J. Phys. Chem. A **1998,** *102,* 6585−6589

ARTICLES

Significant Quenching of the Photoinduced Charge Separated State of Aminophenyl(phenyl)acetylene and *N*,*N*-Dimethylaminophenyl(phenyl)acetylene in Protic Solvents

Yoshinori Hirata* and Tadashi Okada

Department of Chemistry, Graduate school of Engineering Science and Research Center for Materials Science at Extreme Conditions, Osaka University, Toyonaka 560-8531, Japan

Tateo Nomoto

Department of Chemistry, Faculty of Education, Mie University, Tsu 514-0008, Japan

Received: February 3, 1998; In Final Form: April 16, 1998

By using picosecond transient absorption and fluorescence lifetime measurement techniques, we have investigated intramolecular charge separation and charge recombination processes of aminophenyl(phenyl)acetylene and *N*,*N*-dimethylaminophenyl(phenyl)acetylene in various polar solvents. Significant quenching of the intramolecular charge separated state was observed in protic solvents and both the triplet and fluorescence yields were much lower than those in aprotic polar solvents. Such enhancement of the charge recombination was explained by the increase of the radiationless transition probability to the ground electronic state caused by the structural deformation around the amino nitrogen atom. Interaction between the amino nitrogen atom and the oxygen atom of the solvent molecule, which is the hydrogen-bond donor terminal of the network, should play an important role.

Introduction

A conjugated donor−acceptor molecule, *p*-cyano-*p*′-methylthiodiphenylacetylene (MTCN-DPA), was reported to emit fluorescence in various polar solvents from an intramolecular charge separated (CS) state.[1] In the previous paper,[2] we have investigated intramolecular charge separation of *p*-(*N*,*N*-dimethylamino)-*p*′-cyanodiphenylacetylene (DACN-DPA) in various polar solvents. In polar solvents the CS state, which shows transient absorption bands around 400 and 600−700 nm, was observed. Assuming the cavity radius of 6.4 Å, we estimated that the dipole moment of the CS state is about 31 D larger than that in the ground electronic state of DACN-DPA. In alcohols, in addition to the observation of the solvation process of the CS state revealed as a dynamic blue shift of the transient absorption band of the CS state in a few tens of picosecond time scale, we found a shortening of the lifetime of the CS state. The triplet yields were found to be much smaller in alcohols compared with those in aprotic polar solvents.

It is known that the specific interaction between solute and protic solvent molecules, which cannot be rationalized from the macroscopic properties of solvent such as dielectric constant and viscosity, plays an important role in electron-transfer processes of the solute. Fluorescence quenching of tetramethyl-*p*-phenylenediamine (TMPD) in water[3] and the dynamic behavior of the ion pair state of TMPD in alcohols,[4] can be examples of the specific solute−solvent interaction. Photophysical properties and their solvent effects of dye molecules such as rhodamines[5] and coumarins[6] have been reported. The rate constants of the internal conversion from the S_1 state of 7-aminocoumarin derivatives increase strongly upon the alkylation of the amino groups.[6] Strong fluorescence quenching of the diethylamino derivative observed in water was explained by the solute−solvent hydrogen bond. Although the mechanism is not established yet, the above-mentioned enhancement of the charge recombination of DACN-DPA in alcoholic solvents[2] should be an appearance of such a specific solvent effect.

In this paper, by using picosecond transient absorption spectral measurement techniques, we have investigated the intramolecular charge-transfer process of aminophenyl(phenyl)acetylene (AM-DPA) and *N*,*N*-dimethylaminophenyl(phenyl)acetylene (DA-DPA). Although these molecules have only an electron donating group, in various polar solvents intramolecular charge separation was observed and absorption spectra of the CS state were quite similar to those of DACN-DPA, which has both the electron donating and electron accepting groups. Moreover, a significant shortening of the CS state lifetime in protic solvents was observed. We proposed that a specific interaction between the amino group and the solvent oligomer is responsible for the enhancement of the charge recombination.

To avoid confusion about our notation of the excited singlet states of AM-DPA and DA-DPA, we will define them here. Two locally excited singlet states are observed in nonpolar solvents. One is the lowest excited singlet state (S_1) of which the lifetime is a few hundreds of picosecond, and another is the short-lived S_2 state, which is located slightly above the S_1 state. The former is nonfluorescent, while the latter is fluorescent.[7,8] Although the CS state is the lowest excited singlet state

---

* Corresponding author. E-mail: hirata@chem.es.osaka-u.ac.jp.

