BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 764—769(1972)

Laser Photolysis Studies on the Formation of Solvated Ion Radicals in the Pyrene—*N*,*N*-Dimethylaniline System in Various Solvents

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(Received August 27, 1971)

Formation of solvated ion radicals in the pyrene-*N*,*N*-dimethylaniline (DMA) system (which is a typical one showing heteroexcimer (HE) fluorescence) in various solvents has been studied by means of the laser photolysis and transient photoconductivity as well as transient absorption measurements. Ion radical formation due to the encounter collision between an excited pyrene and DMA in moderately as well as in strongly polar solvents has been established. This result is quite important in explaining the experimentally observed relation between the solvent dependent HE fluorescence quantum yield and decay time.

In relation to the electron transfer mechanism of fluorescence quenching in solution, somewhat detailed studies concerning the solvent effects on the HE fluorescence have been carried out.[1,2] According to those investigations, the fluorescence yield as well as fluorescence decay time of HE decrease as the solvent polarity is increased, where the solvent dependence of the fluorescence yield is much stronger than the decay time. One of the present authors (N.M.)[1] has interpreted this result as due to the decrease of the radiative transition probability and the increase of the radiationless transition probability of HE as the solvent polarity is increased. On the other hand, Weller and coworkers[2] have proposed an alternative interpretation for this phenomenon. They assumed the competition of the following two processes for an aromatic hydrocarbon (acceptor) and an aromatic amine (donor) system

$$A^* + D \xrightarrow{k_C} (A^- \cdot D^+)^*$$

$$A^* + D \xrightarrow{k_I} (A_s^- \cdots D_s^+)$$

where $(A^- \cdot D^+)^*$ is the fluorescent HE and $(A_s^- \cdots D_s^+)$ represents solvent-shared ion-pair which is non-fluorescent. It is assumed that the rate of process k_I increases with the increase of the solvent polarity, while process k_C is independent of the solvent polarity.

In order to examine the validity of the assumption of the existence of the non-fluorescent ion-pair state in a solvent which is not very polar, we have undertaken nsec laser photolysis studies on aromatic hydrocarbon-amine system in various solvents. If the dissociation of the ion-pair $(A_s^- \cdots D_s^+)$ into the solvated ion radicals $(A_s^- + D_s^+)$ occurs to some extent in a solvent which is more or less polar, it may be possible to confirm the existence of the dissociated ions by means of the nsec laser photolysis and conductivity measurements. Of course, it may be also possible to observe the non-fluorescent ion-pair and/or the solvated ion radicals by means of the nsec laser photolysis and the measurement of absorption spectra of ions as well as time variations of absorption intensities. However, the sensitivity of the detection by photoconductivity measurements may be higher than that by the absorption spectral measurements. Accordingly, the method of the nsec laser photolysis and conductivity measurement appears to be quite suitable for the detection of ion radicals of rather small concentration in the solvent which is not very polar.

In the following, we show the results of our measurements on the ion radical formation in the pyrene-*N*,*N*-dimethylaniline (DMA) system in various solvents with different polarities.

Experimental

We have used a Q-switched ruby laser (Japan Electron Optics, JLR-O2A) with the out-put power of about 1.5 joule.

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[1] N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).

[2] H. Knibbe, K. Röllig, F. P. Schäfer, and A. Weller, *J. Chem. Phys.* **47**, 1184 (1967).

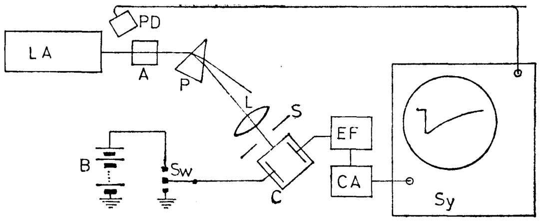

Fig. 1. Schematic diagram of the apparatus for the transient photoconductivity measurement. LA: Q-switched ruby laser, PD: photo-diode, A: ADP frequency doubler, P: prism for separating the 694 and 347 nm beams, L: lense, S: slit, C: cuvette, B: battery, SW: switch, EF: emitter follower amplifier, CA: cascade amplifier type CA-2, Sy: Tektronix 585A oscilloscope.

