The Formation and Dissociation of the Solvated Ion-pair in the Excited Pyrene–Dicyanobenzene System

Tetsuro Hino, Hiroshi Masuhara*, and Noboru Mataga
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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Nanosecond laser photolysis has been applied to investigate the photochemical primary processes of the pyrene-*p*-dicyanobenzene system in some solvents. The solvated ion-pair is formed by the excitation and its yield increases as the dielectric constant of the solvent does; this was explained with the empirical equation proposed previously. The dissociation of the solvated ion-pair to free ions was directly observed in moderately polar solvents and the rate constant of the dissociation was determined, which is in agreement with the values calculated by Eigen's equation. The role of the ion-pair formation in the fluorescence quenching was discussed on the basis of the present results, and it was concluded that some unknown quenching processes other than the triplet formation compete with the solvation to ion-pairs.

We have been studying the ionic photodissociation processes of the excited electron donor-acceptor (EDA) systems by using the nanosecond laser photolysis method. The excited singlet and triplet states of EDA complexes, which are stable in the ground state, and exciplexes are all called excited EDA systems in the present paper. These systems are suitable for clarifying the relation between photophysical as well as photochemical primary processes and molecular interactions. Ionic photodissociation to the donor cation and the acceptor anion in polar solvents is one of the important primary processes and has been referred to in many fields of chemistry. The results obtained by laser photolysis are summarized as follows: (1) Several different dissociation patterns have been demonstrated. Dissociations from the excited singlet or triplet states are known in the case of EDA complexes, while the problem in the case of exciplexes is not about the spin state but about the excited state relaxed or nonrelaxed with respect to the solvation.[1)] (2) The important role of the nonrelaxed state in the dissociation process was confirmed.[1a),2)] The dissociation of pyrene–*N*,*N*-dimethylaniline (DMA) and *s*-tetracyanobenzene–toluene systems occurs from the excited singlet state nonrelaxed with respect to the solvent orientation. (3) A new empirical equation for the relationship between the yield and the solvent dielectric constant was proposed. The solvent effect on the ionic photodissociation seems to be well explained in terms of the dielectric constant.[1a)] (4) Ionic dissociation yields of several EDA systems in acetonitrile depend upon the chemical property of the quencher and not on the strength of the EDA interaction.[3)]

In the present work we will show another kind of ionic dissociation process: namely, the results for the formation and dissociation processes of the solvated ion-pair will be shown in the case of the pyrene–*p*-dicyanobenzene(DCNB) system.

Experimental

The transient absorption spectral and photocurrent measurements were performed by using the same apparatus as reported previously.[4)] The exciting pulse of 347 nm was produced through the ADP frequency doubler with a conversion efficiency of *ca.* 8%. The ADP crystal was set in an air bath to control the temperature. The fluctuation was ±0.6 °C. The temperature matched and phase matched ADP gives a constant output of the exciting pulse.

Pyrene was chromatographically purified. DCNB was recrystallized several times and sublimated. All the solvents were spectrograde (Dotite, Nakarai, or Merck) and used without further purification. Pyridine was dried over potassium hydroxide and distilled. The concentration of pyrene was adjusted to give an appropriate absorbance (0.1—0.4) at 347 nm, which is a suitable condition for the present laser photolysis measurements. The concentration of DCNB was determined so as to quench the pyrene fluorescence more than 90%. The solutions were completely degassed by usual freeze-pump-thaw method.

Results and Discussion

The Formation and Dissociation Processes of the Solvated Ion-Pair in the Pyrene–DCNB System. The transient absorption spectra of the pyrene–DCNB–dichloromethane system shown in Fig. 1 were obtained at 50 ns after the laser excitation. These spectra can be reproduced with the superposition of the bands of the pyrene cation, the DCNB anion, and the triplet pyrene. The ionic species and the triplet pyrene are produced immediately after the excitation with the pulse. The kinetic relation between the transmittance at 445 nm (the pyrene cation) and the photocurrent is given in Fig. 2. The transmittance is almost constant in the course of a few μs, while the peak photocurrent is attained in several hundred nanoseconds. The difference of the time dependence between the transmittance and the current may be ascribed to an ionic transient, which gives no current but shows an absorption similar to that of the pyrene cation. This transient may be an ion-pair of the pyrene cation and the DCNB anion or the pyrene–DCNB exciplex, since the absorption spectra of both species are expected to be reproduced with the superposition of the bands of the pyrene cation and the DCNB anion.[5)] Because the lifetime of the exciplex in the dichloromethane solution is ∼30 ns, a curve of photocurrent rising more quickly than the observed one should be found if the free ions were formed from the exciplex. Therefore, the present transient seems to be an ion-pair of the pyrene cation and the DCNB anion, which is of course completely solvated. The latter ion-pair is produced rapidly by

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* To whom all correspondence should be addressed.