S1089-5639(98)00991-8 CCC: $15.00

in polar solvents, we use S_1 for the locally excited state which has the same character as the lowest excited singlet state in nonpolar solvents. In polar solvents, both the locally excited S_2 and CS states emit fluorescence.

Experimental Section

Picosecond transient absorption spectra were measured by using a dye laser photolysis system pumped by the second harmonic of a mode-locked Nd^{3+}:YAG laser (Quantel, Picochrome YG-503C/PTL-10). The details of this system were described elsewhere.[9] The sample was excited with the second harmonics of a rhodamine-6G (295 nm) or rhodamine-640 (313 nm) laser and a transient absorption spectrum between 380 and 980 nm was measured by using a picosecond white light generated in a H_2O/D_2O mixture. Typically the signal was averaged over 30 shots. To correct the transient absorption spectrum for the dispersion of the probe light, we measured the optical Kerr effect of CCl_4 and determined the wavelength-dependent arrival times of the picosecond white light at the sample cell.

Fluorescence lifetimes were measured by using a streak camera (Hamamatsu C2830 temporal disperser with H2547 fast scan unit). The fluorescence was excited with the second harmonics of the dye laser (295 nm) and was collected at right angles. After passing through a color glass filter and a monochromator, the fluorescence was temporally dispersed by a streak camera and the signals of typically 16 shots were accumulated on a CCD chip. The two-dimensional data were averaged over 30−100 cycles of measurement on the controller of the streak camera and were transferred to the microcomputer for further data analysis.

Synthesis of AM-DPA and DA-DPA was given elsewhere.[10] The concentration of the sample solutions was about 2×10^{-4} M. Spectrograde *n*-hexane, diethyl ether, tetrahydrofuran (THF), methanol, ethanol, 2-propanol, 1-butanol, *N,N*-dimethylformamide (DMF), and acetonitrile were used without further purification. 1,2-Dimethoxyethane and 1-propanol (GR-Grade) were purified by fractional distillation and formamide (FA) and *N*-methylformamide (DMF) were distilled under reduced pressure. Methanol-*O-d* (99.5 atom % D) was used without further purification. All the samples prepared in quartz cells of 1-cm optical path length were deaerated by flushing an Ar or N_2 stream. No significant degradation of the sample was observed in all solvents used for the transient absorption measurements. The measurements were carried out at room temperature (23 ± 1 °C).

Results and Discussion

Absorption and Fluorescence Spectra. Figure 1 shows absorption and fluorescence spectra of AM-DPA in various solvents. In nonpolar solvents such as *n*-hexane, the fluorescence spectrum of AM-DPA had maxima at 327 and 338 nm, while the absorption spectrum had a maximum at 300 nm and shoulders around 310−320 nm. In polar solvents AM-DPA showed a broad fluorescence with a large solvatochromic shift. A shoulder was observed in diethyl ether and THF around 420−460 nm and in acetonitrile a band maximum appeared at 480 nm. Although the solvent effects of the absorption spectrum were not so significant as those of the fluorescence spectrum, the first absorption band in polar solvents showed a slight broadening, a solvent dependent small red shift, and an increase of absorbance in the red tail region.

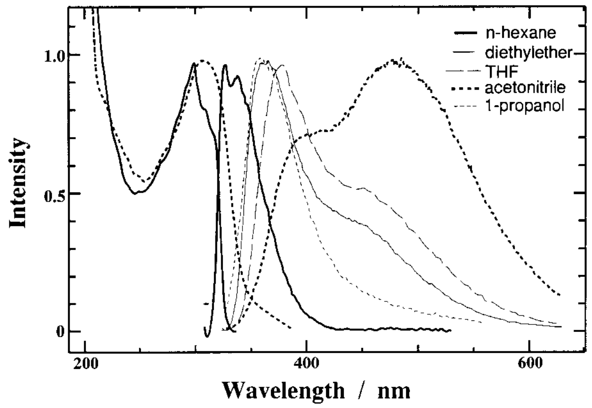


Figure 1. Absorption and fluorescence spectra of AM-DPA in *n*-hexane, diethyl ether, THF, acetonitrile, and 1-propanol.

