Photoionization and Ion Pair Formation of *N*,*N*-Diethyl-*p*-phenylenediamine in Various Polar Solvents

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By using transient absorption and photoconductivity measurement techniques, we have investigated the photoionization process of *N*,*N*-diethyl-*p*-phenylenediamine in various polar solvents. Significant excitation wavelength and excitation intensity effects were observed in alcoholic solvents. The slowly rising component of the photoconductivity in hundreds of nanoseconds or longer time scale is ascribed to the dissociation of the monophotonically produced ion pairs. In addition, a photoconductivity signal that has almost the same duration as the excitation laser pulse and is due to the geminate pair formed via the two-photon ionization is clearly observed with the 248-nm excitation. On the other hand, the biphotonic process was negligible with the 351-nm excitation in ethanol and 1-propanol. The monophotonically formed long-lived ion pair did not contribute to the conductivity. The long lifetime of the ion pair indicates that not only the Coulombic interaction but also the exciplex-like specific interaction is important.

Ionization is one of the most important photochemical primary processes and a great many publications concerned with the photoionization of solute molecules in the liquid phase can be found.[1] The ionization energies of the solute molecules in polar solvents are much lower than those in non-polar solvents, which reflects the large stabilization of the charges in polar solvents. In the beginning of the 1980s we reported that aromatic diamines with low oxidation potentials such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD)[2–4] and 2,7-bis(*N*,*N*-dimethylamino)tetrahydropyrene (BDATP)[5,6] in the highly polar solvents can eject an electron from their fluorescent state. The long-lived ion pair produced in this process plays an important role as a precursor of the free ions.

The ionization energy of TMPD is about 54000 $\mathrm{cm^{-1}}$ in vacuum[7] and ~41000 $\mathrm{cm^{-1}}$ in non-polar solvents,[8] while the lowest excited singlet state is located about 28000 $\mathrm{cm^{-1}}$ above the ground state. Therefore, a quite large stabilization of charges brought by the polar solvation is necessary to eject an electron from the fluorescent state. Since the S_1 states of the diamines do not have large dipole moments, the appearance of sites that are formed by the fluctuation of the solvent molecules and that can significantly stabilize the charges plays an important role in the ionization process.[9] The large stabilization of the charges may require correlated motions of the solvent molecules extending over a wide region around the solute molecule, which makes the ionization a slow process in the nanosecond time scale. This kind of solvent dynamics should be important for the elucidation of the various kinds of reaction mechanisms in the solution phase.

Among the various polar solvents, 2-propanol has been chosen for the investigation of the photoionization of TMPD. Many different techniques, including the transient absorption,[3,4] photoconductivity,[3,10] and time resolved EPR[11,12] measurements have been used. The observed phenomena seem to strongly depend on the experimental techniques and the character of the excitation light source. By using picosecond transient absorption measurements, we can observe the ionization from the S_1 state of the amine,[3–6] as well as the two-photon ionization in the singlet channel, while the two-photon ionization via the T_1 state of TMPD is reported to be observed by the time resolved EPR study.[12] Addition of a small amount of naphthalene, which acts as a triplet quencher, to the TMPD in 2-propanol system does not affect the ionization yield, in spite of the significant shortening of the $T_n \leftarrow T_1$ absorption and a formation of the triplet naphthalene.[3] Therefore, electron ejection from the T_1 state of TMPD can be neglected.

By using photoconductivity measurement techniques, we found that the lifetime of the ion pair of TMPD in 2-propanol was as long as 2.6 μs.[3] On the other hand, Tanimoto et al. investigated the external magnetic field effect of the photoconductivity and reported a shorter lifetime of about 700 ns.[10] They suggested that the different excitation wavelength can be a reason for the poor reproducibility. Not only the excitation wavelength but the duration of the excitation laser pulse was different for these investigations; as Avdievich et al. pointed out,[12] the experimental conditions affect the photoionization mechanism. In order to find the reason for this poor reproducibility, we measured the photoionization of *N*,*N*-diethyl-*p*-phenylenediamine (DEPD) in various polar solvents. The oxidation potential of *N*,*N*-dimethyl-*p*-phenylenediamine, of which the structure is similar to DEPD, is known to be 0.25 V,[13] therefore, we can expect that the oxidation potential of DEPD will also be slightly higher than that of TMPD.