Table 1. The dissociation rate constants of the solvated ion-pair to free ions

Solvent	k_{exp}	τ_f	$1/\tau_f$	k_{diss}	τ_{max}[a)]
Dichloromethane	$1.3\times10^7\,\mathrm{s}^{-1}$	28 ns	$3.5\times10^7\,\mathrm{s}^{-1}$	1.5×10^7	400 ns
1,2-Dichloroethane	0.9×10^7	short	large	2.4×10^7	
Pyridine	$9\ \times10^7$	short	large	6.3×10^7	20 ns
Acetone	rapid[b)]	—		1.4×10^9	immediately
Acetonitrile	rapid[b)]	—		4.3×10^9	immediately

a) τ_{max} is the time when the peak photocurrent is attained after the excitation. b) The rising curve is identical with a time-integrated function of an exciting pulse.

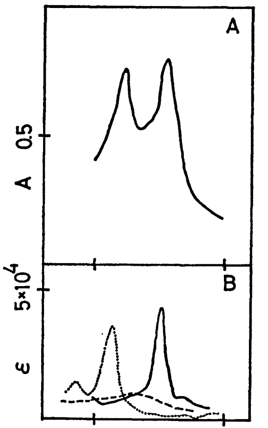

Fig. 1. The transient absorption spectra of the pyrene-DCNB-dichloromethane system obtained at 50 ns after the laser oscillation (A). The reference spectra (B) of the pyrene cation (——), the triplet pyrene (······) and the DCNB anion (----).

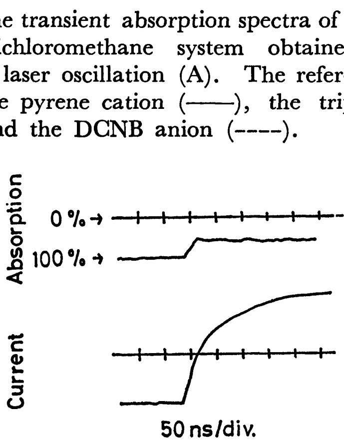

Fig. 2. The kinetic relation between the absorption (the pyrene cation at 445 nm) and the photocurrent of the pyrene-DCNB-dichloromethane system.

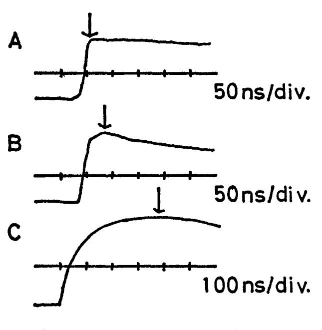

Fig. 3. The oscillogram of the rise of the transient photocurrent, (A) in acetonitrile, (B) in pyridine and (C) in dichloromethane. The vertical arrow (↓) shows the time when the maximum value was obtained.

laser excitation and dissociates gradually into free ions.

The solvent effect on the dissociation process is shown in Fig. 3. Faster rising curves are obtained in solvents with higher polarity, and the maximum value of the photocurrent in acetonitrile is reached immediately after excitation. These solvent effects are consistent with the following theoretical estimation of reaction rates. The rate constant of the diffusion-controlled dissociation was calculated by Eq. (1).[6,7)]

$$k_{\mathrm{diss}} = 4\pi N'(D_{\mathrm{A}^-}+D_{\mathrm{D}^+})a\delta/\Delta V(1-\exp(-\delta)) \tag{1}$$

where $\delta=e^2/\varepsilon kTa$ and $\Delta V=4\pi N'a^3/3$. The notations are the same as in Ref. 7. The encounter distance a was assumed to be 7 Å. The experimental rate constant (k_{exp}) was determined from the exponential growth curve of the photocurrent. The results obtained are listed in Table 1. The k_{exp} in these solvents is almost identical with k_{diss}, but not with $1/\tau_f$. Thus the present solvent effect is well explained by assuming the diffusion-controlled dissociation mechanism.

As mentioned in the previous paper[1a)], the ionic dissociation of the pyrene–DMA system occurs in the excited state nonrelaxed with respect to the solvation. Although the energy levels of the initial encounter complex, the solvated ion-pair, and the free ions of the pyrene–DMA system are almost equal to those of the pyrene–DCNB system, their dissociation processes are not similar. This difference may be characteristic of the "chemical property" of the quencher, although the precise nature of the "chemical property" is still unknown. Recently we have studied the ionic photodissociation of various pyrene-quencher systems in polar solvents and found no general relation between the yield of free ions and the strength of the EDA interaction.[3)] It was emphasized that the "chemical property" of the quencher is a key for understanding the ionic photodissociation mechanism.

