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Dynamic Behaviors of the Electron Donor-Acceptor Complex in its Lowest Excited Singlet State

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Dynamic behaviors of the weak electron donor-acceptor (EDA) complex in its lowest excited singlet state have been investigated by the nsec flash photolysis method and measurements of fluorescence and transient photocurrent. In polar solvents the weak EDA complex in its lowest excited singlet state dissociates spontaneously into ions. The dynamic behaviors of *s*-tetracyanobenzene(TCNB)-benzene and TCNB-toluene complexes were studied in some solvents and the existence of the direct radiationless process at the excited Franck-Condon (FC) state as well as in the course of relaxation process from the excited FC state to the fluorescent state has been confirmed in the case of 1,2-dichloroethane solution. The nature of the intra-complex radiationless processes was discussed on the basis of this result. It has been pointed out that the lifetime of excited states is of crucial importance for understanding the dynamic behaviors of excited weak EDA complexes.

EDA complexes which are fluorescent in solution at room temperature are rather scarce. However, one can observe at room temperature the fluorescence of complexes of some acceptors such as TCNB, tetrachlorophthalic anhydride (TCPA) and pyromelitic dianhydride (PMDA) with hydrocarbon donors.[1-6] From the study of solvent effects on the fluorescence of these complexes, it has been shown that the low fluorescence yield in nonpolar solvents can be ascribed to a small value of radiative rate constant k_f while, in polar solvents, it can be attributed to a large value of radiationless rate constant k_n.[2,3,6] In order to understand the results, the effect of solvent and temperature on fluorescence spectra, fluorescence quantum yield and fluorescence decay times of TCNB complexes were investigated. A small value of k_f was ascribed to the large difference in electronic structure between the fluorescent and ground states.[2] The important role of surrounding environments in the relaxation process, through which the fluorescent state is produced from the excited FC state, was made clear.[2,7,8]

Recently, we have shown that the ionic dissociation of TCNB-toluene complex in the lowest excited singlet state occurs in acetonitrile.[9] Detailed studies on the ionic dissociation of excited EDA complexes may provide useful information for understanding radiationless transitions as well as primary processes of photochemical reactions of EDA complexes. It is well-known that the ionic dissociation of heteroexcimer or the electron transfer in the encounter collision in the excited state can occur easily in polar solvents.[10] However, there are only a few studies on ionic dissociation of the excited EDA complexes which are stable in the ground state.[11,12] In these

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[11] F. S. Stewart and M. Eisner, *Mol. Phys.*, **12**, 173 (1967); D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965); E. M. Kosower and L. Lindquist, *Tetrahedron Lett.*, **50**, 4481 (1965); R. F. Cozzes and T. A. Cover, *J. Phys. Chem.*, **74**, 3003 (1970); W. C. Meyer, *ibid.*, **74**, 2118 (1970).

[12] R. Potashnik, C. R. Goldschmidt, and M. Ottolenghi, *ibid.*, **73**, 3170 (1969).

studies, the absorption spectra of produced ion radicals were measured by only the conventional flash photolysis method and no direct observation on the primary process of the production of ion radicals in nsec time region was performed. However, the study on the primary processes of ionic photodissociation of EDA complexes is indispensable in order to obtain a correct picture of the dynamic behaviors of excited complexes.

In the present paper the results of our studies on the ionic photodissociation of various weak EDA complexes in various solvents will be described, and the mechanisms of the ionic photodissociation as well as other radiationless processes in these complexes will be discussed in detail.

Experimental

We used a Q-switched ruby laser (Japan Electron Optics, JLR-02A) with out put of *ca.* 1.5 J. The exciting light pulse of 347 nm was produced through ADP frequency doubler with conversion efficiency of *ca.* 8%. The output of an exciting pulse was measured with a ballistic thermopile TRG model 100 (HADRON). The light pulse has a duration of 15—20 nsec. The absorption spectra of ions produced by exciting the complex at the charge-transfer (CT) absorption band were measured photographically by using laser-breakdown sparks in O_2 and Xe gases as spectroflashes.[13] The rise and decay curves of ions were observed by the nsec flash photolysis method we developed. Since a 50 Ω resistor is equipped to photomultiplier to obtain nsec time resolution, a monitoring light intensity falling onto the photomultiplier must be far greater than that of a conventional flash photolysis.[14] We used a Xe flash lamp as monitoring light, the duration of which was adjusted to *ca.* 300 μsec. A block diagram of the present nsec flash photolysis apparatus is shown in Fig. 1. The timing circuit using a cathode-coupled multivibrator makes the adjustment of an exciting pulse to the peak intensity of the monitoring flash lamp easy and linear.[15]