In this paper, we report the results of the picosecond transient absorption and the nanosecond photoconductivity measurements of DEPD and TMPD in various polar solvents. The electron ejection occurred from the S_1 state of the diamine and the long-lived ion pair was formed in nitriles and normal alcohols, in 2-propanol, however monophotonic ionization was not observed. In addition to the ionization from the fluorescent state, the biphotonic ionization was observed in alcohols with the

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248-nm excitation and in nitriles with the excitation at 351 and 248 nm. When one used the nanosecond laser pulse as an excitation light source, the 248-nm excitation gave a much higher efficiency of the biphotonic ionization than the 351-nm excitation in alcoholic solvents under our experimental conditions. The observed strong dependence of the ionization mechanism on the excitation wavelength and the excitation intensity can be a reason for the poor reproducibility of the lifetime of the ion pair of TMPD in 2-propanol.

Experimental

Picosecond transient absorption spectra were measured by using the mode-locked Nd^{3+}:YAG laser (Ekspla PL2143) photolysis system with the double beam detection configuration. The laser was operated at 10 Hz and the sample was excited with third harmonics (355 nm, ~3 mJ/pulse) of the laser. The transient absorption spectrum between 390 and 960 nm was measured by using picosecond white light generated in H_2O/D_2O mixture. The probe beams before and after passing through the sample cell were introduced into a pair of glass fibers connected to the monochromators equipped with the CCD detectors (Ocean Optics SD2000). The second-order diffraction was eliminated by placing a glass filter in front of the CCD detector. The output signals were transferred to the microcomputer. Typically, 30 shots of the signals were averaged and then the transient absorption spectrum was calculated. LabView (National Instruments) was used for the acquisition and processing of the data. The time resolution of the system was about 25 ps.

The photoconductivity was excited with an excimer laser (Lambda Physik Compex 102; XeF for 351 nm and KrF for 248 nm), of which the pulse width was about 20 ns. The bias of 45 V cm^{-1} was applied across a pair of platinum plates in the quartz cell. The signal was fed to a wide band amplifier (Hewlett-Packard 8447D) and was recorded on a digital oscilloscope (Tektronix TDS2024).

DEPD was obtained from its sulfate (Wako GR-grade) by dissolving in water and precipitating out the free amines with addition of ammonia. The precipitate was purified by sublimation in vacuo; the samples under N_2 atmosphere were kept in a freezer. The ∞-pure grade of hexane, acetonitrile, methanol, ethanol, 1-propanol, and 2-propanol obtained from Wako Chemical were used without further purification. Propiononitrile and butyronitrile were purified by fractional distillation after refluxing with calcium hydride.

The concentration of the samples for the transient absorption measurements was adjusted to give an absorbance of ~2 at 355 nm in the 1-cm optical path length cell. The absorbance of the samples used for the photoconductivity measurements was adjusted to ~1 at the excitation wavelength. The samples were deaerated by bubbling with pure nitrogen gas prior to the measurements. All the measurements were performed at room temperature (23 °C).

Results and Discussion

Figure 1 demonstrates the picosecond time resolved absorption spectra of DEPD in acetonitrile. The spectrum observed at the delay time of 5 ns can be due to the cation band and a small amount of the $T_n \leftarrow T_1$ absorption of DEPD. The cation radical of DEPD generally known as Wurster's red has a spectrum with the maxima around 513 and 557 nm. Although the spectrum of Wurster's red is shifted to the blue about 1690 cm^{-1} compared with that of Wurster's blue, the radical cation of TMPD, their spectral features are similar to each other. The $T_n \leftarrow T_1$ absorption spectrum of DEPD has a rather similar spectrum to that of the radical cation. Such similarities are also known for TMPD.[14] At short delay times, the spectrum with the maxima around 610 and 656 nm was observed. Because of an agreement between the decay time of the transient absorbance measured at 656 nm and the fluorescence lifetime (1.2 and 4.8 ns in acetonitrile and hexane, respectively), the band was assigned to the $S_n \leftarrow S_1$ transition of DEPD.