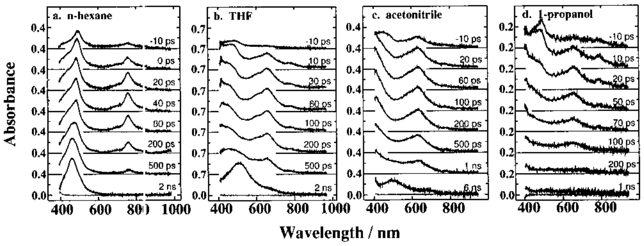


Figure 2. Picosecond time-resolved absorption spectra of AM-DPA in (a) *n*-hexane, (b) THF, (c) acetonitrile, and (d) 1-propanol. Baselines (the signal without the excitation) are also given in the bottom of the figure. Delay times after the laser pulse excitation are shown in the figure.

At wavelengths shorter than 400 nm, a short-lived fluorescence of which the lifetime was shorter than the effective time resolution of the apparatus (~60 ps) was observed. On the other hand, the fluorescence lifetimes measured at longer wavelengths were about 0.50, 0.91, and 1.3 ns in diethyl ether, THF, and acetonitrile, respectively. In 1-propanol the fluorescence band maximum was similar to that in diethyl ether but no shoulder in the longer wavelength region was observed. The fluorescence yield was smaller than that in aprotic polar solvents and the fluorescence lifetime was shorter than our time resolution. In nonpolar solvents, the fluorescence state of AM-DPA is neither the CS state nor the S_1 state, but it was known to be the second excited singlet state (S_2).[7] The $S_1 \leftarrow S_0$ transition is dipole forbidden, therefore the first absorption band around 300 nm is due to the S_2 state.

These results indicate that the fluorescence band in the longer wavelength region (shoulder in diethyl ether and THF and the peak in acetonitrile) can be ascribed to the CS state, which was reported for MTCN-DPA[1] and DACN-DPA[2] in polar solvents. Taking into account the results of the transient absorption spectra discussed in the following subsection, we can safely assign the short-lived fluorescence observed at the shorter wavelengths to the S_2 state of AM-DPA. A similar behavior was observed for DA-DPA.

Transient Absorption Spectra. Picosecond time-resolved absorption spectra of AM-DPA and DA-DPA in various solvents are shown in Figures 2 and 3, respectively. Immediately after the laser pulse excitation, the $S_n \leftarrow S_2$ absorption appears around 510 nm in *n*-hexane (Figure 2a) and the spectrum was rapidly replaced by the $S_n \leftarrow S_1$ band of which the peaks appear at 480 and 760 nm. The lifetime of the S_2 state of AM-DPA is reported to be about 8 ps at room temperature.[7] At the longer delay times, the $T_n \leftarrow T_1$ absorption band was observed around 460 nm. The $S_n \leftarrow S_1$ and $T_n \leftarrow T_1$ absorption bands of DA-DPA in *n*-hexane are reported to be observed at 830 and 530 nm, respectively (Figure 3a).[8]

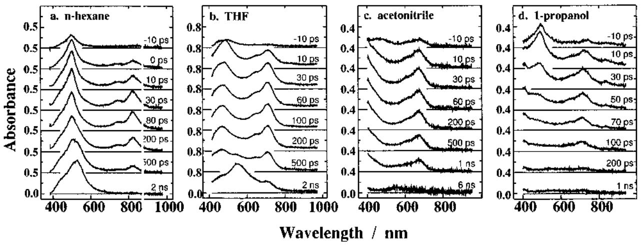


Figure 3. Picosecond time-resolved absorption spectra of DA-DPA in (a) *n*-hexane, (b) THF, (c) acetonitrile, and (d) 1-propanol. Baselines (the signal without the excitation) are also given in the bottom of the figure. Delay times after the laser pulse excitation are shown in the figure.