The exciting light pulse of 347 nm was produced through the ADP frequency doubler with conversion efficiency of about 8%. The light pulse has a duration of 15—20 nsec.

The optical arrangement for the photocurrent measurments is shown in Fig. 1. The position of the quartz cuvette for the measurement of photocurrents or transient spectra was settled by using the light beam of a He-Ne gas laser which reproduced the optical path of 347 nm pulse. The optical path of the 347 nm beam was recorded by burned spots on coloured paper produced by irradiating with the 347 nm pulse.

The quartz cuvette for the photocurrent measurments contains two 9 mm×10 mm Ni plate electrodes spaced each other by 7 mm. The direct irradiation on the electrodes was avoided by putting an optical slit on the front face of the cuvette. The supplied D.C. voltage between electrodes was adjusted in the range from 90 V to 540 V. Current signal obtained was converted to voltage signal through a 50Ω resister or home-made emitter follower amplifiers, the frequency characteristics of which covered the range from about 2 kHz to 150 MHz. The input impedance of our emitter followers was 13.2, 4.12, and 0.887 kΩ, respectively. Some weaker signals of photocurrent were measured by using Iwatsu cascade amplifier type CA-2. The time constant of the electronic circuit was less than 5 nsec when a 50Ω resister was used. In the other cases where the amplifiers were used, the time constant of the electronic circuit increased because of stray capacities of the cuvette and cables. The DC dark current was omitted by using the AC coupling of an emitter follower as well as the AC coupling of an input of Tektronix 585 A oscilloscope. For examining the effect of the exciting light intensity on the photocurrent, the intensity of the laser pulse was varied by using neutral filters composed of wire gauzes.

Transient absorption spectra of ion radicals produced by laser photolysis were measured by means of the methods explained in detail elsewhere.[3] The absorption spectra of ion radicals were photographed by using laser breakdown sparks in O_2 and Xe gases as spectroflashes. On the other hand, the spectra as well as time variations of their intensities were measured by using a Xe flash lamp as a monitoring light source.

Acetonitrile was refluxed repeatedly over phosphorus pentoxide, distilled into potassium carbonate and fractionally distilled. Merck spectrograde *n*-hexane, toluene, ethylether, monochlolobenzene, ethylene dichloride, methylethylketone, and acetone were used without further purification. Pyrene was chromatographed on activated alumina and silica gel, and extensively zone-refined. DMA was refluxed with acetic anhydride, washed with water, dried over potassium hydroxide, and distilled in vacuum several times. All the solutions measured were deaerated completely by repeated freeze-pump-thaw cycles.

Results and Discussion

Generally speaking, the photocurrent density may be given by,

$$i(t) = \sum_j z_j e n_j(t) \mu_j E_{\mathrm{eff}} \qquad (1)$$

where $z_j e$, μ_j and $n_j(t)$ represent an electric charge, the mobility of j-th carrier and its number in unit volume, respectively. E_{eff} is an effective electric field working on the carriers.

In the case of three compoment system of pyrene-DMA-solvent, the charge carriers may be mainly pyrene anions and DMA cations. We have confirmed the simultaneous production of these anions and cations by means of the laser photolysis and the measurement of the transient absorption spectra. For example, the spectra observed in acetonitrile and pyridine are indicated in Fig. 2 where the absorption bands appearing in the region from 440 to 510 nm can be ascribed to those of pyrene anion and DMA cation and those around 400 nm are due to the T-T absorption of pyrene.[4]

The effective electric field may be given by, $E_{\mathrm{eff}} = E_{\mathrm{app}}/\varepsilon$, where E_{app} is an applied electric field and ε is