The Solvent Effect on the Yield of the Ion-pair Formation. The relative yield of ionic species (ion-pair or free ions) in acetonitrile and in dichloromethane was obtained by absorption spectral measurements. The ratio of the yields obtained immediately after the excitation in the former and the latter solvents was 1 : 0.25. On the other hand, the ratio obtained by comparing the maximum value of the transient photocurrent was 1 : 0.22. Since free ions are favored in acetonitrile,[8)] the above agreement of the ratios for the spectral and the photocurrent data means that most of the ion-pair dissociate into ions even in dichloromethane. Therefore, the yield of ion-pair formation in some solvents may be estimated by examining the photo-

TABLE 2. QUANTUM YIELDS OF THE ION-PAIR FORMATION

Solvents	ε	ϕ_{pc}[a)]	ϕ_{ab}[b)]
Dichloromethane	8.93	0.08	0.25
1,2-Dichloroethane	10.4	0.11	
Pyridine	12.4	0.14	
Acetone	20.7	0.32	
Acetonitrile	37.5	0.38	1.00

a) ϕ_{pc} are the absolute yields obtained from the photocurrent data. b) ϕ_{ab} are the relative yields obtained from the absorption spectral measurements.

current data. As shown in Table 1, the rate constant of dissociation is larger than 10^7 s^{-1}, while the rate of the recombination of free ions is calculated to be 10^5—10^6 s^{-1}, since the rate constant of the diffusion-controlled process is 10^{10} M^{-1} s^{-1} and the concentration of ions is 10^{-4}—10^{-5} M. Since the decay of free ions due to the recombination is almost negligible at an early stage after the excitation, the dissociation may be approximately completed. Then the values of the current are proportional to the yield of the ion-pairs. The obtained yields are listed in Table 2.

The yield increases as the solvent polarity (dielectric constant) increases. The present results can be well explained with the following empirical equation for the relationship between the yield (ϕ) and the solvent dielectric constant (ε), proposed in the previous work[1a)].

$$\log\left(\frac{1}{\phi}-1\right)=\frac{p}{\varepsilon}+q \tag{2}$$

where p and q represent constants. It has been pointed out[1a)] that the following two conclusions are given when Eq. (2) is satisfied: (1) The ionic photodissociation depending upon ε competes with the other radiationless processes independent of ε. (2) The identical dissociation mechanism is expected in various solvents. Therefore it may be concluded that the free ions in acetonitrile are also formed through the ion-pair and that some radiationless process independent of the solvent dielectric constant competes with the ion-pair formation.

Discussion on the Fluorescence Quenching Mechanism. The fluorescence quenching process has been studied in detail in various solvents by Mataga *et al.*[2,4b,9)] and by Weller *et al.*[7)] One of the main quenching processes has been pointed out to be the formation of the solvated ion-pair competing with the exciplex formation.[7)] However, there have been no observations concerning the dynamic behavior of the solvated ion-pair up to now, and the formation and dissociation processes of the solvated ion-pair have been made clear in the present work for the first time.

A quantitative analysis of the produced intermediates seems important for understanding the quenching processes. The yield of ions and the triplet molecule are estimated in the usual way.[4)] The yields of ions in acetonitrile and in dichloromethane were 0.38 and 0.08, respectively. On the other hand, the yields of the pyrene triplet in acetonitrile and in dichloromethane were 0.11 and 0.07, respectively. The sum of these yields is smaller than unity in both solvents and the residual radiationless transitions may compete with the above processes. This conclusion is in good agreement with the above result of the solvent effect on the ion-pair yield. Such a degradation process has not always been postulated in the previous papers. However, the former process seems to be important for elucidating the fluorescence quenching process due to the electron transfer in the excited EDA systems. This conclusion is consistent with the results of ionic photodissociation of pyrene–DMA, pyrene–electron acceptors, and tetracycnobenzene–aromatic hydrocarbon systems.[1,3,4a)]

Finally, the intersystem crossing process of the present system should be mentioned. In dichloromethane solution an appreciable amount of triplet molecules is formed at 50 ns (shown in Fig. 1) after the laser oscillation, when the decay of the ion-pair can be neglected. Therefore, a triplet formation through the solvated ion-pair of the present type may be excluded. Recently, similar results have been reported,[10)] although the nature of this particular behavior is not clear.

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