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Ionic Photodissociation of Electron Donor-Acceptor Complexes

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Ionic photodissociation of electron donor-acceptor (EDA) complexes of *s*-tetracyanobenzene (TCNB) and pyromellitic dianhydride (PMDA) with 2-methyltetrahydrofuran (MTHF) has been investigated by means of nsec flash photolysis and transient photocurrent measurements. The solvent-shared ion-pair of TCNB anion and MTHF cation is formed from the excited charge-transfer (CT) singlet state of a TCNB–MTHF complex, dissociating into solvated ions. TCNB complexes with aromatic hydrocarbons dissociate directly into ions from the lowest excited CT singlet state. Dissociation of PMDA complexes occurs in the CT triplet state in nonpolar solvents and mainly in the excited CT singlet state in polar solvents. The relative rate constant of radiationless process, which competes with ionic dissociation in the excited singlet state, can be deduced from the effect of solvent on ionic photodissociation. It has been confirmed for the first time that the ionic dissociation of a TCNB–benzene–1,2-dichloroethane (DCE) system occurs in the excited Franck-Condon (FC) state. It is pointed out that the latter dissociation mechanism is not inconsistent with all the results obtained for TCNB and PMDA complexes under various conditions.

Ionic photodissociation is one of the most important processes of EDA complexes. At the present stage of our investigation on the electronic structures and dynamic behaviors of EDA complexes in the excited state, the results on weak EDA complexes may be summarized as follows. TCNB complexes with methyl-substituted benzenes as well as some other aromatic donors such as naphthalene in polar solvents dissociate into ions in the excited singlet state, while in nonpolar solvents, ionic dissociation does not occur but only the CT fluorescence is observed.[1,2] It has become clear that a TCNB-α-methylstyrene complex in amylalcohol at low temperature dissociates in the CT triplet state.[3] Dissociation of PMDA complexes with mesitylene and hexamethylbenzene (HMB) occurs also in the CT triplet state.[4] The dissociative state of tetracyanoethylene (TCNE) complexes with tetrahydrofuran (THF), dimethylsulfoxide, *N,N*-dimethylformamide and acetone donors was concluded to be CT triplet state by means of ESR experiments.[5,6] A flash photolysis study on a TCNE–THF complex gave the same conclusion.[7] The present work deals with the complex formation and ionic dissociation of TNCB–MTHF and PMDA–MTHF complexes. The dissociation mechanism of TCNB complexes will be discussed in detail on the basis of present and previous results.

Experimental

Experimental methods are the same as reported previously.[2] Acetonitrile and butyronitrile were refluxed over phosphorus pentoxide and distilled from anhydrous calcium carbonate. MTHF was refluxed over metallic sodium for a few hours, distilled and stocked in a vacuum. Spectrograde DCE, 1,4-dioxane, THF, ethanol (Nakarai Chemicals) and benzene (Merck) were used without further purification. TCNB, PMDA and naphthalene were the same samples as used before.[2] All the solutions were degassed by the usual freeze-pump-thaw method.

Results

Absorption and Luminescence Spectra of MTHF Complexes. The absorption spectra of TCNB–MTHF–DCE and PMDA–MTHF–DCE systems are given in Figs. 1 and 2, respectively. As the concentration of the donor increases, the intensity of the absorption band of the acceptor decreases, the swelling and tail appearing at 280 and 330 nm, respectively. The isosbestic points can be recognized in both systems. A spectrum, obtained by normalizing spectra (a) and (c) at the 320 nm peak and subtracting the former from the latter, has broad bands with peaks at 280 and 323 nm. Both bands satisfy approximately the relation between the absorption maxima of TCNB complexes and the ioniza-

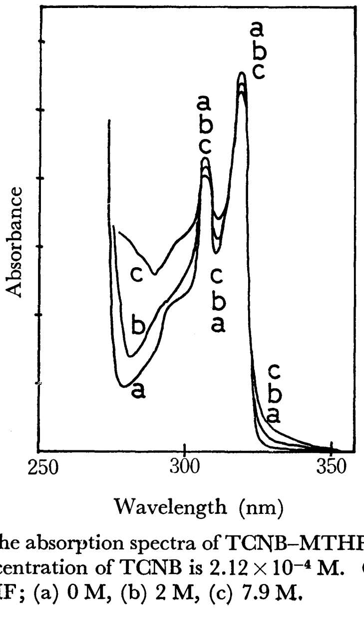

Fig. 1. The absorption spectra of TCNB–MTHF–DCE system; the concentration of TCNB is 2.12×10^{-4} M. Concentrations of MTHF; (a) 0 M, (b) 2 M, (c) 7.9 M.