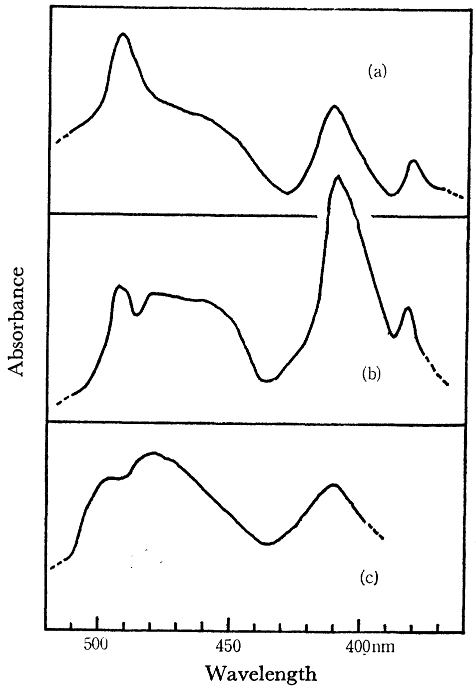

Fig. 2. Transient absorption spectra measured photographically by using laser break down sparks in O_2 and Xe gas. [Pyrene]$=5\times10^{-4}$ M, [DMA]$=8\times10^{-2}$ M
(a) acetonitrile solution. O_2 spark.
(b) acetonitrile solution. Xe spark.
(c) pyridine solution. O_2 spark.

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[3] H. Masuhara, M. Shimada, N. Tsujino, and N. Mataga, This Bulletin, to be published.

[4] T. Okada, H. Oohari, and N. Mataga, This Bulletin, **43**, 2750 (1970).

the static dielectric constant of solution. Accordingly, Eq. (1) can be reduced to the following.

$$i(t) = en(t)(\mu_{\text{anion}}+\mu_{\text{cation}})E_{\text{app}}/\varepsilon \qquad (2)$$

For the actual evaluation of the concentrations of produced ions in various solvents from the observed photocurrent, the value of the mobility of ion radicals in each solvent is necessary. Because the concentration of ions is rather low, we assume here that the mobility is independent of the ion concentration and is inversely proportional to the viscosity η of the solvent.[5] Then, the concentration of ions may be proportional to the product of (photocurrent) $\times\eta\times\varepsilon$.

In the case of the three component system, the ion radicals may be produced by the encounter collision between A* and D, and the produced ions may decay mainly due to the recombination reaction, *i.e.* electron transfer from anion to cation. Since the concentration of DMA in the present study is approximately 10^{-2}—10^{-1} M, the formation of ion radicals seems to occur very rapidly during nsec time region. Actually, we have confirmed that the formation of ion radicals is quite rapid and the rise curve of the photocurrent is the same as that of a time-integrated function of a 347 nm pulse. As an example, the rise curve of photocurrent and that of the optical absorption at 493 nm (pyrene anion) of the pyrene-DMA-acctonitrile system are indicated in Fig. 3 together with the shape of an exciting light pulse.

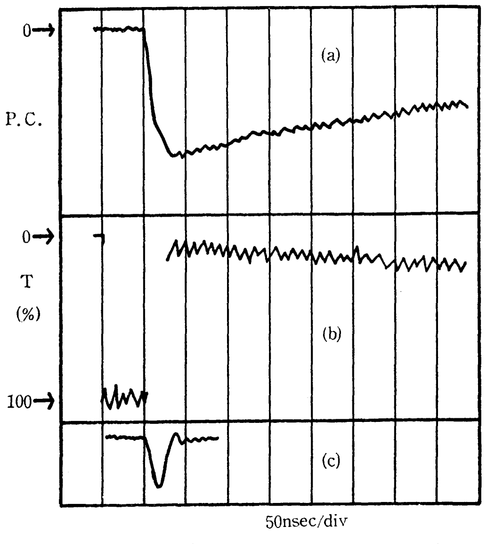

Fig. 3. The rise curve of photocurrent and that of the optical absorption of pyrene anion in the case of pyrene-DMA-acetonitrile system. Concentrations of pyrene and DMA are the same as those in Fig. 2.
(a) photocurrent. (b) transmittance at 493 nm. (c) shape of an exciting light pulse.