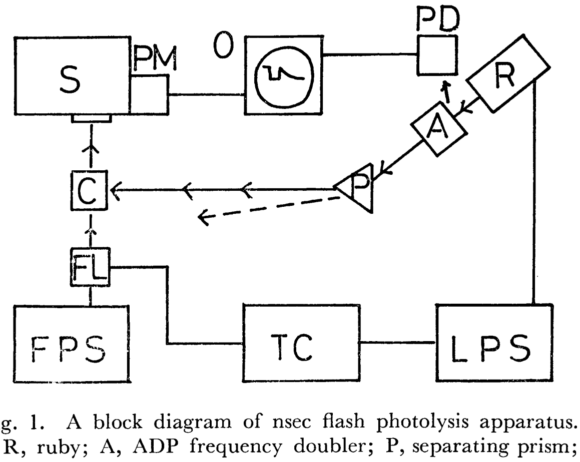

Fig. 1. A block diagram of nsec flash photolysis apparatus. R, ruby; A, ADP frequency doubler; P, separating prism; C, sample cell; LPS, laser power supply; TC, timing circuit; FPS, flash power supply; FL, monitoring flash lamp; S, Nalumi R21 spectrograph; PM, RCA 1P28 or Hamamatsu TV R406 photomultiplier; PD, Hewlet-Packard 5082—4220 photodiode; O, Tektronix 585A synchroscope.

The ion radicals produced were also observed by measuring the photocurrent induced by laser excitation. Although the details of the measurement of the photocurrent will be reported by Taniguchi and Mataga,[16] some fundamental points are given here. Direct irradiation on the electrodes was avoided by focusing the 347 nm pulse. The electrodes were Ni plates of 9 mm × 10 mm set 7 mm apart from each other. To obtain nsec time resolution a 50 Ω resistor was used and the supplied DC voltage between electrodes was adjusted from 90 V to 540 V. The time constant of the electronic circuit is less than 5 nsec. The DC dark current was omitted by using the ac coupling of the input of a Tektronix 585 A synchroscope. For examining the effect of the excitation light intensity on the photocurrent, the normal laser pulse was reduced by using neutral filters composed of wire gauzes. The filters reduced the light intensity to 0.3%, 13%, 32%, and 68%. Some weaker signals of photocurrent were measured by using an Iwatsu cascade amplifier CA-2.

The fluorescence spectra and relative quantum yields of the fluorescence were measured with an Aminco-Bowman spectrophotofluorometer.

The temperature effect on ionic dissociation was studied by measuring the laser-induced photocurrent at various temperatures. The cell for the measurements of photocurrent was fitted into a copper-cellholder, which was coupled to a tank filled with liquid N_2. The whole system was contained in a quartz dewar, the bottom of which is unsilvered to permit photoexcitation. The temperature was measured with a Cu-constantan thermopile and a micro volt meter model AM 1001 (Ohkura Electric Co.).

Acetonitrile, mesitylene, and α-methylstyrene were purified by distillation. Benzene, toluene, and ethyl ether (Merk spectrograde), and ethyl alcohol, isopropyl alcohol, acetone and 1,2-dichloroethane (Nakarai Chemicals, spectrograde) were used without further purification. TCNB, TCPA, and hexamethylbenzene (HMB) were the same as used before.[2] PMDA was purified by repeated recrystallization from ethyl acetate. All the solutions were carefully degassed by the usual method.

Results and Discussion

Absorption Spectra of the Transient Acceptor Anion Produced by Laser Photolysis. The spectra obtained by exciting TCNB-toluene complex to its lowest excited singlet state in acetonitrile solution are shown in Fig. 2. Since the observed transient absorption spectra are identical with those of TCNB anion,[17] it has been proved that the excitation of this complex by light absorption at the CT band leads to the ionic dissociation in acetonitrile solution. This anion decays rather slowly in the course of tens of μsec. Some parts of the produced anions are quite stable and observable even by a usual spectrophotometer. It was not possible to identify the transient spectra of

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[13] J. R. Novak and M. W. Windsor, *Proc. Roy. Soc. Ser. A*, **308**, 95 (1968).