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[1] H. Masuhara, M. Shimada, and N. Mataga, This Bulletin, **43**, 3316 (1970).

[2] H. Masuhara, M. Shimada, N. Tsujino, and N. Mataga, *ibid.*, **44**, 3310 (1971).

[3] M. Irie, S. Tomimoto, and K. Hayashi, *J. Phys. Chem.*, **76**, 1419 (1972).

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

[5] D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

[6] F. E. Stewart, M. Eisner, and W. R. Carper, *ibid.*, **44**, 2866 (1966).

[7] Y. Achiha, S. Katsumata, and K. Kimura, *Chem. Phys. Lett.*, **13**, 213 (1972); This Bulletin, **45**, 1272 (1972).

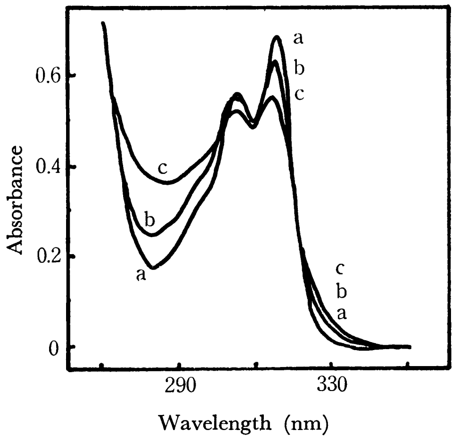

Fig. 2. The absorption spectra of a PMDA–MTHF–DCE system; the concentration of PMDA is 2.61×10^{-4} M. Concentrations of MTHF; (a) 0 M, (b) 2 M, (c) 7.9 M.

tion potential of the donor,[8] although the precise value of the ionization potential of MTHF is not known. Hence, they may be assigned to CT transitions of MTHF complexes with TCNB and PMDA. Absorption spectra were measured with a high concentration of the acceptor, and the molar extinction coefficient of the CT band as well as the equilibrium constant of the complex formation were evaluated. Since the original band of the acceptor has a small absorption intensity in the wavelength region examined, the following equation was used.

$$\varepsilon^* - \varepsilon_A = (\varepsilon - \varepsilon_A)/(1+1/Kc_D)$$

$$\varepsilon^* = D/c_A l$$

where D is the absorbance at the wavelength examined and l is the optical path length of the cell in cm. ε_A and ε represent molar extinction coefficients of the acceptor and the EDA complex at that wavelength, respectively. c_A and c_D are the concentrations of the donor and the acceptor, respectively. K is the equilibrium constant. The results for the TCNB–MTHF–DCE system are shown in Fig. 3, where the measurements were made at 350 nm. The complex formation of MTHF, a weak electron-donor reagent, with TCNB and PMDA is thus confirmed. K was obtained as 0.45 and ε was calculated to be 6 at 350 nm. The extinction coefficients of CT bands at 323 and 280 nm were 700 and 1100, respectively.

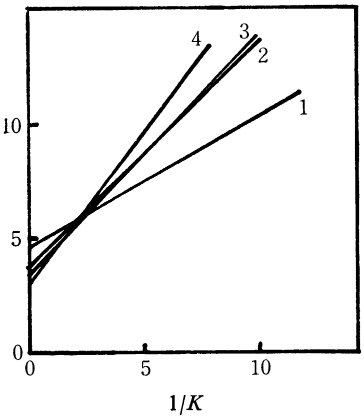

Fig. 3. The relation between ε and $1/K$ of a TCNB–MTHF–DCE system; the concentration of TCNB is 1.06×10^{-2} M. Concentrations of MTHF; (1) 3.36 M, (2) 1.38 M, (3) 0.99 M, (4) 0.49 M.