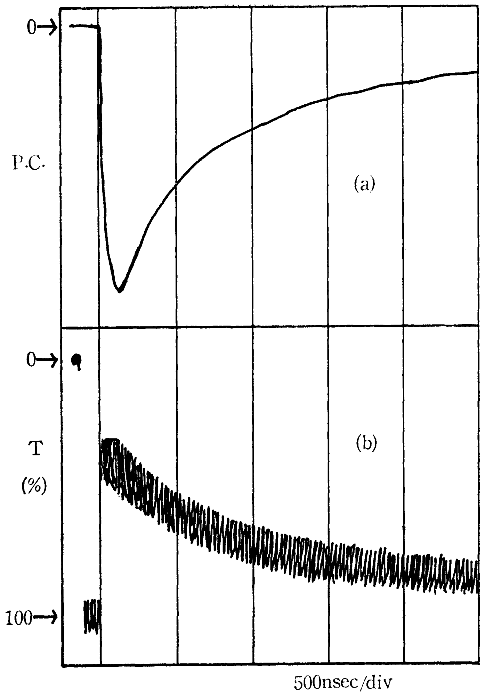

Fig. 4. The decay process of ions in the case of pyrene-DMA-acetone system. Concentrations of pyrene and DMA are the same as those of Fig. 2
(a) photocurrent (b) transmittance at 493 nm.

Since the concentration of the produced ion radicals may be rather small, the rate of the disappearance of ions due to the recombination reaction will be much slower compared to the rate of their production. We have confirmed that the photocurrent as well as the absorbance due to the ions decay slowly during times of μsec. As an example, the observed results for pyrene-DMA-acetone system are shown in Fig. 4.

If the decay of ions is mainly due to the bimolecular reaction between the acceptor anion and the donor cation radicals, both of the reciprocal of the photocurrent and that of the absorbance due to the ions should be proportional to time. This requirement is well satisfied as it is indicated in Fig. 5 for the same system as in Fig. 4. The difference in the slope between (a) and (b) in Fig. 5 can be ascribed to the difference in the initial concentrations of produced ions.

Now, because the formation of ion radicals is quite

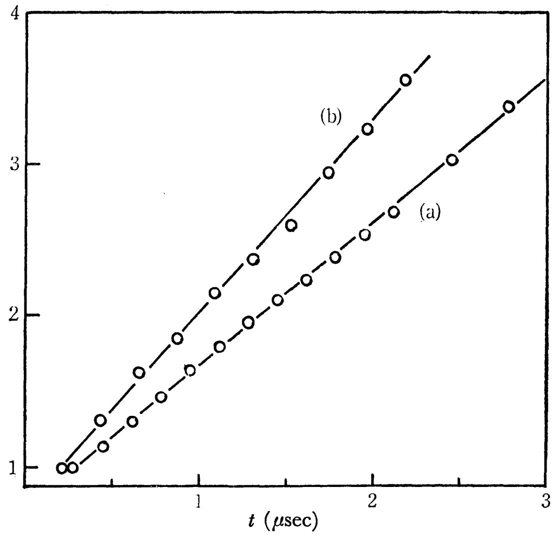

Fig. 5. The reciprocal of the photocurrent *vs.* time relation (a) and the reciprocal of the absorbance *vs.* time relation (b). The same system as indicated in Fig. 4.

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[5] J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Vol. 1, Plenum Press, New York (1970).

rapid while they decay slowly during times of μsec as it is described above, the value of the peak photocurrent obtained immediately after the excitation appears to be proportional to the concentration of dissociated ions. However, there is another problem to be taken into account for the evaluation of ion concentrations in various solvents. Since the light pulse in the present work is fairly strong, it may be possible that the ionization of pyrene due to the double photon absorption occurs and that we are observing the photoconductivity due to pyrene cations and solvated electrons. In order to examine this problem, we have investigated the effect of the exciting light intensity on the peak photocurrent. As an example, the result for pyrene-DMA-acetonitrile system is indicated in Fig. 6, from which one can see that the ionic dissociation in this case is a one photon process. Therefore, in these systems of pyrene-DMA-solvent, the most predominant process leading to the photoionization appears to be the encounter collision between DMA and excited pyrene molecule followed by one electron transfer from DMA to pyrene.