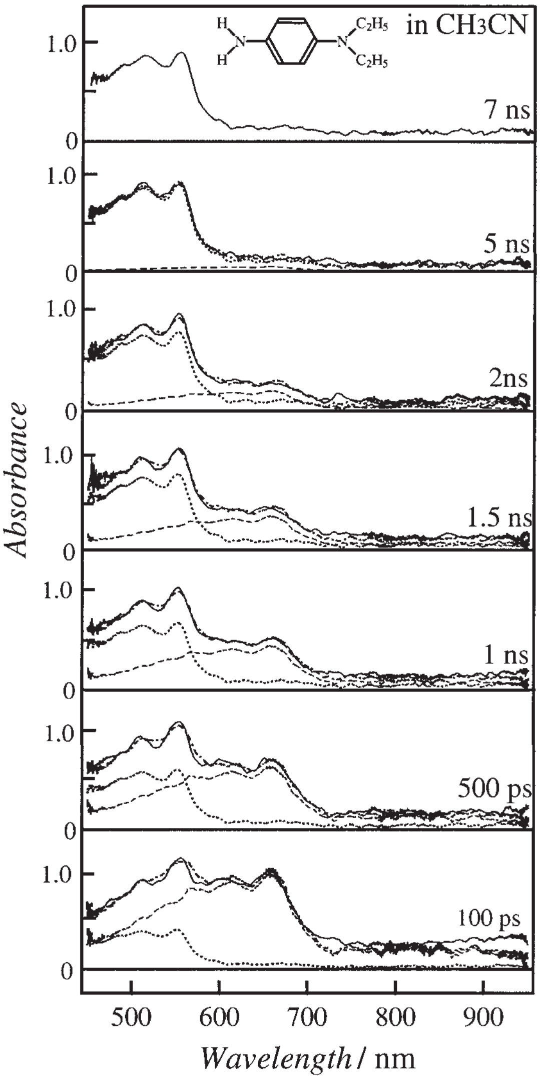

Fig. 1. Picosecond transient absorption spectra of DEPD in acetonitrile excited at 351 nm. The contributions of the cation and $S_n \leftarrow S_1$ bands evaluated with the spectral decomposition are shown by the dotted and broken lines, respectively, and the dash–dot lines are their sum. The delay times after the laser pulse excitation are indicated in the figure.

Because the cation band and the $S_n \leftarrow S_1$ absorption of DEPD were overlapped, we decomposed the measured spectra into their components. The spectrum measured in acetonitrile at 7 ns after the excitation was used for the reference spectrum of the cation radical. The $S_n \leftarrow S_1$ absorption spectrum showed a solvent effect; thus, after applying a certain amount

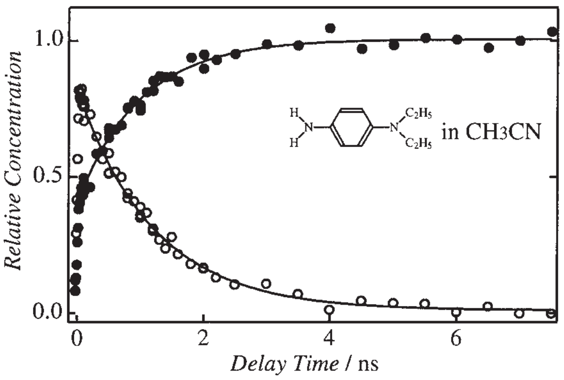

Fig. 2. Time dependence of the relative concentrations of the S_1 state (open circles) and the radical cation (closed circles) of DEPD in acetonitrile. The solid lines show the results of the fitting.