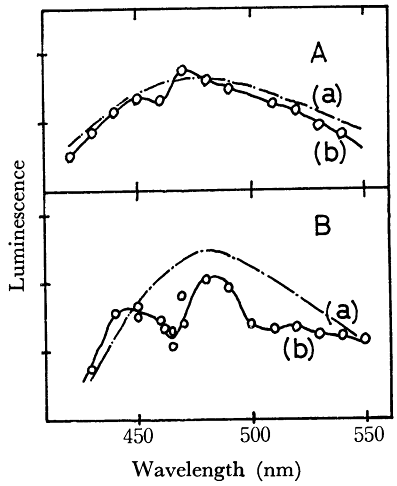

Fig. 4. Fluorescence spectra of a TCNB–MTHF complex at room temperature (A), and at 77 K (B): (a) —— by spectrophotofluorometer, (b) —○—○— by laser excitation.

Fluorescence spectra of the TCNB–MTHF complex observed at room temperature and at 77 K by exciting the CT absorption band are shown in Fig. 4. The fluorescence lifetime at room temperature is *ca.* 5 ns at all the wavelengths in the fluorescence band, while at 77 K the lifetime depends on the fluorescence wavelength. It increases from *ca.* 20 to 40 ns as the wavelength increases. A re-absorption of the CT fluorescence by the excited complex or by photoproduced transients was observed in the case of laser excitation. A phosphorescence spectrum of the TCNB–MTHF complex has a peak at about 500 nm with a lifetime 28.4 ms. Flourescence of the PMDA–MTHF complex has a peak at 390 nm with a very short lifetime (a few ns). No re-absorption effect by laser excitation was observed.

Ionic Dissociation of MTHF Complexes. The transient absorption spectrum obtained by exciting the TCNB–MTHF complex at 347 nm is shown in Fig. 5. Since the absorption spectrum on the wave-

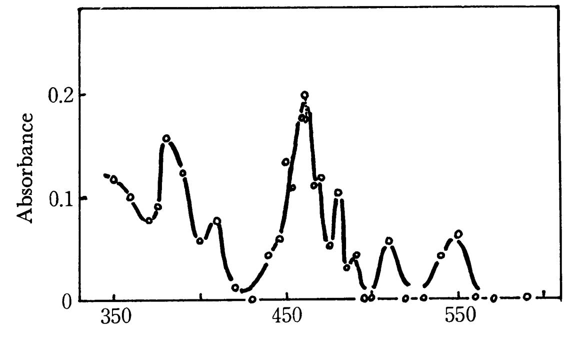

Fig. 5. The transient absorption spectra observed immediately after excitation of a TCNB–MTHF complex; the concentration of TCNB is 0.1 M.

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[8] N. Mataga and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 3144 (1969).

length region smaller than 500 nm is similar to that of TCNB anion, it is confirmed that the excitation of the complex leads to ionic dissociation. On the other hand, the bands in the wavelength region greater than 500 nm, which cannot be observed by the ordinary stationary measurements, may be due to the excited state of a photoproduct, since the absorbances of these bands increase by the irradiation of CT band with a steady Xe-lamp. The kinetic relation between the transmittance at 462 nm and the transient photocurrent is given in Fig. 6. The transimittance is almost constant in the course of several μs after excitation, while the peak photocurrent is attained during *ca.* 2 μs. The current decays slowly ($\tau_{1/2}$~10 μs). The difference between transmittance and photocurrent may be ascribed to a transient, which gives no current but shows an absorption spectrum similar to that of TCNB anion. The transient is deemed to be an ion-pair of TCNB anion and MTHF cation, which is produced rapidly by laser excitation, dissociating gradually into ions. The results in the case of the aerated system are the same as those in the degassed case.

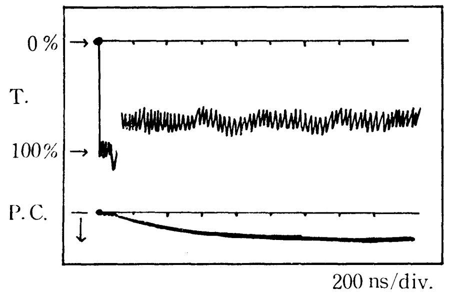

Fig. 6. The kinetic relation between the transient photocurrent and the transmittance of a TCNB anion at 462 nm, induced by exciting TCNB-MTHF complex.