In THF and acetonitrile immediately after the excitation of AM-DPA, the transient absorption spectra peaked at 480 (Figure 2b) and 460 nm (Figure 2c) were observed. Although the peak position was slightly shorter than that of the $S_n \leftarrow S_2$ band in *n*-hexane, these short-lived bands (20 and 7 ps in THF and acetonitrile, respectively) can be ascribed to the S_2 state. The S_2 band disappeared with increasing delay time and was replaced by the bands peaked at 660 and 640 nm in THF and acetonitrile, respectively. The lifetimes of the red bands were estimated to be about 0.9 and 1.3 ns in THF and acetonitrile, respectively, which show good agreement with the fluorescence lifetimes measured at longer than 480 nm. Therefore the transient absorption band in the red region should be ascribed to the CS state of AM-DPA. The band observed between a few tens and hundreds of picosecond region and peaked at 400 nm or shorter should be due to the CS state, too. In THF and acetonitrile, the S_1 band was hardly observed.

The long-lived absorption band observed around 500 nm can be assigned to the $T_n \leftarrow T_1$ transition of AM-DPA. Assuming that the extinction coefficient of the $T_n \leftarrow T_1$ absorption at the peak wavelength is solvent independent, we can estimate the triplet yield in acetonitrile to be about 30% of that in THF. The triplet yield seemed to decrease with increasing solvent dielectric constant of aprotic polar solvents. A quite similar behavior was observed for DM-DPA; however, the bands of the CS state and the triplet state were observed around 670−710 and 550 nm, respectively. The spectrum of the CS state resembled that of DACN-DPA in polar solvents.[11]

In 1-propanol (Figure 2d) immediately after the excitation, a transient absorption band appeared around 490 nm. From the similarity of the peak position and the band shape to those of the $S_n \leftarrow S_2$ absorption band observed in *n*-hexane, we can safely assign the 490-nm band to the $S_n \leftarrow S_2$ transition of AM-DPA. The 490-nm band was rapidly replaced by the red bands (660 and 790 nm for AM-DPA 720 and 830 nm for DA-DPA). From the similarity of the peak position, the 660 and 720 nm bands should be due to the CS state, while the 790 and 830 nm bands are ascribed to the $S_n \leftarrow S_1$ transition. These bands were short-lived, and at the delay time longer than 200 ps, only a quite weak and broad transient absorption was observed. The long-lived band seemed to be a superposition of the CS state and T_1 bands.

In the previous paper,[2] we find that the band maximum of the CS state of DACN-DPA in the red region shows a dynamic blue shift in alcoholic solvents and is a good indicator of the local polarity of the solution. As shown in Figure 4, the band maximum of the CS state of AM-DPA and DA-DPA also showed a similar relation. In aprotic polar solvents (1−8), the solvent dependence appeared to be on a different straight line from that in alcohols (9−12). The polarity of the environment in alcohols seemed to be lower than was expected from the polar parameter, which was widely known for the Mataga−Lippert plots of many systems.[12] On the contrary, a larger blue shift than expected from the polar parameter was observed in NMF (15) and FA (16).

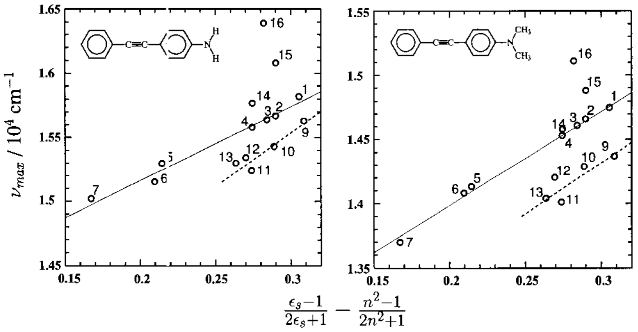


Figure 4. Plots of the band maximum of the CS state band of AM-DPA and DA-DPA in the red region against the polarity parameter of solvents. The numbering for the solvents is the same as that in Table 1: 1, acetonitrile; 2, propionitrile; 3, acetone; 4, *n*-butyronitrile; 5, THF; 6, 1,2-dimethoxyethane; 7, diethyl ether; 9, methanol; 10, ethanol; 11, 1-propanol; 12, 2-propanol; 13, 1-butanol; 14, DMF; 15, NMF; 16, FA.

