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Picosecond Laser Photolysis Studies on the Photoreduction of Excited Benzophenone by Diphenylamine in Solutions

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The mechanism of photoreduction of benzophenone (BP) by diphenylamine (DPA) in isooctane as well as acetonitrile and other polar solvents has been investigated by means of picosecond laser photolysis and time-resolved transient absorption spectral measurements. The results of measurements have demonstrated clearly that the hydrogen abstraction and charge transfer (CT) or ion pair (IP) state formation by electron transfer are competing at encounter between triplet benzophenone ($^3BP^*$) and DPA both in nonpolar and polar solvent, and the CT or IP state relaxed with respect to the donor acceptor configurations and solvation does not contribute to the ketyl radical formation. It has been concluded that the very short-lived CT state at encounter between $^3BP^*$ and DPA plays a crucial role in the hydrogen abstraction reaction, i.e. the mutual orientation of $^3BP^*$ and DPA in this very short-lived CT state at encounter will determine the successive process, the formation of the ketyl radical or relaxed CT or IP state.

The photoinduced electron transfer (ET) and subsequent dynamic processes are the most fundamental and important problems in photochemical primary processes in condensed phase.[1–4] The elucidation of the factors controlling the behaviors of the ET state in the photochemical reaction is of crucial importance.

The photoreduction of excited triplet benzophenone ($^3BP^*$) in solution has been extensively studied and a number of results have been reported.[5–25] Especially, much attention has been paid to the hydrogen abstraction of $^3BP^*$ from aliphatic as well as aromatic amines. The reaction yield of the hydrogen abstraction from the amine is usually very high and the reaction rate is rather close to that of the diffusion-controlled reaction. This efficient and rapid reduction process has been considered to be due to the participation of the charge-transfer (CT) interaction between $^3BP^*$ and amines in the reaction, since the rate of the hydrogen abstraction of $^3BP^*$ from 2-propanol is about 10^3 times smaller than those from amines. On the basis of such results, Cohen et al. proposed[7] the reaction mechanism of the hydrogen abstraction of $^3BP^*$ from amines, which assumed the CT complex or ion-pair formation followed by proton transfer;

$$^3BP^* + AH \xrightarrow[\text{transfer}]{\text{electron}} {}^3(BP^- \cdots AH^+) \xrightarrow[\text{transfer}]{\text{proton}} (BPH + A)$$

where AH is an amine and BPH is a ketyl radical.

Arimitsu et al. investigated[8,9] the quenching of $^3BP^*$ by various kinds of amines by observing the transient absorption with a nanosecond laser photolysis method. On the basis of the observed dependence of the yield of the BPH radical on the oxidation potential of the amine, they concluded that the BPH formation was in competition with the production of the solvated free ion. In other word, it was considered that the CT or the ion-pair (IP) state prior to the solvation was the species undergoing the proton transfer leading to the BPH formation and that this proton transfer in the IP state competed with the solvation leading to the ionic dissociation. On the other hands, Peters and co-workers[10–13] investigated the picosecond dynamics of the excited benzophenone and amine systems. On the basis of the observed time-dependent spectral shift of the benzophenone anion radical, they concluded that the structural change of the solvent separated IP formed by the ET between $^3BP^*$ and amine, to the contact IP was the key process for the proton transfer to take place.

Summarizing the above extensive studies on the photoreduction of the excited benzophenone at the present stage of the investigation, the dependence of the proton-transfer process on the structure of the intermediate CT or IP state seems to be an important point for the elucidation of the reaction mechanism. In this respect, we have conducted detailed picosecond and femtosecond laser photolysis studies on the reaction of excited benzophenone with various aromatic and aliphatic amines in nonpolar as well as polar solvents. Owing to these investigations with more direct and quantitative time-resolved spectral measurements, the reaction mechanisms have now become much clearer.

In the present paper, results of the picosecond laser photolysis studies on the reactions of the excited benzophenone with diphenylamine in several solvents of different polarity will be reported. The relation between the CT or IP state formation and the hydrogen abstraction process will be discussed and the mechanisms of the hydrogen abstraction will be reconsidered including the photochemistry of the excited singlet state benzophenone.

Experimental

Laser Photolysis Apparatus and Purification of Samples. A microcomputer-controlled picosecond laser photolysis system with a repetitive Nd^{3+}:YAG laser was used to measure transient absorption spectra in the picosecond and a few nanoseconds time region. The details of this system have been reported elsewhere.[16,17] For the measurement of the time profiles of the transient absorbance in a few nanoseconds to a few hundreds nanoseconds time region, a kinetic spectroscopy system[18] with a pulsed Xe lamp as a monitoring light, a photodetector, and a fast storage oscilloscope, was used. In both of these measurements, samples were excited by a single 355 nm pulse with 22 ps fwhm. For the transient absorption spectral measurements in longer time region, an excimer laser photolysis system with 351 nm excitation pulse was used.[19]

Benzophenone (Wako, Special Guarantee) was purified by repeated recrystallization from ethanol and sublimation. Diphenylamine (Wako, Special Guarantee) was purified by repeated recrystallization from isooctane. Isooctane (2,2,4-trimethylpentane), acetonitrile, 2-propanol, and ethyl acetate (Merck Uvasol) for the laser photolysis measurements were used without further purification. Samples were deaerated by N_2 purging. All the measurements were performed at room temperature (22±3 °C).