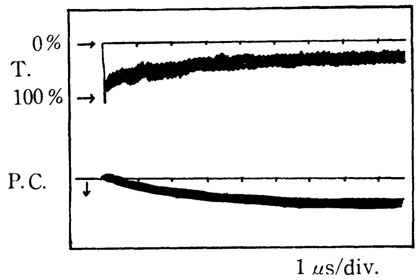

Fig. 7. The kinetic relation between the transient photocurrent and the transmittance of a PMDA anion at 660 nm, induced by exciting a PMDA-MTHF complex.

The dissociation process was also examined in an ethanol solution, where the volume ratio of MTHF to ethanol was 1: 1. The transient absorption was similar to that of a TCNB anion. The transmittance was constant with respect to time, while most of the photocurrent was induced rapidly, the delayed (~100 ns) photocurrent being also detected.

Assuming that an extinction coefficient of the ion-pair is equal to that of the dissociated ions, the quantum yields of dissociation as well as ion-pair formation for the systems of TCNB-MTHF and TCNB-MTHF-ethanol were estimated according to the same method as reported previously.[2] Values for the quantum yield were 0.03 and 0.089, respectively.

Since all the measurements were carried out under a high concentration of TCNB, effect of the direct excitation of the tail of the original TCNB band should be examined. A small and rapidly rising photocurrent was induced in the TCNB-DCE system, which may be due to ionization of TCNB itself. A slowly rising curve of laser-induced photocurrent similar to that of the TCNB-MTHF system was observed by exciting the TCNB-MTHF-DCE system, where the concentration of TCNB was equal to that of the TCNB-DCE system. Thus, it might be concluded that the present results are due to the ionic dissociation of the TCNB-MTHF complex.

We have confirmed that a PMDA anion is produced by exciting a PMDA-MTHF complex with a 347 nm laser pulse at room temperature. Oscillograms showing the transmittance at the wavelength of the PMDA anion absorption (660 nm) as well as a laser-induced photocurrent are given in Fig. 7. The peak photocurrent was measured at *ca.* 8 μs after excitation. It decayed slowly ($\tau_{1/2}$~300 μs). The rise curve of the photocurrent is in good agreement with that of absorption band of a PMDA anion. At 77 K the measurement of transient absorption spectra is impossible because of a laser-induced cracking of an MTHF rigid solution. No appropriate condition could be found in which the rise of a PMDA anion can be related to the decay of the phosphorescence. In the aerated system the peak photocurrent was measured at *ca.* 2.5 μs after excitation, its value being *ca.* one fifth of that in the degassed system.

The effect of solvents on the dissociation of a PMDA-MTHF complex was examined by photocurrent measurement. A schematic representation of oscillograms is given in Fig. 8. In a DCE solution, the peak photocurrent was reached slowly, while in polar solvents such as acetonitrile and butyronitrile rapid as well as slow productions of ions were observed. The rise of a laser-induced photocurrent is in good agreement with

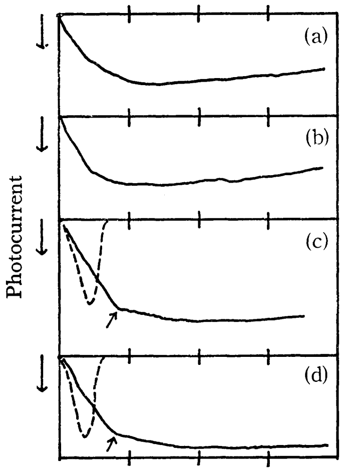

Fig. 8. The rise and decay curves of photocurrent induced by exciting a PMDA-MTHF complex. Solvents; (a) Without other solvent, (b) DCE, (c) butyronitrile, (d) acetonitrile. Horizontal scale; (a), (b) 5 μsec per division, (c), (d) 50 nsec per division. ------Observed exciting pulse.

that of transmittance of a PMDA anion in the case of a PMDA–MTHF–acetonitrile system. The photocurrent of a PMDA–acetonitrile system was also confirmed under the same concentration of PMDA as that of a PMDA–MTHF–acetonitrile system. Only rapid rise of the photocurrent was observed, which is *ca.* one fifth of that of a PMDA–MTHF–acetonitrile system. Hence, the present result is concluded to be due to the dissociation of a PMDA–MTHF complex.