[14] G. Porter and M. R. Topp, *ibid.*, **315**, 163 (1970).

[15] J. Millman and H. Taub, "Pulse and Digital Circuits," McGraw-Hill, New York (1966), p. 187.

[16] Y. Taniguchi and N. Mataga, Preprint for the Symposium on Photochemistry, Kyoto, 1970.

[17] M. Sofue and S. Nagakura, This Bulletin, **38**, 1048 (1965); A. Ishitani and S. Nagakura, *Theor. Chem. Acta* (Berl.), **4**, 236 (1966).

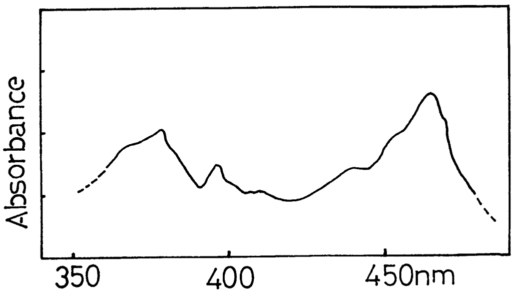

Fig. 2. The transient absorption spectra of the TCNB-toluene-acetonitrile system. Concentration of TCNB, 6×10^{-3} M. Volume ratio of toluene *vs.* acetonitrile, 1 : 2.

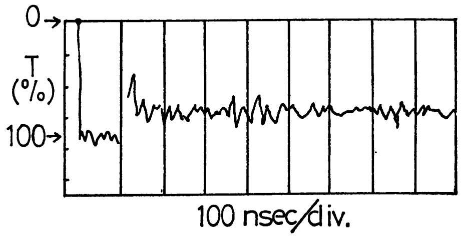

Fig. 3. The rise of TCNB anion produced by exciting the TCNB-α-methylstyrene-acetonitrile system. Observed at 465 nm.

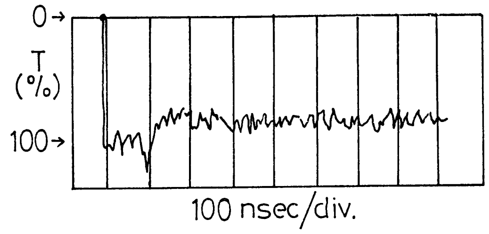

Fig. 4. The rise of PMDA anion produced by exciting the PMDA-mesitylene-acetonitrile system. Observed at 665 nm.

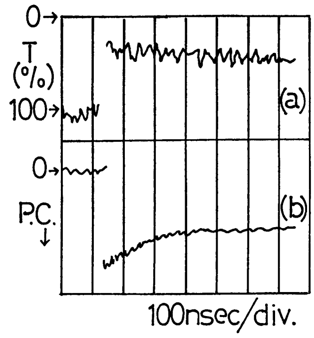

Fig. 5. The kinetic relation between transient photocurrent and transmittance of TCNB anion, produced by exciting the TCNB-toluene-acetonitrile system.
(a) transmittance at 465 nm (b) photocurrent.

toluene cation, which may be ascribed to the fact that the absorption band of cation which lies at *ca.* 460 nm[18] may be hidden behind the strong band of TCNB anion.

We have also made some investigations in other polar solvents, fixing volume ratio of donor solvent *vs.* polar solvent to 1 : 2. The transient spectra due to TCNB anion produced by exciting the TCNB-toluene complex at the CT band were observed also in acetone, isopropyl alcohol and ethyl alcohol. We examined the ionic dissociation of other TCNB complexes by means of the laser photolysis method and observed the absorption spectra of TCNB anion in acetonitrile solution in the cases of TCNB-benzene and TCNB-mesitylene complexes. In the case of the latter, the spectra were also taken by using the fluorescence of cyclohexane solution of tetraphenylbutadiene as a flash light, a technique used by Porter and Topp.[13] Since the fluorescence lifetime of tetraphenylbutadiene is short, the fluorescence light pulse has the same shape in time as an exciting laser pulse. Accordingly, this technique is convenient for observing the species produced rapidly. The acceptor anion was detected also in the cases of TCNB-α-methylstyrene and PMDA-mesitylene complexes with nsec flash photolysis. Thus, the ionic dissociation caused by exciting the CT band in polar solvents has been observed commonly for various weak EDA complexes.

