acetonitrile and acetone solution in the case of the pyrene–DCNB system.<sup>5</sup> Weak exciplex fluorescence can be observed only in considerably less polar solvents, and  $\tau_d < \tau_f$  just as in the case of pyrene–DMA. For example,  $\tau_d = 5.5 \pm 0.3$  ns,  $\tau_f = 5.7 \pm 0.1$  ns in pyridine,  $\tau_d = 28.3 \pm 1.5$  ns,  $\tau_f = 47.0 \pm 0.4$  ns in *o*-dichlorobenzene and  $\tau_d = 46.0 \pm 1.6$  ns,  $\tau_f = 56.2 \pm 0.4$  ns in tetrahydrofuran.<sup>5</sup> Moreover, we have confirmed by means of the transient absorption measurements in the ps–several hundred ns regime that a large amount of the geminate ion pairs undergoes the CR deactivation even in acetonitrile solution in the 10 ns regime. These results indicate that we must assume the existence of several different kinds of ion pairs also in the pyrene–DCNB system.

Although the free energy of the ion pair state estimated from the oxidation–reduction potentials is almost the same for pyrene–DMA and pyrene–DCNB in the same solvent, the behavior of the geminate ion pairs and exciplexes are quite different, namely the CR deactivation process is more predominant in the pyrene–DCNB system. In addition, the initial yield of the ions of this system also depends upon the solvent polarity and decreases with a decrease of solvent polarity as in the case of the pyrene–DMA system.

Summarizing the above results, the photoinduced CS and CR processes in pyrene–DMA and pyrene–DCNB systems may be represented as follows.



In Eq. (1), the process  $\tau_g^{-1}$  represents the rapid non-radiative deactivation in the course of ET or immediately after ET before solvated geminate ion pair formation.

In addition to the above results with aromatic amine and aromatic cyano compound quenchers, we show here another example of the dependence of the photoinduced ET process and the behavior of the produced ion pairs upon the nature of the quencher in the case of the pyrene–aliphatic amine system. As an example, the transient absorption spectra of the pyrene–TEA system in pyridine are shown in Fig. 1. Similar time-resolved spectra were also observed in acetonitrile and acetone solution, and the ion band

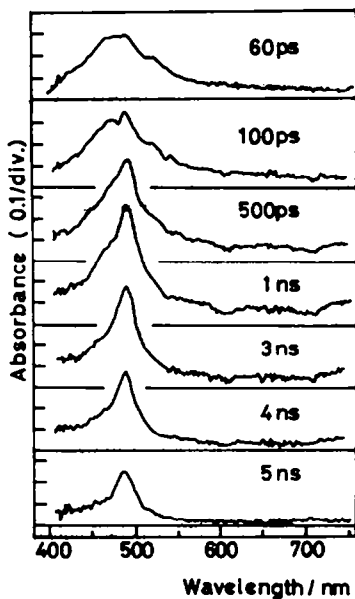


Fig. 1. Time-resolved transient absorption spectra of the pyrene-TEA system in pyridine. [TEA] = 0.53 M. The delay times from the exciting pulse are indicated.

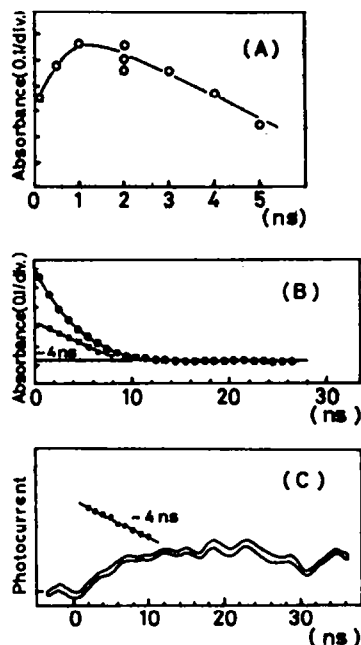
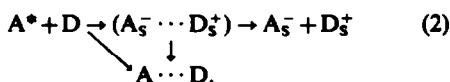


Fig. 2. The rise and decay curve of the transient absorbance of the pyrene anion band in the 100 ps–a few ns regime (A), its decay curve in the 10 ns regime (B), and the rise curve of the ps laser induced transient photocurrent (C) of the pyrene-TEA system in pyridine. The plateau region in (B) is due to the absorbance of dissociated ions.

in acetonitrile is considerably sharper than in other solvents.