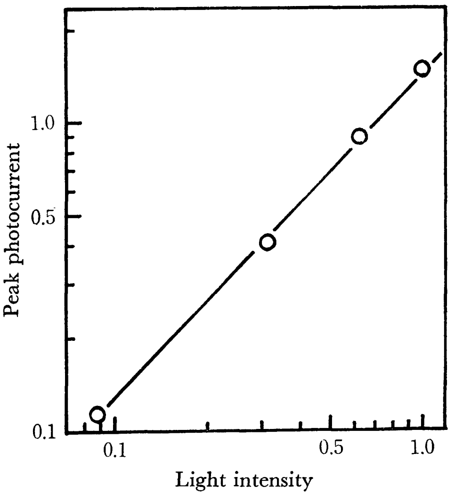

Fig. 6. The effect of exciting light intensity on the peak photocurrent of pyrene-DMA-acetonitrile system. Concentrations of pyrene and DMA are the same as those of Fig. 2, respectively.

In the actual experimental measurements, we have checked not only the photocurrent of the pyrene-DMA system in a solvent but also that of the two component system, pyrene or DMA in the same solvent, as well as that of the pure solvent. We have confirmed that the laser induced photoconductivity of a DMA-solvent system and also that of the pure solvent are negligibly small compared with that of the pyrene-DMA system in the same solvent. However, the photocurrent of pyrene-solvent two component system was not negligible compared with that of the three component system, especially in the case of less polar solvent. For example, the observed value of photocurrent of pyrene-acetonitrile system was *ca.* 5% of that of pyrene-DMA-acetonitrile system. The percentage of the photocurrent of pyrene-solvent system to that of the corresponding three component system becomes larger as the dielectric constant of solvent is decreased. Namely, it is 10% in acetone and pyridine, 30% in methylene dichloride, 50% in monochlorobenzene, and almost 100% in ethylether. These results indicate that the photoionization of pyrene-DMA-solvent system is affected by the solvent polarity more strongly than that of pyrene-solvent two component system.

The laser induced ionization of two component system is not limited to the case of pyrene-solvent systems. Although the details of our studies on the laser induced ionization of various aromatic molecules in organic solvents will be published elsewhere, some fundamental points will be given here.

According to our investigations, this photoionization is mainly caused by a biphotonic process which is a direct two quantum absorption by the ground state to give a high energy state which ionizes. Our studies have indicated further that the photoionization is partially due to mono-photonic absorption process, where the electron transfer from the excited Franck-Condon state of the solute to the solvent molecules seems to occur. At any rate, the laser induced ionization of the pyrene-solvent system is a very rapid process (faster than the encounter collision between A* and D). Therefore, in a rough approximation, the amount of ion radicals produced by the encounter collison between A* and D may be given by subtracting the value of photocurrent of two component system from that of the corresponding three component system. In this way, we have evaluated the relative concentrations of ions given in Table 1.

Although it was not possible to observe the ion radical formation due to the encounter collision between A* and D in *n*-hexane by means of the photocurrent measurements, we have observed transient absorption bands quite similar to those of pyrene anion in the case of pyrene-DMA-*n*-hexane system. The decay curve of the transient absorption at 719 nm is shown in Fig. 7

Table 1. OBSERVED RELATIVE CONCENTRATION OF IONS, I_C, FREE ENERGIES OF HE STATE, ΔF(HE), THE SOLVATED IONPAIR STATE, $\Delta F(A_S^- \cdots D_S^+)$, AND THE DISSOCIATED ION RADICAL STATE, $\Delta F(A_S^- + D_S^+)$, ABOVE THE GOUND STATE, A+D. FREE ENERGIES ARE GIVEN IN UNITS OF eV.

Solvent	ε	ΔF (HE)	ΔF $(A_S^- \cdots D_S^+)$	ΔF $(A_S^- + D_S^+)$	I_C[a]
Acetonitrile	37.5	3.02	2.80	2.86	1.0
Acetone	20.7	3.03	2.85	2.95	0.3_0
Methylethyl ketone	18.5	3.03	2.86	2.97	0.2_1
Pyridine	12.3	3.03	2.92	3.08	0.1_1
Ethylene chloride	10.4	3.04	2.95	3.15	0.01_4
Methylene chloride	9.08	3.04	2.98	3.20	0.01_0
Chlorobenzene	5.62	3.06	3.12	3.48	0.004
n-Hexane	1.89	3.28	3.84	4.93	—

[a] Strictly speaking, not only the dependence of mobility on the solvent viscosity but also its dependence on the degree of solvation of ions should be taken into consideration in the evaluation of I_C values. The mobility will be smaller in the case of stronger solvation in polar solvents, leading to the stronger dependence of I_C value on the solvent polarity than indicated here.