Kinetic Analyses by the Measurements of Fluorescence, Absorption and Photocurrent in Nsec Time Region. The rise and decay curves of acceptor anion were obtained by nsec flash photolysis technique developed in the present work. The oscillograms showing rapid production of acceptor ions in the systems of TCNB-α-methylstyrene-acetonitrile, PMDA-mesitylene-acetonitrile and TCNB-toluene-acetonitrile, are given in Figs. 3, 4 and 5(a), respectively. Such a rapid production of acceptor anion was also observed in the case of TCNB-toluene-acetone. The S_n–S_1 spectra of TCNB-toluene and TCNB-benzene complexes recently reported[7,19,20] are similar to the spectra of TCNB anion. We cannot distinguish the solvated anion from the excited singlet EDA complex having the structure of "contact ion-pair"[7,19] by measuring and comparing only the shape of the absorption spectra, although behavior of this anion, *e.g.* the decay processes is different from that of the excited singlet EDA complex.

We have measured the photocurrent induced by laser excitation of weak EDA complexes in various solvents since this may be another useful and important method for examining ionic photodissociation. It has been shown that the obtained photocurrent is due to the dissociated ions, by comparing the rise and decay curves of the photocurrent with those of absorption of acceptor anion. The kinetic relation between transient photocurrent and transient absorption are given in Fig. 5. The rise curve and earlier stage of decay of the photocurrent are almost the same as those of absorption of TCNB anion.[21]

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18) T. Shida and H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).

19) H. Masuhara and N. Mataga, *Chem. Phys. Lett.*, **6**, 608 (1970).

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21) A difference in photocurrent and absorption arises in the later stage of decay. This might be due to secondary reactions as well as the dark current caused by the dark reaction occurring at electrodes because of high applied electric field. The observed photocurrent induced by laser excitation can be ascribed to the dissociated ion radicals.

The rise curve of photocurrent in the case of TCNB-toluene-acetonitrile system and an excitation laser pulse are given in Fig. 6. The shape of the rise curve is the same as that of a time-integrated function of a 347 nm pulse. We have obtained the same results for all the complexes in various solvents at room temperature.

We can observe both the CT fluorescence of TCNB-benzene and the photocurrent due to dissociated ions in the case of 1,2-dichloroethane solution. As indicated in Fig. 7, the fluorescence decay is rather fast corresponding to the rapid production of ions in this solution.

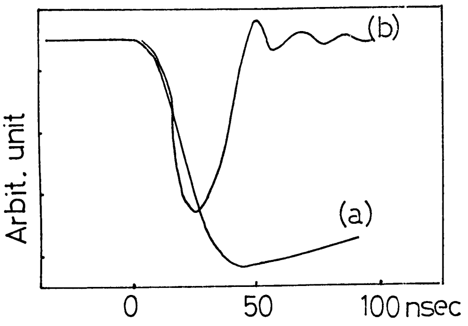

Fig. 6. The rise and decay of photocurrent in the case of the TCNB-toluene-acetonitrile system.
(a) transient photocurrent (b) shape of an exciting pulse.

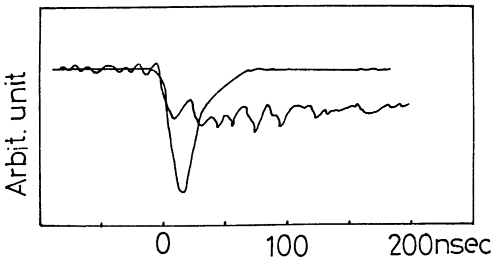

Fig. 7. The kinetic relation between photocurrent and CT fluorescence in the case of the TCNB-benzene-1,2-dichloroethane system.

The photocurrent of aerated TCNB-toluene-acetonitrile system was also measured. It was found that production of TCNB anion in the aerated system was almost the same as that in the degassed system. The decay of ions in aerated solution is, of course, faster than that in degassed solution.

Ionic Dissociation of Weak EDA Complexes in Their Lowest Excited Singlet States. All the results seem to show that ionic dissociation of these complexes occurs in the lowest excited singlet state. However, a two-step process with an excited state as an intermediate and a collision process between excited EDA complexes followed by ionic dissociation should be examined to elucidate the primary process of the dissociation, since a laser pulse is an intense exciting light. First the effect of excitation light intensity on the photocurrent was examined.