In acetonitrile solution, after the rise of the pyrene anion band with rise time  $\tau_r \sim 380$  ps ([TEA] = 0.53 M), the absorbance did not show any decay in the ns–100 ns regime, and the photocurrent rise time  $\tau_d < 2$  ns. The quantum yield of the free ion formation estimated from the absorbance was 0.57. These results indicate that all geminate ion pairs in acetonitrile undergo dissociation and the quantum yield of the geminate ion pair formation is 0.57. Accordingly, rapid CR deactivation will take place in the course of ET, to which the destabilization of the ground state due to the pyramidal  $\rightarrow$  planar structural change, leading to the enhancement of the non-radiative deactivation, will contribute.

In acetone and pyridine solutions of pyrene-TEA, however, we can observe the decay of ion absorbance in the few ns–10 ns regime and the absorbance decay time agrees approximately with the rise time of the photocurrent. Observed results of pyridine solution are shown in Fig. 2. These results indicate clearly that the CR deactivation of the geminate ion pair can compete with its dissociation which has become slower in less polar solvents. It should be noted that, contrary to the results of pyrene-DMA and pyrene-DCNB,  $\tau_d \sim \tau_r$  in pyrene-TEA system, for which the reaction scheme may be given by



The fact that such various kinds of geminate ion pairs as observed in the case of pyrene-DMA and pyrene-DCNB systems do not exist in the pyrene-TEA system

might be due to the severe restriction of the conformation of the ET state.

We have observed also considerably smaller free ion yield compared to that of the pyrene-DMA system when several other aliphatic amines are used as electron donors. The yield becomes especially small ( $\sim 0.1$ ) when aliphatic diamines such as dabco, tetramethylethylenediamine and dimethylpiperazine are used as donors, which indicate that the interaction with pyrene responsible for the CR deactivation of the ion pair is stronger in the case of these diamines. It should be noted here that, although no deactivation process from the relaxed geminate ion pair can be observed in the pyrene-TEA system in acetonitrile, it is possible to observe such a process even in acetonitrile when dabco is used as donor. The initial yield of the geminate ion pair of the pyrene-dabco-acetonitrile system was 0.43 and this ion pair undergoes the CR deactivation and dissociation with a decay time of 140 ps, finally giving the free ions with a quantum yield of 0.1.

Details of the transient absorption spectral measurements of typical exciplex systems in the ps– $\mu$ s regime will be published elsewhere.<sup>7</sup>

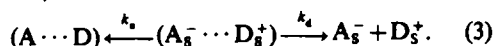
In contrast to the above exciplex systems, solvated radical ions or geminate ion pairs produced from the  $S_1$  state have hardly been detected in the case of porphyrin-quinone intermolecular exciplex systems in considerably or strongly polar solvents. We have observed transient absorption spectra of non-fluorescent short-lived ( $\tau \sim 40$  ps) exciplex (contact ion pair) of ethyletioporphyrin-toluquinone (TQ) and nanoethylporphyrin-TQ systems in benzene solution.<sup>8</sup> In strongly polar solvents, however, the energy gap  $|\Delta G_p|$  between the ion pair state and the

ground state may become considerably smaller due to the strong solvation. Moreover, the strong solvation will cause some change in the nature of the ion pair state. These effects of solvation will lead to the solvation-induced ultrafast CR deactivation ( $k_r \approx 10^{11} \sim 10^{12} \text{ s}^{-1}$ ) of the porphyrin-quinone ion pair state.<sup>8</sup> In any way, when compared to the ion pairs of the typical exciplex systems, this is a remarkable example of the dependence of CR rate constant upon the energy gap  $\Delta G_{ip}$ .

## 2. Charge recombination deactivation and dissociation processes from the excited singlet state of EDA complexes

We discuss here some examples of CR deactivation and dissociation processes from the ion pairs formed by excitation of ground state EDA complexes in polar solvents and dependence of CR deactivation rate constant  $k_r$  upon  $|\Delta G_{ip}|$  as well as molecular nature of donor and acceptor.