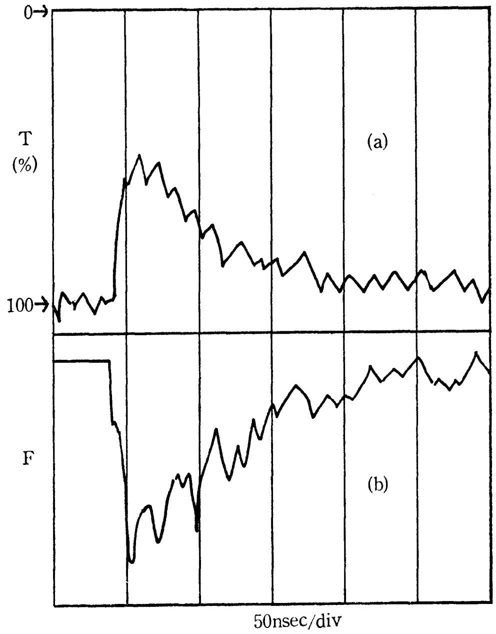

Fig. 7. Rise and decay curves of absorption at 719 nm (a) and those of pyrene-DMA HE fluorescence (b) in the case of *n*-hexane solution. Concentrations of pyrene and DMA are the same as those of Fig. 2, respectively.

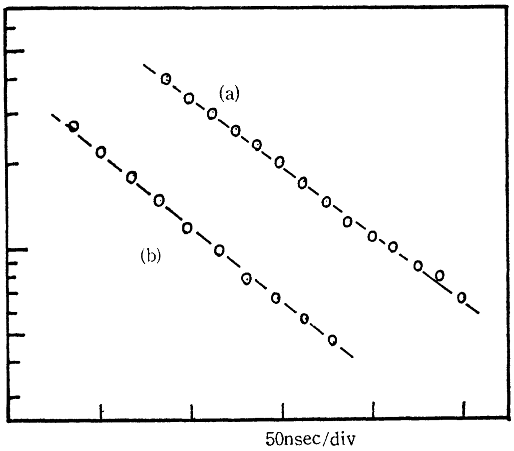

Fig. 8. Semilogarithmic plots of decay curves of Fig. 7.
(a) absorption (b) fluorescence

together with the fluorescence decay curve of the pyrene-DMA HE. Semi-logarithmic plots of these decay curves are indicated in Fig. 8. One can see clearly from Fig. 8 that both decay curves are single exponential and they have approximately the same decay constant. Accordingly, the transient absorption bands similar to those of pyrene anion can be assigned to those of pyrene-DMA HE. Thus, the pyrene-DMA HE seems to have a quite polar electronic structure even in the *n*-hexane solution.

Now let us return to the discussion on the results given in Table 1. In Table 1, free energies of the HE state, ΔF(HE), the solvated ion-pair state, $\Delta F(A_s^- \cdots D_s^+)$, and the dissociated ion radical state, $\Delta F(A_s^- + D_s^+)$, respectively above the ground state, A+D, in various solvents are given together with the relative yield of the dissociated ions, I_C. ΔF(HE) has been evaluated by means of the relation,

$$\Delta F(\mathrm{HE}) = \Delta F(\mathrm{A}^* + \mathrm{D}) + \Delta F_c(\varepsilon) \tag{3}$$

where $\Delta F(\mathrm{A}^* + \mathrm{D})$ has been estimated to be 3.346 eV, the excitation energy of pyrene to the fluorescent state, and $\Delta F_C(\varepsilon)$ is the free energy change associated with the formation of the HE in a solvent with dielectric constant ε, which can be calculated according to,

$$\Delta F_c(\varepsilon) = \Delta F_c(n\text{-hexane}) - \left(\frac{\varepsilon-1}{2\varepsilon-1} - 0.186\right)(\vec{\mu}_c^{\,2}/a^3) \tag{4}$$