In general, the photocurrent density is given by[22)]

$$i(t) = \sum_j Z_j e n_j(t) \mu_j E \tag{1}$$

where Z_j, μ_j, and $n_j(t)$ represent electric charge, mobility, and number of the carrier j in unit volume, respectively. E is an applied electric field. In the present system of weak EDA complexes, the charge carriers are acceptor anions and donor cations, and the equation is reduced to

$$i(t) = en(t)(\mu_{\text{anion}}+\mu_{\text{cation}})E. \tag{2}$$

Since both ions are simultaneously produced by laser excitation and disappear by recombination reaction, we have

$$\frac{\mathrm{d}n}{\mathrm{d}t} = aI - bn^2, \tag{3}$$

where a and b represent rate constants of production and disappearance of ions, respectively. I is an intensity of the exciting pulse.

In the case of EDA complexes in various solvents at room temperature, the dissociation into ion radicals occurs quite rapidly in nsec time region while they decay slowly during time more than ten μsec. Thus the peak photocurrent obtained immediately after excitation is proportional to the concentration of the dissociated ions. The effect of excitation light intensity on the peak photocurrent of TCNB-toluene-acetonitrile system is given in Fig. 8. The linear relation shows that this ionic dissociation is a one-photon process.[23)]

The effect of the excitation light intensity on the production of ions has been studied also by means of nsec flash photolysis and measurement of the transient absorption band. The observed results on the TCNB-toluene-acetone system, also indicating a one-photon process, are given in Fig. 9.

We have investigated the temperature effect on ionic dissociation in the case of TCNB-toluene-ethyl alcohol system. The volume ratio of toluene *vs.* ethyl alcohol was set to 1 : 10, in which case a rigid

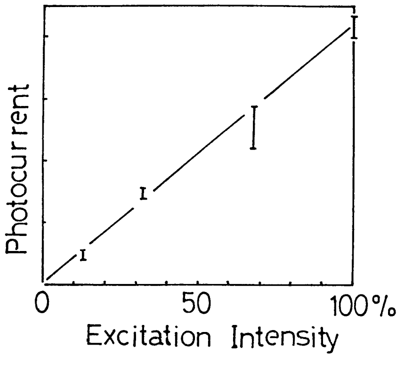

Fig. 8. The effect of exciting light intensity on the peak photocurrent of the TCNB-toluene-acetonitrile system. Optical density at 347 nm is *ca.* 0.1.

[22)] G. E. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **44**, 3179 (1966); H. S. Pilloff and A. C. Albrecht, *ibid.*, **49**, 4891 (1968); T. Imura, N. Yamamoto, and H. Tsubomura, This Bulletin, **43**, 1670 (1970).

[23)] The effect of excitation light intensity on ionic dissociation was examined under rather low solute concentration. In the case of high concentration (O. D. at 347 nm ~1.0), a saturation effect of photocurrent was caused by high intensity laser excitation.

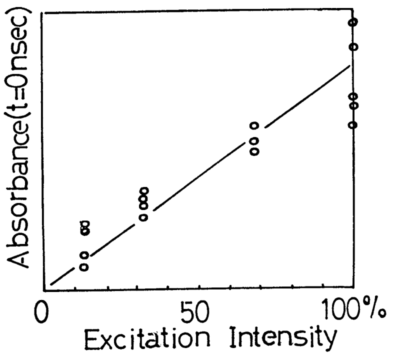

Fig. 9. The effect of exciting light intensity on the transient absorption of TCNB anion produced by irradiating the TCNB-toluene-acetone system. Observed at 462 nm. Optical density at 347 nm is *ca.* 1.0.

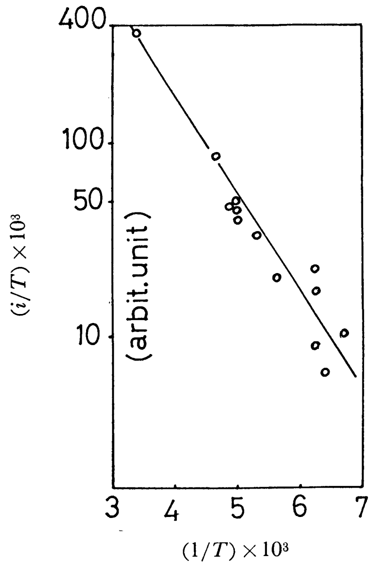

Fig. 10. $\log(i/T)$ *vs.* $(1/T)$ relation observed for the TCNB-toluene-ethanol system.