of the shift, the spectrum measured in hexane at the delay time of 100 ps was used as the reference of the $S_n \leftarrow S_1$ band. The shifts to the red were 17 and 28 nm in acetonitrile and in alcohols, respectively. The spectra of the components and their sums are also shown in Fig. 1. The relative concentrations of the components against the delay times after the laser pulse excitation are plotted in Fig. 2. Since the time constants for the decay of the S_1 state and the formation of the cation radical were found to be 1.2 and 1.0 ns, respectively, which showed an agreement within the experimental error and were about 4 times shorter than the fluorescence lifetime in hexane. Therefore we can conclude that the ionization occurs from the fluorescence state of DEPD in acetonitrile.

In addition to the rise of 1.0 ns, the instrumentally limited rapid formation of the cation radical was found. Because the ratio of the transient absorbance of the cation band and the $S_n \leftarrow S_1$ absorption at the origin of the delay time decreased with decreasing excitation intensity, the rapid rise was due to the multiphoton (probably two-photon) ionization. Under our experimental conditions, the multiphoton ionization in methanol had a larger contribution than that in the acetonitrile solution. In methanol, ethanol, and 1-propanol, both the monophotonic and the multiphotonic ionizations were observed; the relative contribution of the multiphoton process increased with decreasing dielectric constant of the solvent. Although the dielectric constants of 1- and 2-propanols are similar, the monophotonic ionization was not observed in 2-propanol. In alcohols, the absorption band ascribed to the solvated electron can be observed in the long wavelength region, where the cation radical and the S_1 state of DEPD do not have large extinction coefficients. The lifetimes of the S_1 state were estimated to be 2.5, 4.7, and 4.3 ns in methanol, ethanol, and 1-propanol, respectively. In acetonitrile the lifetime of the S_1 state of DEPD was similar to that of TMPD, while in alcohols DEPD had the shorter S_1 state lifetimes.

Time profiles of the photoconductivity of DEPD in various alcohols excited at 351 and 248 nm are displayed in Fig. 3. In methanol, the rise of the photoconductivity was essentially limited by the instrumental response time and little decay was observed in the time region of hundreds of nanoseconds. Although the excitation wavelength did not affect the time profile in this solvent, a significant excitation wavelength effect was observed in other alcohols.