The first term denotes the free energy change in *n*-hexane which has been estimated to be about −0.066 eV[6] and the second term the difference in solvation free energy of the complex with dielectric constant ε and *n*-hexane. a and $\vec{\mu}_C$ in the second term represent respectively the cavity radius in Onsager's theory of reaction field and dipole moment of the HE, and the value of $(\vec{\mu}_c^{\,2}/a^3)$ has been estimated to be 0.8 eV[7] by applying the equation,

$$hc\bar{\nu}_f \approx -\left(\frac{2(\varepsilon-1)}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)(\vec{\mu}_c^{\,2}/a^3) \tag{5}$$

for the observed values of fluorescence wave numbers. (n is the refractive index of the solvent). $\Delta F(A_s^- \cdots D_s^+)$ can be calculated according to,

$$\Delta F(\mathrm{A_s}^- \cdots \mathrm{D_s}^+) = (E^+ - E^-) - (e^2/\varepsilon R_0) + \Delta F_s \tag{6}$$

The first term represents the difference between the oxidation potential of the donor and the reduction potential of the acceptor in acetonitrile, the second term the Coulomb attraction energy between the ions A_s^- and D_s^+ separated by the distance R_0 (assumed to be 7 Å), and the third term denotes the difference of the free solvation energies of ions in acetonitrile ($\varepsilon = 37.5$) and a solvent with dielectric constant ε. ΔF_S can be calculated with the aid of Born's equation,

$$\Delta F_s = (e^2/2)\left(\frac{1}{R_+} - \frac{1}{R_-}\right)\left(\frac{1}{\varepsilon} - \frac{1}{37.5}\right) \tag{7}$$

where we have assumed $R_+ \approx R_- \approx 3.5$ Å. Finally, $\Delta F(A_s^- + D_s^+)$ is given simply by

$$\Delta F(\mathrm{A_s}^- + \mathrm{D_s}^+) = \Delta F(\mathrm{A_s}^- \cdots \mathrm{D_s}^+) + e^2/\varepsilon R_0 \tag{8}$$

The calculated ΔF values and the observed I_C values are plotted against ε values in Fig. 9 for convenience's sake.[8]

One can see clearly from Fig. 9 that the I_C value increases strongly and the $\Delta F(A_s^- + D_s^+)$ as well as $\Delta F(A_s^- \cdots D_s^+)$ values are lowered remarkably as the solvent dielectric constant is increased. The increase of the I_C value is especially notable for the range of $\varepsilon \gtrsim 10$. Thus, in these rather polar solvents with ε values larger than 10, the existence of the dissociated ions has been clearly proved by the present study. In the range of $\varepsilon \approx 5$—10, although the experimental errors for the

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[6] Unpublished result by T. Okada, H. Matsui, and N. Mataga.

[7] Unpublished result by T. Okada and N. Mataga.

[8] Quite similar plots of ΔF(HE) and $\Delta F(\mathrm{A_s}^- \cdots \mathrm{D_s}^+)$ against ε value have been given already by Weller. A. Weller, in Nobel Symposium 5, Fast Reactions and Primary Processes in Chemical Kinetics (S. Claesson, ed.,) Almqvist and Wiksell, Stockholm (1967), p. 413.

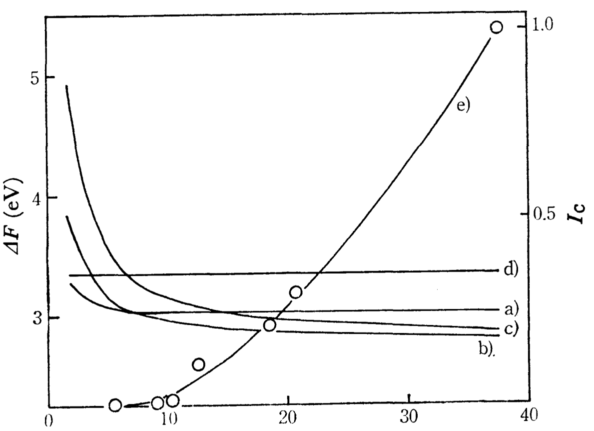

Fig. 9. Plots of ΔF values and I_C values given in Table 1 against ε values of solvents.
(a) ΔF(HE) (b) $\Delta F(A^-{}_s \cdots D^+{}_s)$ (c) $\Delta F(A^-{}_s + D^+{}_s)$
(d) $\Delta F(A^* + D)$ (e) I_C

determination of I_C values are rather large, the existence of a small quantity of dissociated ions produced by the encounter collision seems to be certain. However, the formation of such ions was not observable in the range of ε smaller than 5.