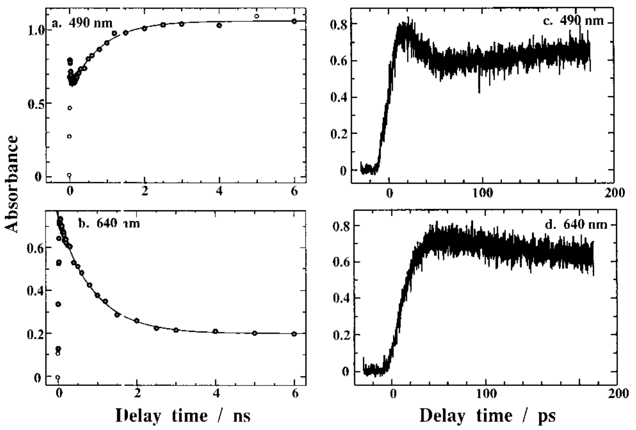


Figure 5. Time dependence of the transient absorbance of AM-DPA in THF. The monitoring wavelengths are indicated in the figure, and two time scales are given.

Time Dependence of the Transient Absorbance. Figure 5 shows the time dependence of the transient absorbance of AM-DPA in THF. The decay curve measured at 640 nm (Figure 5b) can be analyzed as a biexponential function. The longer lived component, which should be due to T_1, was essentially constant between 3 and 6 ns, while the lifetime of the short-lived component (about 0.9 ns) agreed with the rise time of the long-lived component measured at 490 nm. In the short delay time region, at 490 nm the instrumentally limited rise was followed by a rapid decay of about 15 ps. At 640 nm a rise time of about 13 ps was observed. On the basis of the picosecond transient absorption spectra, the rapid decay observed at 490 nm should be due to the decay of S_2, while the rise at 640 nm was ascribed to the formation of the CS state. The triplet state was formed via the charge recombination. The decay time of the CS state measured around 640 nm (700 nm for DA-DPA) in the various solvents are listed in Table 1.

In less polar solvents such as diethyl ether, the $S_n \leftarrow S_1$ absorption was observed at shorter than several hundred picosecond delay times. The decay time of the S_1 state appeared to be the same as that of the CS state. The results imply that the charge recombination to form the S_1 state cannot be negligible. Such decay channel should be closed in the highly

TABLE 1: Fluorescence Lifetimes of the CS State and Decay Times of the Transient Absorbance Monitored in the Red Region for AM-DPA and DA-DPA in Various Polar Solvents

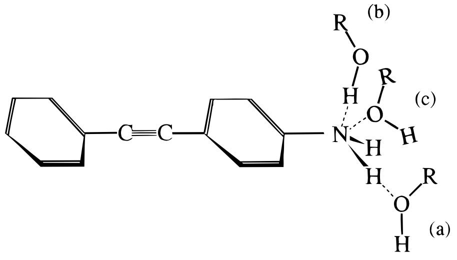
		AM-DPA		DA-DPA	
	solvent	τ_f/ns	τ_d (CS)/ns	τ_f/ns	τ_d (CS)/ns
1	acetonitrile	1.41	1.3 ± 0.1	1.76	1.8 ± 0.1
2	propionitrile	1.51	1.5 ± 0.3	1.92	2.3 ± 0.3
4	*n*-butyronitrile	1.6	1.4 ± 0.2	2.5	2.4 ± 0.4
5	THF	1.02	0.91 ± 0.07	1.48	1.4 ± 0.06
7	diethyl ether	0.50	0.47 ± 0.05	0.72	0.69 ± 0.06
8	*p*-dioxane	0.66	0.63 ± 0.07	1.03	1.0 ± 0.1
9	methanol	<0.06	1.6×10^{-2}	<0.06	1.7×10^{-2}
	methanol-*O*-*d*	<0.06	1.5×10^{-2}	<0.06	1.7×10^{-2}
10	ethanol	<0.06	2.3×10^{-2}	<0.06	2.7×10^{-2}
11	1-propanol	<0.06	$(2.9 \pm 0.3) \times 10^{-2}$	<0.06	$(3.2 \pm 0.3) \times 10^{-2}$
12	2-propanol	~ 0.08	$(8.0 \pm 0.4) \times 10^{-2}$	~ 0.08	$(8.2 \pm 0.5) \times 10^{-2}$
13	1-butanol	<0.06	$(4.7 \pm 0.3) \times 10^{-2}$	<0.06	$(5.2 \pm 0.3) \times 10^{-2}$
14	DMF	1.3	1.3 ± 0.2	2.1	2.2 ± 0.3
15	NMF	~ 0.07	$(5.8 \pm 0.5) \times 10^{-2}$	~ 0.08	$(8.4 \pm 0.7) \times 10^{-2}$
16	FA	~ 0.07	$(5.8 \pm 0.6) \times 10^{-2}$	~ 0.08	$(7.8 \pm 0.6) \times 10^{-2}$