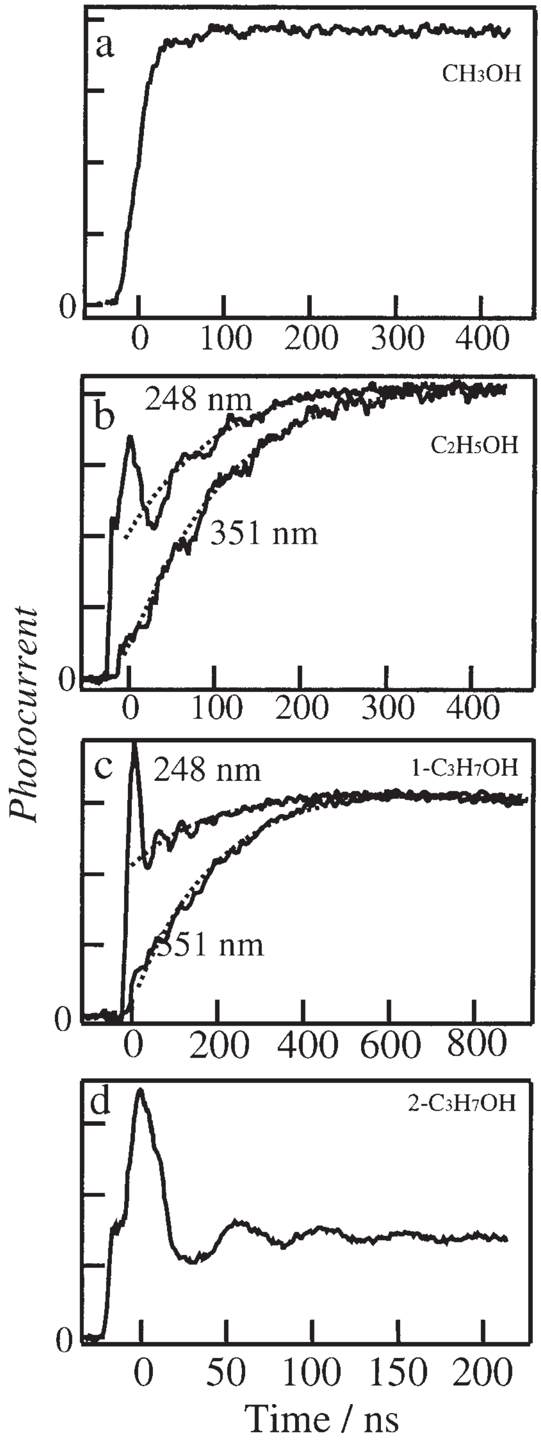

Fig. 3. Time dependence of the transient photoconductivity of DEPD in alcohols excited with the 20-ns laser pulse. The dotted lines in b and c are the results of the fitting. The solvents and the excitation wavelength are indicated in the figure.

As shown by the dotted lines in Figs. 3b and 3c, the rise curve of the photoconductivity in ethanol and 1-propanol observed with the 351-nm excitation was well reproduced by a double exponential function. One component was due to a rise and the other was a decay. Although the decay of the photoconductivity might not be exponential, the time scale of the decay was much longer than that of the rise. Thus, the details of the decay did not give a significant influence with the evaluation of the rise time. The rise times so obtained were about 100 and 220 ns in ethanol and 1-propanol, respectively; these were much longer than the rise times of the cation radical obtained from the transient absorption measurements. Therefore the initially formed cation radical is a part of the ion pair that cannot give photoconductivity. Similar mechanisms were reported for various diamines in polar solvents.[2–6,15]

On the other hand, the time profile observed with 248-nm excitation seems to be much more complicated. A spike, of which the width was essentially limited by the instrumental response time, was followed by a slow rise. Ignoring the spike, we analyzed the time dependence of the photoconductivity in the delay times of >40 ns and the time constants of the slowly rising component were determined to be 110 and 200 ns in ethanol and 1-propanol, respectively; such values were very similar to the rise times observed with the 351-nm excitation. Extrapolating the fitting curve to the origin of the delay time, we estimated the contributions of the rapidly and slowly rising components. In alcohols the ionization yield showed a strong dependence on the dielectric constant of the solvent. The intensity of the photoconductivity observed in methanol was almost one order of magnitude larger than the intensities in ethanol and 1-propanol.

Since both the monophotonic and multiphotonic processes are important mechanism for the ionization of DEPD in polar solvents, we performed the excitation intensity dependence measurements of the photoconductivity. In case of the 351-nm excitation, only with very high excitation intensities of $>10^{11}$ W m^{-2}, a small amount of the rapidly rising component was observed in ethanol and 1-propanol. The slope of the logarithmic plot of the slowly rising component in ethanol against the logarithm of the excitation intensity was found to be 0.97. Therefore under our experimental conditions of the nanosecond laser pulse excitation, monophotonic process was dominant with the 351-nm excitation while the multiphoton process, which gave the rapid rise of the photoconductivity, can be observed only with the very high excitation intensity.

The time profiles of the photoconductivity in ethanol with the 248-nm excitation at several excitation intensities are shown in Fig. 4. The contributions of the spike and the rapidly rising component decreased with decreasing excitation intensity. Figure 5 displays the excitation intensity dependence of the rapidly and slowly rising components that are evaluated from the fitting in the delay times of >40 ns. The slopes of the logarithmic plot were found to be 2.1 and 0.96 for the rapidly and slowly rising components, respectively. The results indicate that the rapidly rising component is due to the biphotonic ionization, while the slowly rising component is due to the monophotonic ionization. The spike was also due to the biphotonic ionization.