We also made an investigation on TCNB–1,4-dioxane, PMDA–1,4-dioxane and PMDA–THF complexes in DCE solutions. The peak photocurrents were observed at several μs after excitation, the delayed formation of ions being confirmed. The effect of excitation light intensity on the production of ions was examined by transient photocurrent measurement. Since the decay of a photocurrent is slower than the rise, the peak photocurrent is approximately proportional to the concentration of dissociated ions. The linear relations obtained between the excitation light intensity and the peak photocurrent show that the ionic dissociation of the present complexes in several solvents is a one-photon process.

Ionic Dissociation of TCNB and PMDA Complexes with Benzene and Naphthalene Donors. TCNB complexes with benzene and naphthalene donors and a PMDA–benzene complex were investigated in several solvents. The transient photocurrent measurements show that these complexes dissociate into ions immediately after excitation. The PMDA–benzene complex was examined in DCE and acetonitrile, where the volume ratio of benzene donor *vs.* solvent was fixed to 1 : 2. The results obtained on the TCNB–naphthalene complex are listed in Table 1, where the values of dielectric constant and viscosity coefficient are corrected by the method described previously. Although the measurement of the photocurrent has been reported,[2] we examined the TCNB–benzene–DCE system in more detail, with a 1 : 2 volume ratio of benzene to DCE. The rise and decay curves obtained for the fluorescence and photocurrent are shown in Figs. 9A and B. The observed fluorescence lifetime is about 20 ns. The simulated curves, considering a duration of an exciting pulse, are given in Fig. 9C, where (a), (b), and (c) represent the observed exciting pulse and the rise curves of radical ions from the fluorescent state ($\tau \sim 20$ ns) and excited FC states, respectively. The present observation of photocurrent agrees with (c). From an examination of the effect of excitation light intensity upon photocurrent, it has been confirmed that this ionic dissociation is a one-photon process. The photocurrent of TCNB in DCE was confirmed to be much smaller than that of the present system.

TABLE 1. IONIC DISSOCIATION OF TCNB–NAPHTHALENE COMPLEX IN ITS LOWEST EXCITED SINGLET STATE

Solvent	$\varepsilon^{a)}$	$\varphi_{\text{ion}}{}^{b)}$
Ethylether	4.34	0.0019
DCE	10.36	0.095
Butyronitrile	20.3	0.24
Acetonitrile	27.5	0.57
Standard[c)]	25.8[d)]	1.00

a) Dielectric constant of solvent.
b) Relative quantum yields of ionic dissociation determined by measurement of photocurrent.
c) The TCNB–toluene–acetonitrile system.[2)]
d) Calculated dielectric constant.[2)]

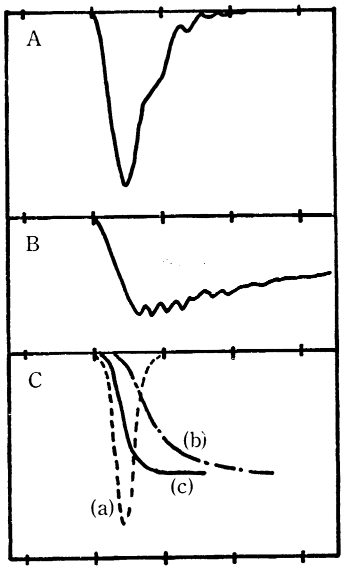

Fig. 9. TCNB–benzene–DCE system.
A. The rise and decay of fluorescence.
B. The rise and decay of laser-induced photocurrent.
C. The simulated rise and decay curves of photocurrent;
(a) Observed exciting pulse, $p(t')$,
(b) $\int_0^t p(t')\,(1-\exp(-(t'-t)/\tau))\,dt'$, $\tau \sim 20$ ns,
(c) $\int_0^t p(t')dt'$.