glass was formed at liquid nitrogen temperature. Mobility μ and dielectric constant ε of solvent undergo changes with change of temperature. It is well known that mobility μ is proportional to diffusion-controlled rate constant k, which is approximately proportional to T/η,[24] where η and T represent viscosity coefficient and temperature, respectively. Moreover, the relation $\log\eta\sim1/T$ holds in the case of the glass-forming solvent mixtures.[25] Thus, log (i/T), where i is the peak photocurrent, should be proportional to $1/T$. It is necessary, however, to correct the peak photocurrent with respect to the dielectric constant of mixed solvent. In the present work, we have neglected the contribution of toluene to dielectric constant of mixed solvent and taken into consideration only the change of dielectric constant of ethylalcohol due to the change of temperature. The results are given in Fig. 10, which shows a linear relation between log (i/T) and $(1/T)$. This can be ascribed to the fact that the quantum yield of dissociation is constant, independent of temperature, indicating spontaneous dissociation (without activation energy) of this complex in ethyl alcohol.

From the results it can be concluded that the weak EDA complexes (which are stable in the ground state) dissociate spontaneously into ions in their excited CT singlet states in polar solvents.

Dynamic Behaviors of TCNB-Benzene and TCNB-Toluene Complexes in Various Solvents. The dynamic behaviors of excited TCNB-benzene and TCNB-toluene complexes in various solvents were studied in detail, fixing the volume ratio of the donor solvent *vs.* another solvent to 1 : 2. The lifetime and relative quantum yield of fluorescence, exciting the CT band at 347 nm, were measured by the usual method.[2] The relative quantum yields of ionic dissociation were obtained by correcting photocurrent with respect to the strength of applied electric field, the distribution and number of exciting photons, viscosity and dielectric constant of mixed solvents and by comparing the peak photocurrent. Viscosity η and dielectric constant ε of a mixed solvent were calculated approximately by equations $\eta=\sum_i v_i\eta_i$ and $\varepsilon=\sum_i v_i\varepsilon_i$, where η_i, ε_i, and v_i represent viscosity, dielectric constant, and volume fraction of the solvent i, respectively.

Estimation of the order of magnitude of the absolute quantum yield of dissociation for the systems of TCNB benzene-acetonitrile and TCNB-α-methylstyrene-acetonitrile was made as follows. (1) The distribution of exciting photons was assumed to be uniform in the effective irradiation spot on the front face of the cell, which was determined from a burned spot on a color sheet produced by a 347 nm pulse. (2) The distribution of the produced TCNB anion in the monitoring portion of the sample cell was averaged. (3) The concentration of the produced anion was calculated, using an optical density of TCNB anion obtained immediately after the excitation (Fig. 5 (a)) and assuming molecular extinction coefficient at 465 nm to be *ca.* 10^4. (4) The quantum yield was put equal to the number of anions divided by the number of exciting photons which were measured to be 1.7×10^{17} per pulse by the TRG 100 thermopile. All the results on TCNB-benzene and TCNB-toluene complexes are listed in Tables 1 and 2.

We see that the decrease of φ_f from benzene to 1,2-dichloroethane solutions is larger than that of τ_f. This result can be explained on the basis of the following two alternative models. (a) The radiative transition probability of fluorescence k_f decreases and the radiationless transition probability increases with the increase of the solvent polarity, due to the strong interaction between the complex and solvent. (b) The direct radiationless process arises from the excited FC state as well as in the course of the relaxation process from the excited FC state to the fluorescent state. This radiationless process as well as the usual one from the fluorescent state increase as the solvent polarity is increased, while the k_f value

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[24] M. Smoluchowski, *Z. Physik. Chem.*, **92**, 129 (1917).

[25] F. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

TABLE 1. DYNAMIC BEHAVIORS OF TCNB-BENZENE COMPLEX IN ITS LOWEST EXCITED SINGLET STATE

Solvent	ε_{mix} a)	Fluorescence lifetime	φ_f b)	φ_{ion} b)	φ_{nf} b,c)
Benzene	2.3	∼100 nsec	0.009 (1.0) e)	0	0.91
Ethyl ether	3.7		0.02 (0.23)	0	0.98
1,2-Dichloroethane	7.7	20 d)	0.004 (0.04)	0.001 (0.0015)	0.995
Acetone	14.6			0.035 (0.35)	0.965
Acetonitrile	25.8			0.1 (1.0)	0.9

a) Calculated dielectric constants.

b) φ_f, φ_{ion}, and φ_{nf} represent absolute quantum yields of fluorescence, ionic dissociation, and intra-complex radiationless transition, respectively.

c) φ_{nf} does not contain ionic dissociation and was estimated by the relation $\varphi_{nf}=1-\varphi_f-\varphi_{ion}$.

d) The fluorescence decay curve was observed by exciting the complex with N_2 gas laser. The N_2 laser was the same as that described in Ref. 8.

e) The values in parentheses are relative quantum yields.