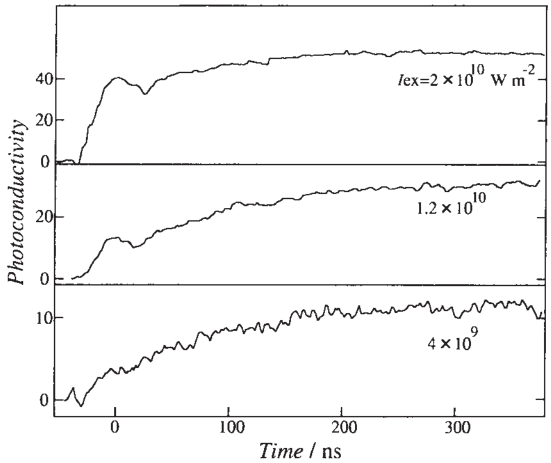

Fig. 4. Excitation intensity dependence of the time profiles of the photoconductivity of DEPD in ethanol. The relative intensity of the excitation laser pulse are indicated in the figure.

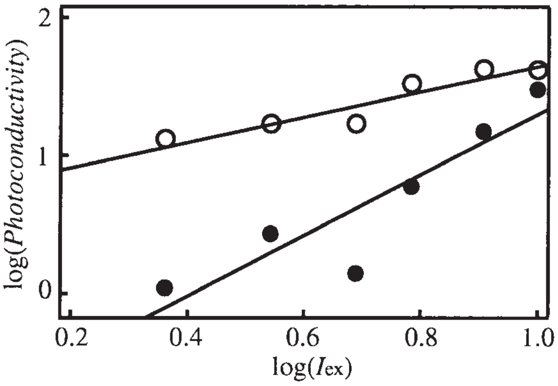

Fig. 5. Logarithmic plots of the rapidly and slowly rising components of the transient photoconductivity of DEPD in ethanol.

In spite of the similar dielectric constants of 1- and 2-propanols, as shown in Fig. 3c and 3d, quite different time profiles of the photoconductivity were observed in these solvents. In 2-propanol, the spike was followed by the decay and no slow rise was observed. The excitation intensity dependence suggests that the signal in 2-propanol was due to the biphotonic ionization. The results of not observing the monophotonic ionization in 2-propanol were consistent with the results of the transient absorption measurements. The band maximum of the solvated electron in 2-propanol is around 644 nm and is longer than that in 1-propanol;[16] the difference can be an indication of the small solvation energy of the electron in 2-propanol. The small stabilization energy of the charges created in 2-propanol may affect the photoionization mechanism of DEPD.

The observation of the spike with the instrumentally limited time width indicates rapid recombination or disappearance of the polarization that occurs within the duration of the excitation laser pulse. Such a rapid decay of the photoconductivity may be due to the geminate ion pair. The polarization of the geminate ion pair under the influence of the external electric field was suggested to give a transient dc-photoconductivity.[17]

Although we cannot separate the contributions of the monophotonic and biphotonic ionizations in methanol because of the short lifetimes of the ion pair states, not observing the spike in methanol means that the escape probability of the geminate pair is large in this solvent. Since no spike but the slow rise was observed in ethanol and 1-propanol with the 351-nm excitation, the long-lived ion pair had a smaller distance between the ions compared with the geminate ion pair and could not give the large conductivity signal. The long lifetime of the ion pair suggests that not only the Coulombic interaction but also the exciplex-like specific interaction that prevents the recombination of the ions is important.

The excitation wavelength effect was not so significant in nitriles as in ethanol and 1-propanol. The biphotonic ionization with the 351-nm excitation, which was a minor process in ethanol and 1-propanol, was clearly observed in propiononitrile and butyronitrile. As shown in Fig. 6, the rise of the photoconductivity in acetonitrile was rapid. The long lived component and a small portion of the decaying component with a time constant of about 70 ns, which was due to the formation of the dimer anion of acetonitrile,[5] were observed. The spike was not observed in this solvent. On the other hand, in propiononitrile and butyronitrile, the instrumentally limited rapid decay was followed by the decay with a time constant of about 500 ns and the slow decay component in the microsecond time scale.