Discussion

The Electronic Structure of a TCNB–MTHF Complex in the Ground and Excited States. It has been shown that the 1st and the 2nd CT absorption bands of TCNB–mesitylene and TCNB–HMB complexes are due to transitions from the highest occupied molecular orbital (MO) of the donor to the lowest and the 2nd lowest vacant MO's of the acceptor, respectively.[9] In the case of benzene and toluene donors the 2nd CT band was not observable since there are absorption bands of the donor in this wavelength region. In the case of the TCNB–MTHF complex, two CT bands were observed since there is no absorption band of the donor. The energy gap between the 1st and the 2nd new bands was estimated to be 0.56 eV, from the observed frequencies of the two bands. The value differs somewhat from the gap between the lowest and the 2nd lowest MO's of TCNB (0.68 eV). The difference may be related to the relative locations of the CT and the original bands of TCNB. In the case of mesitylene and HMB donors, two CT's are observed in the wavelength region longer than the original TCNB band, which results in the small configuration interaction (CI) between the CT and the locally excited (LE) configurations. On the other hand, the CT bands of

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[9] S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

the present complex were observed in the same wavelength region as that of the original bands of the acceptor. Hence, it is expected that the extent of CI between the CT and the LE configurations is rather large. Thus, the energy gap between the two bands of the TCNB–MTHF complex is not connected directly with the gap between two MO energies.

According to Iwata *et al.*,[9] the CT degree in the excited singlet FC state of TCNB complexes increases as the ionization potensial of the donor decreases. The ionization potential of MTHF is not known but may be larger than that of benzene (9.24 eV), since the ionization potensial of THF is 9.49 eV. The large interaction between the CT and the LE configurations is expected in the TCNB–MTHF complex. The LE character in the excited FC state may be rather high.

Fluorescence spectra of a TCNB–MTHF complex at room temperature show a large Stokes shift of about 10200 cm^{-1}. This can be explained by the same consideration as that on TCNB complexes with other donors. The large Stokes shift of TCNB–methylsubstituted benzene complexes was concluded to be due to differences in energy and geometrical structure between the excited FC and the fluorescent state. This conclusion was deduced from fluorescence studies as well as from direct observations of excited singlet-singlet absorption spectra.[8,10–12] Since the LE character of the excited FC state of the TCNB–MTHF complex seems to be high and the value of Stokes shift is quite large, it is considered by analogy to the case of the TCNB–methylsubstituted benzene complexes that the CT character of the fluorescent state is rather high. The fluorescence spectrum of a TCNB–MTHF complex by laser excitation are re-absorbed by some transients photoproduced from the excited FC state. Absorption spectra of the transient estimated from the re-absorption are similar to those of TCNB anion. Due to the short fluorescence lifetime it was difficult to analyze fluorescence decay curves at several wavelengths, though this is necessary for assigning the transient to the fluorescent state of the complex.[13] Nevertheless, similarity of the spectra of the fluorescent state to those of a TCNB anion is consistent with the large value of the Stokes shift and with the above argument concerning the high CT character of the fluorescent state. Hence, the changes in energy as well as electronic structure of the TCNB–MTHF complex occur in the course of the process from the excited FC to the relaxed fluorescent states, just as in the case of TCNB–methylsubstituted benzene complexes.

The Stokes shift of the present complex at 77 K is almost the same as that at room temperature, differing from the case of TCNB complexes with methylsubstituted benzenes.[8,10] Dependence of fluorescence lifetime on the observed wavelength was not observed in the case of the latter TCNB complexes at 77 K. The fact that the lifetime increases with the fluorescence wavelength may be ascribed to the relaxation process including surrounding molecules from the excited FC state to the equilibrium state. This particular behavior might be due to the fact that the electron donating orbital is the lone pair orbital of oxygen atom and the structural change involving environments is possible even at 77 K.