Of course, the precursor of the dissociated ions is the solvated ion-pair $(A_s^- \cdots D_s^+)$ which is formed by the electron transfer process in the encounter complex. Then, the reaction scheme of the dissociated ion radical formation may be written as

$$A^* + D \rightleftarrows A^* \cdots D \rightleftarrows A_s^- \cdots D_s^+ \rightleftarrows A_s^- + D_s^+ \qquad (9)$$

However, the difference, $\Delta F(A_s^- + D_s^+) - \Delta F(A_s^- \cdots D_s^+)$, is much larger than the thermal energy at room temperature even at $\varepsilon \approx 10$. Accordingly, it might be possible that the dissociation occurs in the non-relaxed state of the ion-pair immediately after the electron transfer, competing with the relaxation process to the equilibrium solvation state of the ion-pair and/or the relaxation process to the ground state, $(A+D)$. At any rate, since the formation of solvated ion radicals in solvents, which are not very polar and where the HE fluorescence is fairly strong, has been proved in this work, the reaction scheme of the competition of the exciplex formation process with the electron transfer process in the encounter complex seems to be more suitable than the assumption of the continuous structural change of HE with the change of solvent polarity. Of course, there should be more or less structural change of HE induced by the solute-solvent interactions, in principle. However, this effect may play rather small role[9] in explaining the experimentally observed relation between the solvent dependent HE fluorescence quantum yield and decay time, in the case of moderately polar solvents.

As we have described already, the formation of dissociated ion radicals was not observable in *n*-hexane. The circumstance was the same also in toluene. One may see from Fig. 9 that not only the formation of the dissociated ions but also the formation of the solvated ion-pairs, $A_s^- \cdots D_s^+$, seems to be rather difficult in *n*-hexane and toluene ($\varepsilon = 2.38$). However, according to the experimental results, the HE fluorescence yield in toluene is only one third of that in *n*-hexane, while the HE fluorescence decay time in toluene is practically the same as that in *n*-hexane.[1] It seems to be rather difficult to explain this result by assuming only the reaction of Eq. (9) which competes with the HE formation process, if the relations between the free energies in Fig. 9 are approximately correct.

Possible explanations for the observed results in toluene solution may be as follows. (a) Toluene molecules will make a specific short range interaction with the ions in the solvated ion-pair $(A_s^- \cdots D_s^+)$ in addition to the long range dielectric interactions. This short range interaction (for which the π-electron system of toluene might be playing some role) may lower the $\Delta F(A_s^- \cdots D_s^+)$ value in toluene solution more strongly than indicated in Fig. 9, which makes possible the reaction of Eq. (9) to occur considerably. This is a kind of structural change of the complex involving the surrounding solvent molecules. (b) Owing to a specific interaction of excited molecules with π-electron systems of toluene, there arises some quenching process in the course of HE formation reaction *i.e.* in the encounter complex, as follows.

$$\begin{array}{l} A^* + D \rightleftarrows A^* \cdots D \longrightarrow (A^- \cdot D^+)^* \\ \qquad\qquad\qquad\ \text{solvent} \searrow \\ \qquad\qquad\qquad\qquad\qquad A + D \text{ or } A^*(T) + D \end{array}$$

where $A^*(T)$ represents the triplet state of pyrene. The quenching process which competes with the HE formation in the encounter complex has been assumed also by Ottolenghi and co-workers[10] in order to interpret quite efficient and very rapid intersystem crossing in some aromatic hydrocarbon-DEA (*N*,*N*-diethylaniline) systems in several solvents. However, it seems to be rather difficult, at the present stage of investigation, to determine the true mechanism of the above described solvent effects on the HE fluorescence in almost non-polar solvents.

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[9] H. Beens, Thesis, Free University, Amsterdam, 1969.

[10] C. R. Goldschmidt, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **75**, 1025 (1971).