The ion pairs of TCNB (1,2,4,5-tetracyano-benzene)-toluene complex in various solvents of different polarity show decay over several hundred ps-ns regime undergoing the deactivation and dissociation.<sup>1c,9</sup>



The lifetime  $\tau = (k_a + k_d)^{-1}$  of the ion pair decreases with an increase in solvent polarity, e.g. from 1100 ps in octanenitrile to 300 ps in acetonitrile, while the dissociation quantum yield  $\phi = k_d/(k_a + k_d)$  increases with an increase in solvent polarity,  $\phi = 0.10$  in octanenitrile and  $\phi = 0.45$  in acetonitrile.<sup>1c,9</sup> Therefore, both  $k_a$  and  $k_d$  increase with an increase in solvent polarity, with the larger extent of the increase of  $k_d$  than that of  $k_a$ . For example,  $k_a = 8.2 \times 10^8 \text{ s}^{-1}$ ,  $k_d = 9.1 \times 10^7 \text{ s}^{-1}$  in octanenitrile and  $k_a = 1.8 \times 10^9 \text{ s}^{-1}$ ,  $k_d = 1.5 \times 10^9 \text{ s}^{-1}$  in acetonitrile. The increase of  $k_a$  can be ascribed to the decrease of  $|\Delta G_{ip}|$  due to the stronger solvation of the ion pair in a more polar solvent.

Contrary to the case of the TCNB-toluene system, EDA complexes of PMDA (pyromellitic dianhydride) with stronger donors like pyrene and DMA do not show the formation of the dissociated ions in polar solvents. This result is rather similar to that of the porphyrin-quinone system in strongly polar solvents. In order to elucidate the mechanism underlying this behavior of PMDA-strong donor complexes we have made transient absorption spectral measurements in the ps-ns regime. As an example, time resolved transient absorption spectra of PMDA-pyrene complex in THF are shown in Fig. 3. The spectra show characteristic PMDA anion like band immediately after excitation with the second harmonic YAG laser pulse. From the analysis of the rise and decay of the transient absorbance taking into consideration the exciting pulse width, the lifetime  $\tau$  of the ion pair state was obtained as follows:  $\tau \lesssim 10, 15, 50$  and 60 ps in acetonitrile, acetone, THF and ethylacetate, respectively. More details of the ps transient absorption as well as fluorescence studies of this system will be published elsewhere.<sup>10</sup>

Since  $k_d \sim 10^9 \text{ s}^{-1}$  even in acetonitrile and becomes much smaller in a less polar solvent, the observed  $\tau$  values indicate the overwhelmingly large  $k_a$  compared

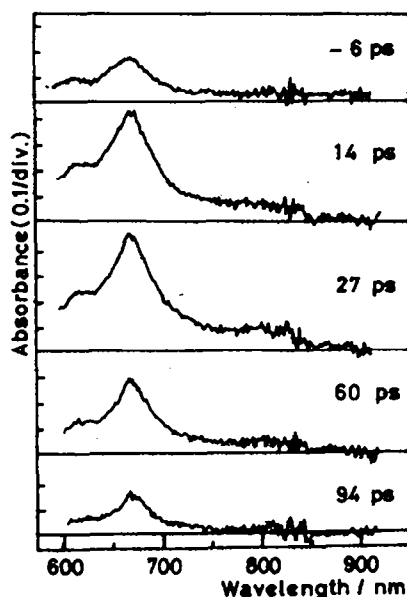


Fig. 3. Time-resolved transient absorption spectra of the singlet excited state of the PMDA-pyrene system in THF. The delay times from the exciting pulse are indicated.

to  $k_d$  in PMDA-pyrene ion pair. This result, together with that of porphyrin-quinone system, is a striking example of the dependence of  $k_a$  upon the energy gap  $\Delta G_{ip}$ .