polar solvents such as acetonitrile and THF because of a large stabilization of the CS state. The microscopic environment in alcohol is not so polar as was expected from the static dielectric constant, since the back electron transfer to the S_1 state was observed in 1-propanol. The similar result was obtained from the solvent dependent shift of the transient absorption spectrum of the CS state as we touched upon. Detailed explanation of the $S_2 \rightarrow S_1$ internal conversion and the contribution of the S_1 state to the intramolecular charge separation and charge recombination of AM-DPA and DA-DPA as well as their temperature dependence will be given elsewhere.[13]

Enhancement of the Charge Recombination in Protic Solvents. In protic solvents, deactivation of the CS state was much faster than that in aprotic polar solvents. The decay times of the transient absorbance of AM-DPA in protic solvents monitored at 650 nm where the contribution of the CS state was predominant are listed in Table 1. In methanol, the shortest lifetime was obtained and the deuterium effect in the hydroxyl group was hardly observed. In normal alcohols, the lifetime seemed to increase with increasing molecular size of the solvent, while in 2-propanol, an almost 2 times slower decay compared with 1-propanol was observed. The lifetimes obtained in FA and NMF were similar to that in 1-butanol, while in DMF the CS state was quite long-lived. Since the triplet yield was low in the protic solvents, the deactivation of the CS state should result in the formation of the S_0 state. These results clearly show that the enhancement of the charge recombination is not due to the effect of the solvent polarity but should be due to a specific solute–solvent interaction in protic solvents. At the present stage of the investigation, because detailed information about the microscopic solvent–solute interaction is not available, we cannot draw a definite picture to explain the experimental results.

One of the most plausible candidates of the specific solute–solvent interaction in protic solvents may be hydrogen bonding. The small deuterium effect of methanol suggests that the interaction between the OH hydrogen atom with the solute molecule is not responsible for the observed quenching of the CS state. Thus the hydrogen bonding interaction with the anionic part of the CS state may be eliminated. In the case of fluorescence quenching of anthraquinone derivatives in alcohol, where the radiationless deactivation of S_1 through hydrogen bonds was believed to be the mechanism, large deuterium isotope effects of the solvent on the nonradiative decay rate were observed.[14]

CHART 1



Interaction a in Chart 1 should not be important because the enhancement of the charge recombination to a similar degree was observed for DA-DPA. Since the nitrogen atom in the amino group of the solute is positively charged in the CS state, interaction b cannot be operative. On the contrary, the interaction between the positively charged nitrogen and the electron rich oxygen atom of the solvent molecule (interaction c) should play an important role. The interaction may cause the deformation of the amino group, which takes a pyramidal structure. Such a deformation should result in the large Franck–Condon factor between the CS and ground states. This can be a mechanism of the rapid charge recombination in protic solvents. Although DMF and ethers can interact with the amino group in the similar manner, no shortening of the CS state lifetime was observed.

The effect of the hydrogen bond on the OH stretching mode was established through infrared absorption measurements.[15] The OH stretching of non-hydrogen-bonded ethanol in CCl_4 appears at 3630 cm^{-1}, while the OH groups at internal positions of hydrogen-bonded oligomers give a broad band around 3330 cm^{-1} and the hydrogen-bonded donor end group of the open-chain oligomers absorbs at $\sim$3500 cm^{-1}.[16] The integrated extinction coefficient of the internal and the hydrogen-bond donor terminal OH groups are 12 and 3.5 times as large as that of the monomer.[17] Both the frequency and the extinction coefficient of the hydrogen-bond acceptor OH group is rather similar to those of the monomer. From these facts, we may expect that the interaction with the hydrogen-bond donor terminal group of the networking solvent molecules is stronger than that with monomers. Such interaction should play an important role in the charge recombination of the CS state.