Since the relative intensity of the spike in nitriles was smaller than that in ethanol and 1-propanol, in nitriles the escape probability of the geminate pair was larger than in alcohols. A strong excitation intensity dependence was observed in propiononitrile and butyronitrile with the 351- and 248-nm excitations. The slowly rising component in these solvents was observed only by the excitation with the very weak laser pulse. The rise times of the slowly rising components were determined to be about 2.5 and 3.7 μs in propiononitrile and butyronitrile, respectively. Although we cannot analyze the time dependence of the photoconductivity in nitriles with very high excitation intensities in a reliable manner, the time constants of the slow rise appeared to be independent of the excitation intensity. Judging from the slopes of the logarithmic plots of the rapidly and slowly rising components, we can conclude that the rapidly and slowly rising components were due to the monophotonic and the biphotonic ionization, respectively.

As shown in Fig. 6d, the time profile of the photoconductivity of TMPD in 2-propanol excited at 248 nm clearly showed the spike and the slow rise in microsecond time region. The time constant of the slow rise was obtained to be about 3.0 μs, which was in an agreement with the reported value with the picosecond 347-nm excitation,[3] where the two-photon ionization was negligibly weak. Although we did not excite the sample with the 308 nm laser pulse and we have no idea about the relative contribution of the biphotonic ionization at this excitation wavelength, our results suggest that special care must be taken to distinguish the contributions of the monophotonic and biphotonic ionization for the measurements of the lifetime of the ion pair.

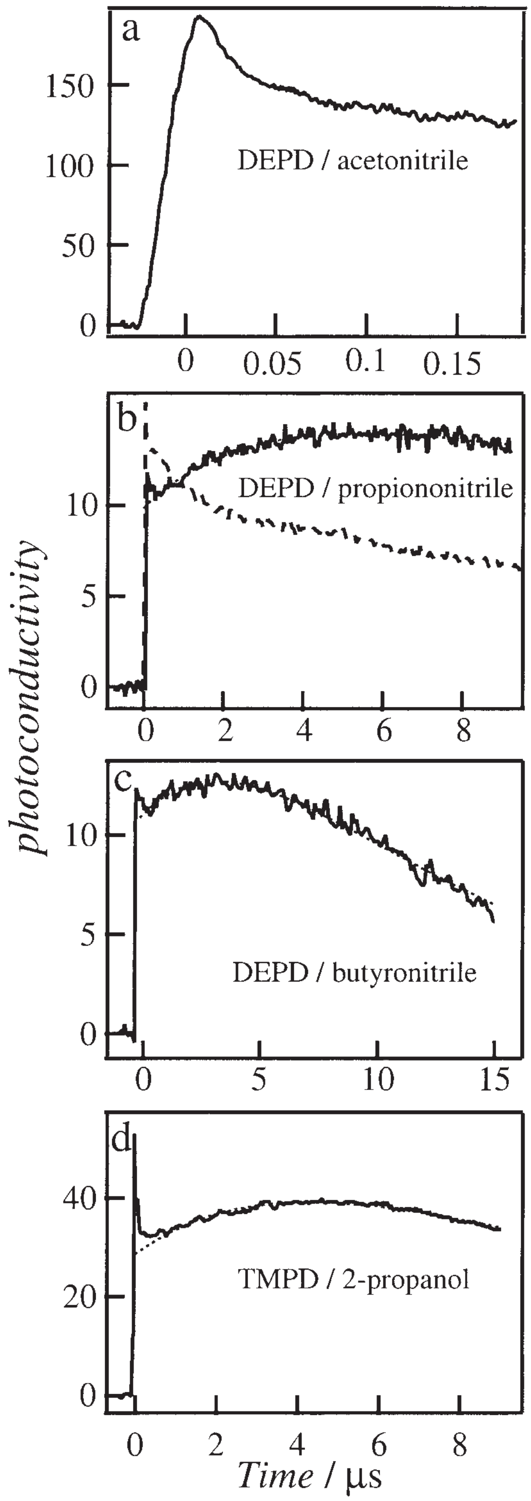

Fig. 6. Time dependence of the transient photoconductivity of DEPD in nitriles (a)–(c) and TMPD in 2-propanol (d). Solvents are indicated in the figure.