In view of the solvation induced ultrafast CR deactivation of porphyrin-quinone and PMDA-pyrene system, without dissociation, part of the previously proposed mechanism of ionic photo-dissociation from the non-relaxed state of some typical exciplex systems and excited EDA complexes<sup>2c-4</sup> of  $\pi-\pi$  type seems to be incorrect. From the results of ps laser photolysis studies of pyrene-DMA, pyrene-DCNB, porphyrin-quinone exciplex systems and TCNB-toluene as well as PMDA-pyrene complexes, it is evident that the relaxed solvated ion pair state is of crucial importance in CR deactivation and dissociation into free ions in these systems.

However, it should be noted that, in the case of the pyrene-TEA system, the CR deactivation in the course of the ET process before the relaxed ion pair state is formed plays an important role. We can observe also ultrafast CR deactivation to the ground state ( $k_a \sim 10^{12} \text{ s}^{-1}$ ) when pyridine, N,N-dimethylformamide and dimethylsulfoxide are used as electron donors in the TCNB complex in acetonitrile solution, although the  $|\Delta G_{ip}|$  of these systems is close to or a little larger than that of the TCNB-toluene-acetonitrile system.<sup>9</sup>

The above results demonstrate clearly the remarkable energy gap dependence of  $k_a$  as well as its strong dependence upon the molecular nature of each donor or acceptor.

## 3. Energy gap dependence of charge recombination process of produced ion pairs in polar solvents—An observation of the Marcus inverted region.

The  $k_a$  values observed for porphyrin-quinone, PMDA-pyrene, TCNB-toluene and pyrene-DMA systems as discussed above are plotted against  $|\Delta G_{ip}|$

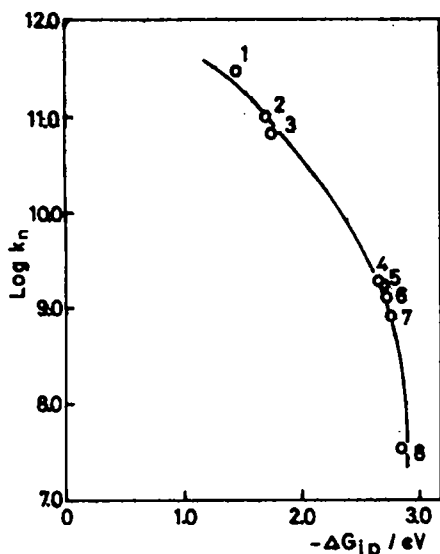


Fig. 4. Dependence of the CR rate constant  $k_r$  upon the energy gap  $\Delta G_{ip}$ : 1, ethyloporphyrin (D)-TQ(A) in acetone (Ref. 8); 2,3, PMDA-pyrene in acetonitrile (2) and acetone (3) (Ref. 10); 4-7, TCNB-toluene in acetonitrile (4), acetone (5), hexanenitrile (6) and octanenitrile (7) (Ref. 9); 8, pyrene-DMA in acetone (Ref. 7).

in Fig. 4. This is a demonstration of the so-called inverted region of Marcus.<sup>11</sup> Moreover, the CR rate constant in a polar solvent also depends strongly upon the molecular nature of the individual electron donor or acceptor ions as we have already discussed in previous sections. For example, exciplex systems containing aliphatic amine donors show more efficient CR reaction than the systems with alkyaniline donors, and similar behaviors of TCNB complexes with pyridine, DMSO, DMF compared to that with toluene are observed.

Contrary to this result of the CR reaction of ion pairs, in many luminescence quenching reactions due

to ET in polar solutions, the quenching rate constant  $k_q$  shows a steep rise around

$$\Delta G_{et}(A^* \cdots B \leftrightarrow A_S^{\pm} \cdots B_S^{\mp}) \sim 0$$

and does not show any decrease from the diffusion-controlled value even in the strongly down-hill region, being insensitive to the energy gap  $\Delta G_{et}$ .<sup>1</sup> We need some unified interpretation for these apparently contradicting results of photoinduced CS reaction and the CR reaction of the produced ion pairs.