Ionic Dissociation of TCNB Complexes. Dissociation mechanism of TCNB complexes should be discussed in detail in consideration of the results of previous[2] and present works. All these complexes with cyclic ethers, methylsubstituted benzenes and naphthalene have a quite polar structure in the fluorescent state and form ion-pair or dissociate into ions rapidly in various solvents. In the case of cyclic ether donors, ions are produced rather slowly through the ion-pair state from the excited CT singlet state in nonpolar and slightly polar solvents. In moderately and strongly polar solvents the new process of direct dissociation, not through the ion-pair, is observed in addition to the above delayed process. Stabilization of ion-pair state may be partially due to the Coulomb attraction force between the cation and the anion. Since the positive charge is localized on an oxygen atom, this attractive force may be rather large. In the case of TCNB complexes with methylsubstituted benzenes, dissociation occurs spontaneously in the lowest excited CT singlet state in various solvents and the ion-pair is not observed. We have pointed out that the ionic dissociation yield increases with the increase of ionization potential of the donor.[2] However, the dissociation yield of a TCNB–naphthalene complex in acetonitrile is larger than that of a TCNB complex with mesitylene, although the ionization potential of naphthalene is lower than that of mesitylene. This may be ascribed to the difference of the Coulomb attractive force between the donor cation and the acceptor anion, if one assumes that the larger Coulomb attraction leads to the stronger nondissociative quenching of the excited state. The Coulomb force between a TCNB anion and a naphthalene cation seems to be rather small, since the positive charge in naphthlene is more delocalized than that in methylsubstituted benzene as well as in cyclic ether. From this consideration and the solvent effect on ionic dissociation of some TCNB complexes, it is concluded that the ionic dissociation of TCNB complexes depends upon the solvation energy on the one hand and upon the Coulomb force between ions on the other.

In the above discussion, the difference of solvation energies of different donor cations was not considered explicitly. The particular behavior of TCNB–cyclic ether complexes may be attributed partly to the property of the donor solvent itself, since cyclic ether is a well-known solvent which stabilizes ion-pair rather than dissociated ions. For example, Briegleb and Lind showed the ion-pair formation in the case of THF–nitrosubstituted benzenes by analyzing an ESR hyperfine pattern.[14] The ion-pair formation was reported

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[10] T. Kobayashi, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 2603 (1971).

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

[12] H. Masuhara and N. Mataga, *Z. Phys. Chem. N. F.*, **80**, 113 (1972).

[13] H. Masuhara and N. Mataga, This Bulletin, **45**, 43 (1972).

[14] G. Briegleb and G. Lind, *Z. Naturforsch.*, **23a**, 1747, 1752 (1968).

also by Pilette and Weiss by analysing the decay of a PMDA anion,[15] produced by exciting the CT bands of PMDA complexes. They interpreted the results in terms of the equilibrium between ion-pair and dissociated ions as well as of the degradation of ion-pairs. In the case of TCNB–methylsubstituted benzene complexes, it is not certain whether the ion-pair was produced or not. Direct observation of the rapid formation of ion-pair was achieved for the first time for a TCNB–MTHF complex.

It should be noted that the ion-pair is a solvent-shared one. From the study on the electronic structure of the EDA complexes we have made it clear that the fluorescent state of these complexes is a contact ion-pair.[11,12] The excited equilibrium state of a TCNB–MTHF complex also seems to be quite polar. The lifetime of this fluorescent ion-pair is *ca.* 5 ns while that of the other ion-pair deduced from the absorption as well as the photocurrent measurement is a few μs. Since the difference of lifetime is very large, the difference between both ion-pairs cannot be ascribed to the difference of relative orientation of the donor cation and the acceptor anion. The long-lived ion-pair observed in μs time region is concluded to be a solvent-shared ion-pair.

Ionic Dissociation of PMDA Complexes. From the delayed formation of a PMDA anion and the oxgen effect on the dissociation, it is concluded that the PMDA–MTHF complex dissociates in the CT triplet state. Ions were produced not through the ion-pair state with rather long life, which differs from that of a TCNB–MTHF complex. This different behavior can be interpreted as follows. In the case of a PMDA–MTHF complex the rate constant of ion-pair formation might be small and in the same order as the dissociation of an ion-pair. Thus, the concentration of the latter is low and not detectable. In polar solvents, however, rapid production of a PMDA anion was observed in addition to the slow formation process. Due to the strong solvation of the donor cation and the acceptor anion by polar solvents, ionic dissociation may compete with intra-complex processes including intersystem crossing in the excited state. This suggests also a delicate balance between intra-complex interaction and solvation.