Conclusion

We investigated the photoionization of DEPD in various polar solvents. The strong excitation wavelength and excitation intensity dependence was observed. With the 351-nm excitation of the alcoholic solutions under our experimental conditions of the nanosecond measurements, the yield of the biphotonic ionization is low. On the other hand, with the 248-nm excitation, in addition to the slowly rising component of the photoconductivity in the hundreds of nanoseconds, which is due to the dissociation of the monophotonically formed ion pair, the spike signal, which is due to the biphotonic ionization was clearly observed. In nitriles, the contribution of the two-photon ionization seems to be large with both the excitation wavelengths.

The spike was ascribed to an induction signal due to the formation of the geminate pair. In contrast to the geminate pair, the long-lived ion pair could not give the dc-conductivity, which implies that the induced polarization and therefore the dipole moment of the long-lived ion pair are much smaller than those of the geminate pair. In spite of the small distance between the ions with the opposite charges, the lifetime of the monophotonically produced ion pair is long, which indicates that the exciplex-like specific interaction plays an important role in preventing the recombination for hundreds of nanoseconds or more.

References

1 H. Labhart and W. Heinzelman, "Organic Molecular Photophysics," ed by J. B. Birks, Wiley-Interscience, London (1973), pp. 457–487, and references therein.

2 Y. Hirata and N. Mataga, *J. Phys. Chem.*, **87**, 1680 (1983).

3 Y. Hirata and N. Mataga, *J. Phys. Chem.*, **87**, 3190 (1983).

4 Y. Hirata and N. Mataga, *J. Phys. Chem.*, **89**, 4031 (1985).

5 Y. Hirata, N. Mataga, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, **86**, 1508 (1982).

6 Y. Hirata, N. Mataga, Y. Sakata, and S. Misumi, *J. Phys. Chem.*, **87**, 1493 (1983).

7 S. L. Murov, I. Carmichael, and G. L. Hug, "Handbook of Photochemistry, 2nd ed," Marcel Dekker, New York (1993).

8 J. Bullot, P. Cordier, and M. Gauthier, *J. Phys. Chem.*, **84**, 3516 (1980).

9 Y. Hirata, Y. Tanaka, and N. Mataga, *Chem. Phys. Lett.*, **1**, 36 (1992).

10 Y. Tanimoto, T. Watanabe, R. Nakagaki, M. Hiramatsu, and S. Nagakura, *Chem. Phys. Lett.*, **116**, 341 (1985).

11 H. Murai and K. Kuwata, *Chem. Phys. Lett.*, **164**, 567 (1989).

12 N. I. Avdievich, A. S. Jeevarajan, and M. D. E. Forbes, *J. Phys. Chem.*, **100**, 5334 (1996).

13 F. B. Kaufman, *J. Am. Chem. Soc.*, **98**, 5339 (1976).

14 H. Tsubomura, N. Yamamoto, K. Kimura, J. Sato, H. Yamada, M. Kato, G. Yamaguchi, and Y. Nakato, *Bull. Chem. Soc. Jpn.*, **38**, 2021 (1965).

15 Y. Hirata, Y. Mori, and N. Mataga, *Chem. Phys. Lett.*, **169**, 427 (1990).

16 L. Kevan, "Advances in Radiation Chemistry," ed by M. Burton and L. Magee, Wiley, New York (1974), Vol. 4.

17 A. V. Tolmachev and B. S. Yakovlev, *Chem. Phys. Lett.*, **113**, 99 (1985).