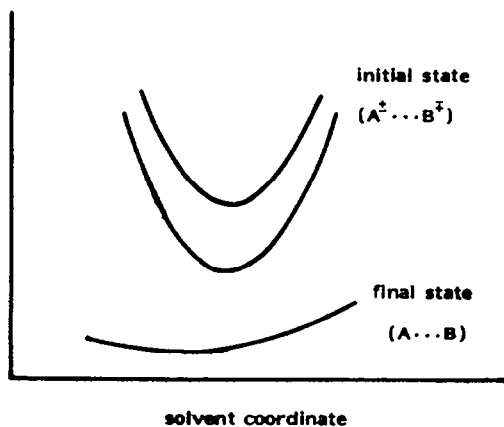
In general, the ET rate constant  $W(\Delta E)$  in the CS and CR reaction can be written by convolution<sup>12</sup>

$$W(\Delta E) = \int_{-\infty}^{\infty} W_q(\Delta E - \epsilon) \mathcal{S}(\epsilon) d\epsilon \quad (4)$$

where  $\Delta E$  is the energy gap between the initial and final states, and  $W_q$  includes the square of the matrix element of electronic interaction responsible for ET as well as the Franck-Condon factor due to the intramolecular vibrational modes, while  $\mathcal{S}(\epsilon)$  is the Franck-Condon factor due to the reorientational phonon of the polar solvent surrounding solute.<sup>12</sup>

By taking into consideration the important fact that the reorientational phonon frequency of the polar solvent surrounding the charged solute is much larger than that surrounding the neutral one, we can explain the above difference between the CR and CS reaction.<sup>12</sup> Numerical calculations of  $W$  by using appropriate approximations show that, in strongly polar solvents, the solvent mode apparently refuses to contribute to the Franck-Condon factor for CR reaction.<sup>12a,c</sup> Accordingly, the CR rate is determined almost exclusively by the intramolecular quantum mode and the magnitude of the electronic interaction responsible for ET.<sup>12a,c</sup> This circumstance can be understood qualitatively from the schematic potential energy surfaces for the solvent mode given in Fig. 5. Compared with the case of the CS reaction where the activation energy originating from the Franck-Condon factor is always small irrespective of the

(a) charge recombination reaction



(b) charge separation reaction

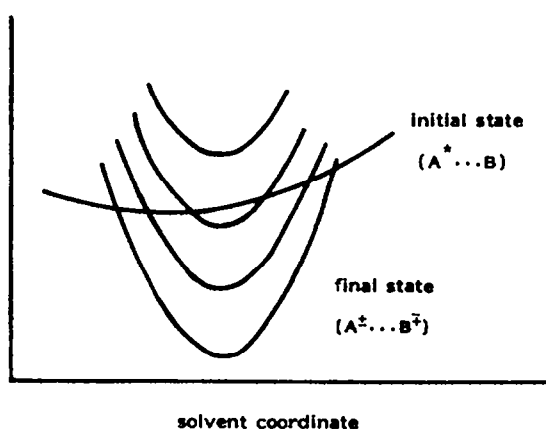


Fig. 5. Schematic potential energy surfaces of the solvent mode in CR (a) and CS (b) reactions in strongly polar solvents.

energy gap,<sup>12a</sup> the solvent phonon mode does not play such a role in the CR reaction.

### EXPERIMENTAL

Transient absorption spectra in the ps–several ns regime were measured by means of a microcomputer-controlled, mode-locked Nd<sup>3+</sup>:YAG laser photolysis system.<sup>13</sup> Transient absorption measurements in the several ns–100 ns regime were made by exciting the sample with the 355 nm ps laser pulse and by observing the time profile of the pyrene anion absorbance using the light pulse produced by focusing the ps fundamental pulse onto a Xe lamp as a spectro-flash. Transient absorption spectra in several ten ns–μs regime were measured with an excimer laser photolysis system.<sup>14</sup> Details of the measurements of ps laser induced photocurrent were given elsewhere.<sup>5</sup> Pyrene and DCNB were purified by repeated recrystallization from ethanol and subsequent vacuum sublimation. PMDA was recrystallized from ethylacetate and sublimated in a vacuum. All other chemicals and solvents were purified by standard method, and all solvents were carefully dried. All sample solutions for the measurement were deaerated by repeated freeze–pump–thaw cycles.

*Acknowledgement*—This work was partly supported by Grant-in-Aid (Nos. 58430003 and 58045097) from the Japanese Ministry of Education Science and Culture to N.M.

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