TABLE 2. IONIC DISSOCIATION OF TCNB-TOLUENE COMPLEX IN ITS LOWEST EXCITED SINGLET STATE

Solvent	ε_{mix}	Relative quantum yield of ionic dissociation	Appearance of absorption band of TCNB anion
Toluene	2.4	∼0	Not observed
Ethyl ether	3.7	∼0	Not observed
1,2-Dichloroethane	7.7	0.01	Not observed
Isopropyl alcohol	13.0	0.29	Observed
Ethyl alcohol	17.0		Observed
Acetonitrile	25.8	1.00	Observed

is not affected by the solvent polarity.

On the other hand, the difference in Stokes shift of fluorescence between TCNB-benzene and TCNB-benzene-1,2-dichloroethane systems can be explained by the usual dielectric theory of the solvent shift of fluorescence spectra.[8] This means that the electronic structure of the excited TCNB-benzene complex is independent of the solvent polarity and a constant value of k_f can be expected. Therefore, at the present stage of investigation the larger decrease of φ_f with the increase of solvent polarity from benzene to 1,2-dichloroethane solutions, compared with the decrease of τ_f, may be ascribed to the existence of the direct radiationless process (b).

From Table 1, we can see the increase of φ_{nf} with the increase of solvent polarity from benzene to 1,2-dichloroethane and the increase of φ_{ion} as well as the decrease of φ_{nf} when the solvent is changed from 1,2-dichloroethane to acetonitrile. These results show that solvent polarity plays an important role not only for ionic dissociation but also for intra-complex radiationless transition.

Ionic Dissociation of Various Weak EDA Complexes. We have studied the ionic photodissociation of various EDA complexes in acetonitrile solution. In the case of liquid donors the volume ratio of the donor *vs.* acetonitrile was fixed to 1 : 2. All the results are listed in Table 3, together with the values of the fluorescence lifetime and the result of S_n–S_1 spectral measurement in nonpolar solvents. The yield of ionic dissociation in acetonitrile solution of TCNB complexes with methyl-substituted benzene decreases from benzene to HMB donors. Together with this decrease arises difficulty to observe S_n–S_1 absorption spectra in nonpolar solvents. The S_n–S_1 spectra of TCNB-HMB complex in methylmethacrylate and TCNB-α-methylstyrene systems have not been observed. However, the S_n–S_1 spectra of TCNB-benzene and TCNB-toluene complexes have been observed easily by analyzing the re-absorption of CT fluorescence[7,19,26] and those of TCNB-mesitylene[27] and PMDA-mesitylene complexes by the nsec flash photolysis method. On the other hand, the electronic structure of excited equilibrium state of TCNB complexes has been shown to depend little upon the donor according to our theoretical consideration.[7] Thus, the above results of decreasing dissociation of TCNB complexes with increasing strength of donor appear to contradict the theoretical consideration. The contradiction can be removed by considering the fluorescence lifetimes of these complexes. Those of TCNB-α-methylstyrene and TCNB-HMB complexes in nonpolar solvents seem to be short, since fluorescence decay function is almost the same in shape as an exciting laser pulse. It seems to be difficult to observe the S_n–S_1 spectra of TCNB-α-methylstyrene and TCNB-HMB complexes because of these short lifetimes, and the dissociation yields of these complexes in polar solvents might be low. Short lifetimes may be due to the large value of intra-complex radiationless transition rate constant. This consideration in terms of short lifetime is, of course, related to that given in the above section.

Related and Future Problems. The present results on the process k_f of TCNB-benzene complex in

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[26] The effect of the re-absorption of CT fluorescence by the excited EDA complex itself was examined in detail. Masuhara and Mataga, This Bulletin, **45**, No. 2 (1972), in press.