In the case of benzene and its derivative donors, dissociation has been confirmed to occur in the lowest CT triplet state. Potashnik *et al.* reported the dissociation from the CT triplet states of PMDA–mesitylene and PMDA–HMB complexes.[4] Recently, this dissociation from the triplet state has been demonstrated also by energy transfer experiments in some solvents.[7] In the present work, we observed the rapid dissociation of a PMDA–benzene complex in DCE as well as in acetonitrile. The rapid dissociation of a PMDA–mesitylene complex in acetonitrile was confirmed previously.[2] In the case of the latter system Achiba *et al.*,[7] have pointed out no participation of the CT triplet state to ionic dissociation. All these results on the PMDA complexes show a delicate effect of environments on the dissociation

The relative rate constant of radiationless processes such as direct degradation as well as intersystem crossing, which compete with ionic dissociation in the excited singlet state, can be deduced from the effect of a solvent on ionic photodissociation. Assuming the same rate constants of photodissociation of TCNB and PMDA complexes, the intersystem crossing process of PMDA complexes may be faster than those of TCNB complexes. The process of PMDA–MTHF is faster than that of PMDA–methylsubstituted benzenes.

Ionic Dissociation from the Excited FC State. Although the dissociative states of EDA complexes have been classified as CT singlet or CT triplet state, the following experimental results seem to suggest the possibility of ionic dissociation in the excited FC state. (1) The electronic structure and geometrical configuration of the fluorescent state differ considerably from those of excited FC state in the case of TCNB complexes. The fluorescent state is therefore produced in nonpolar solvent through relaxation from the excited FC state.[12] In polar solvents, ionic dissociation was observed instead of fluorescence. (2) The intersystem crossing process of TCNB complexes is very rapid and direct formation of the phosphorescent state from the FC state was observed by means of ns flash photolysis studies on the rigid solution of TCNB–toluene complex in the mixture of 2- and 1-propanols.[16] In liquid mixture, ionic dissociation was observed, but not the formation of phosphorescent state. These results suggest that ionic dissociation and intersystem crossing compete with each other in the excited FC state. (3) The solvent effect on the fluorescence quantum yield and lifetime of a TCNB–benzene complex was examined and direct radiationless process was proved to occur from the excited FC state as well as in the course of the relaxation from the excited FC to the relaxed fluorescent states.[2] (4) Energy levels of several states of a TCNB–MTHF complex are given in Fig. 10. The energy levels of a solvent-shared ion-pair as well as dissociated ions are cited from results by Taniguchi *et al.*[17] It should be noted that there is a large gap between the fluorescent and solvent-shared ion-pair states. The ion-pair may be formed from the excited FC state.

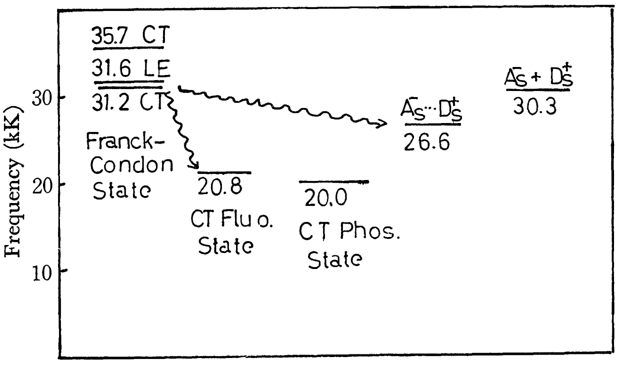

Fig. 10. Energy diagram of a TCNB–MTHF system.

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We have directly confirmed that ions are produced immediately after exciting the CT band of a TCNB–benzene complex in DCE, not through the fluorescent state. It is concluded that the ionic dissociation of the present complex occurs in the excited FC state. This is the first direct observation of rapid dissociation of EDA complexes which are stable in the ground state. In more polar solvents the fluorescence lifetime of this complex is too short to be analysed, while no photocurrent is observed in less polar solvents.[18] Investigations on other systems are difficult because of short fluorescence lifetime. Hence, a TCNB–benzene–DCE system is the only example at the present stage of investigations. All the results obtained for TCNB and PMDA complexes under various conditions are not inconsistent with the present mechanism of dissociation in the excited FC state.

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[18] We used a 50Ω resistor for obtaining ns time resolution.