Monte Carlo simulation of alcohols at 298 K showed that the majority of molecules were in internal positions of the hydrogen-bond network, but still significant percentage (19 and 12% for methanol and 2-propanol, respectively) of molecules were at the chain ends.[18] The longer lifetime in 2-propanol may be due to the steric hindrance. Although in 2-propanol a similar hydrogen-bond network to that in normal alcohols should be presented,[18] the distance between N−O, where the interaction to accelerate the charge recombination was expected to be operative, is shorter than that of the O−O distance in the hydrogen-bond network. In the bulky alcohols such as 2-propanol and *tert*-butyl alcohol, the dynamic behavior of the ion pair state of TMPD was quite different from that in normal alcohols.[4]

By using X-ray diffraction and ab initio molecular orbital calculation, Ohtaki et al.[19] showed that FA and NMF are forming a hydrogen-bond network, but DMF does not form such a hydrogen-bond network. This can rationalize why DMF did not show any specific effect for the charge recombination process. Judging from the extremely large dielectric constants of FA and NMF, hydrogen bonding among solvent molecules should be so strong that the solvent−solute interaction may be less effective, which can be the reason the quenching of the CS state in these solvents was less efficient than that in small alcohols.

Conclusion

We have demonstrated that the CS state is formed from the singlet excited state of AM-DPA and DA-DPA in various polar solvents. In aprotic polar solvents, the rate constant of the charge recombination to the T_1 state seems to decrease with increasing solvent polarity. We confirmed that the polarity of the microscopic environment in alcoholic solvents is lower than we expect from the static dielectric constant. Significant enhancement of the charge recombination to the S_0 state was observed in protic solvents. We proposed the interaction between the amino nitrogen of the solute molecule and the hydrogen-bond donor terminal OH group of solvent oligomers as a quenching mechanism.

References and Notes

(1) Khundkar, L. R.; Stiegman, A. E.; Perry, J. W. *J. Phys. Chem.* **1990**, *94*, 1224.
(2) Hirata, Y.; Okada, T.; Nomoto, T. *Chem. Phys. Lett.* **1997**, *278*, 133.
(3) Hirata, Y.; Tanaka, Y.; Mataga, N. *Chem. Phys. Lett.* **1992**, *193*, 36.
(4) Hirata, Y.; Mataga, N. *J. Phys. Chem.* **1983**, *87*, 3190; Hirata, Y.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 569.
(5) Arbeloa, F. L.;. Arbeloa, T. L.; Estevez, M. J. T.; Arbeloa, I. L. *J. Phys. Chem.* **1991**, *95*, 2203.
(6) Arbeloa, T. L.; Arbeloa, F. L. Tapia, M. J.; Arbeloa, I. L. *J. Phys. Chem.* **1993**, *97*, 4707.
(7) Hirata, Y.; Okada, T.; Nomoto, T. *J. Phys. Chem.* **1993**, *97*, 9677.
(8) Hirata, Y.; Okada, T.; Nomoto, T. *Chem. Phys. Lett.* **1996**, *257*, 513.
(9) Hirata, Y.; Okada, T.; Mataga, N.; Nomoto T. *J. Phys. Chem.* **1992**, *96*, 6559.
(10) Nomoto, T.; Tanaka, F.; Suzuki, N. *Chem. Express* **1991**, *6*, 319.
(11) Hirata, Y.; Okada, T.; Nomoto, T. *Chem. Phys. Lett.* **1993**, *209*, 397.
(12) Mertz, E. L.; Tikhomirov, V. A.; Krishtalik, L. V. *J. Phys. Chem.* **1997**, *101*, 3433.
(13) Hirata, Y.; Gen'nai, K.; Okada, T.; Nomoto, T.; Fisz, J. J. In preparation.
(14) Inoue, H.; Hida, M.; Nakashima, N. Yoshihara, K. *J. Phys. Chem.* **1982**, *86*, 3184.
(15) Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* **1970**, *66*, 1932.
(16) Graener, H.; Ye, T. Q.; Laubereau, A. *J. Chem. Phys.* **1989**, *90*, 3413.
(17) Liddel, U.; Becker, H. E. *Spectrochim. Acta* **1957**, *10*, 79.
(18) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.
(19) Ohtaki, H.; Itoh, S.; Rode, B. M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 271.