[27] H. Masuhara and N. Mataga, Preprints for the 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

Table 3. Ionic dissociation of weak EDA complexes in acetonitrile solution

Acceptor	Donor	I_p	φ_{ion}[a)]	Absorption of TCNB anion	S_n-S_1 spectra[c)]	τ_{fluo}[c)]
TCNB	Benzene	9.24 eV	1.0	Observed	Observed	100 nsec
	Toluene	8.82	0.98	Observed	Observed	100
	Mesitylene	8.39	0.46	Observed	Observed	43[3)]
	α-Methylstyrene	8.36	0.15	Observed	Not observed	S [d)]
	Naphthalene	8.12	Observed			
	HMB	7.85	0.05	Not observed	Not observed	S
	DMA[e)]	7.14	Observed			
	TMPD[e)]	6.6	Observed[b)]			
TCPA	Toluene	8.82	~1.0	Not observed	Not observed	S
PMDA	Mesitylene	8.39	Observed	Observed	Not observed	S

a) Relative quantum yields of ionic dissociation obtained by measurement of photocurrent.
b) The excitation pulse is a 694 nm one of ruby laser.
c) The results in nonpolar solvents.
d) The fluorescence lifetime is short and fluorescence decay function is almost the same in shape as an exciting laser pulse.
e) DMA, *N,N*-dimethylaniline; TMPD, tetramethyl-*p*-phenylenediamine.

polar solvents might be related to the CT and electron-transfer mechanism of the fluorescence quenching of aromatic hydrocarbons. One of the authors (N. M.) reported that the stronger decrease of φ_f of the heteroexcimer (HE), formed by an aromatic hydrocarbon and an aromatic amine, compared to the decay time with the increase of solvent polarity may be ascribed to the decrease of k_f and increase of radiationless process as the solvent polarity is increased.[2,10,28] On the other hand, Weller and his co-workers assumed the existence of non-fluorescent solvated ion-pair state as well as the fluorescent HE state and the competition between two processes of formation of these states.[10,29] According to this interpretation, the low value of φ_f of HE in polar solvents is due to the larger probability of the process leading to the non-fluorescent solvated ion-pair state. Our recent study on HE indicates that the assumption of the existence of the non-fluorescent ion-pair state in a solvent, which is not very polar, is fairly reasonable.[16] Although such a non-fluorescent solvated ion-pair state was not assumed explicitly on TCNB-benzene and TCNB-toluene complexes, it may be related to the direct radiationless processes from the excited FC state as well as in the course of the relaxation process from the excited FC state to the fluorescent state.

We have concluded that short lifetimes of rather stronger complexes may be due to the large value of intra-complex radiationless transition rate constant. In this case there might be also a radiationless process due to the degradation from the excited FC state of the complex in addition to the radiationless processes from the fluorescent state. If this degradation process from the excited FC state exists at all, it will be an interesting subject for investigation.

In contrast to our present results where the dissociation of weak EDA complexes occurs in their lowest excited singlet states, the spontaneous dissociation in the lowest CT triplet state of PMDA-mesitylene complex in ether-isopentane solution at low temperature has been reported.[12] The difference may be ascribed to the difference in solvent and temperature, although atomistic mechanism which determines the different way of dissociation is not very clear. We have confirmed that TCNB-α-methylstyrene complex shows a behavior similar to that of other complexes, *i.e.*, it dissociates in the lowest excited singlet state, although its fluorescence behavior is quite peculiar, giving two fluorescence bands in nonpolar solvents.[30] On the other hand, we have recently found a rather slow rise of the laser-induced photocurrent differing from the present results, in the case of PMDA-2-methyltetrahydrofuran complex.[31]

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28) N. Mataga, T. Okada, and K. Ezumi, *Mol. Phys.*, **10**, 201, 203 (1966); N. Mataga, T. Odaka, and N. Yamamoto, This Bulletin, **39**, 2562 (1966); N. Mataga and K. Ezumi, *ibid.*, **40**, 1355 (1967); N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).

29) H. Beens, H. Knibae, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); H. Knibbe, K. Röllig, F. P. Schäffer, and A. Weller, *ibid.*, **47**, 1184 (1967); H. Knibbe, D. Rehm, and A. Weller, *Z. Physik. Chem.* (Frankfurt am Main), **56**, 95, 99 (1967).

30) M. Irie, S. Tomimoto, and K. Hayashi, Preprint for the Symposium on EDA Complexes, Osaka, 1970.

31) M. Shimada, H. Masuhara, and N. Mataga, Preprint for the Symposium on Photochemistry, Tokyo, 1971.