Extinction Coefficient Used for the Estimation of the Reaction Yield. The extinction coefficient of benzophenone in its triplet state ($^3BP^*$) at 525 nm was reported to be 6500 $M^{-1}\,cm^{-1}$.[20] On the other hand, that for the BPH radical at 545 nm was reported to be 5100 $M^{-1}\,cm^{-1}$.[5] Recently, we have measured the decay process of $^3BP^*$ in 2-methyltetrahydrofuran (MTHF) by means of the picosecond laser photolysis method,[21] the result of which shows that the decay time of $^3BP^*$ in MTHF is 4.1 ns and a fairly large amount of BPH is observed after the decay of $^3BP^*$. By using those extinction coefficients for $^3BP^*$[20] and BPH,[5] the quantum yield of the BPH produced from the initial $^3BP^*$ was obtained to be 0.80. On the other hand, if we assume that the deactivation of $^3BP^*$ is exclusively due to the BPH formation on the basis of the fact that the 4.1 ns decay time in MTHF is extraordinarily shorter than the lifetime of $^3BP^*$ in other solvents, the extinction coefficient at 545 nm is obtained to be 65—70% of that of $^3BP^*$ at 525 nm. Namely, the extinction coefficient of BPH at 545 nm may be 4200—4600 $M^{-1}\,cm^{-1}$, if we set the extinction coefficient of $^3BP^*$ at 525 nm to be 6500 $M^{-1}\,cm^{-1}$. In this study, we have used the extinction coefficient of 4600 $M^{-1}\,cm^{-1}$ for BPH. Moreover, we have assumed that these extinction coefficients for $^3BP^*$ and BPH are independent of the nature of the solvent, for the spectral band shapes and the absorption maxima are almost constant irrespective of the solvent used.

On the other hand, the extinction coefficient of BP^- was reported to be ca. 10000 $M^{-1}\,cm^{-1}$ in the vicinity of 800 nm in MTHF.[22] Although the absorption maximum shifted to shorter wavelength at room temperature in other solvents, the validity of this value for BP^- was supported by the following result. When 1,4-diazabicyclo[2.2.2]octane (DABCO) was used as quencher for $^3BP^*$, only the BP^- was produced in the course of quenching without the BPH formation in tens of nanosecond time region in most solvents.[21] The yield of the IP state produced from $^3BP^*$ was obtained to be 0.8—0.9 if was use the extinction coefficient of 10000 $M^{-1}\,cm^{-1}$ at 720 nm for BP^- and that of 6500 $M^{-1}\,cm^{-1}$ at 525 nm for $^3BP^*$ in acetonitrile. Further, the extinction coefficient of DPA^+ at 675 nm in acetonitrile was estimated to be 25000 $M^{-1}\,cm^{-1}$.[23] In nonpolar solvent, the absorption spectrum of DPA^+ was rather broad and the absorption maximum shifted to 695 nm.[24] The half width of this absorption band around 695 nm was ca. 3000 cm^{-1} in cyclohexane.[24] On the other hand, the half width of this absorption band in acetonitrile, where the absorption maximum located at 675 nm, was 1100 cm^{-1}. Hence, it is plausible that the extinction coefficient of DPA^+ in isooctane is smaller than that in acetonitrile at the absorption maximum. In order to obtain the extinction coefficient of DPA^+ in isooctane, we have assumed that the extinction coefficient is inversely proportional to the half width of the absorption band. Then, the extinction coefficient of DPA^+ in isooctane was estimated to be 9000 $M^{-1}\,cm^{-1}$ at 695 nm. In ethyl acetate and in 2-propanol, the extinction coefficient of DPA^+ was set to 25000 cm^{-1}, since the absorption maximum was around at 675—680 nm and spectral band shape in these solvents were close to that in acetonitrile.

In order to obtain the reaction yield of the IP, ($BP^- \cdots DPA^+$), the extinction coefficients of BP^- and DPA^+ should be added. The spectral band shape of BP^- was reported to be solvent-dependent.[23] In 2-propanol, the absorption maximum of BP^- is located in the vicinity of 640 nm, while that in acetonitrile was around 700 nm.[21] In this study, we have obtained the extinction coefficient of BP^- at the absorption maximum of DPA^+ in each solvent from the transient absorption spectrum of IP or CT state of the BP-*N*,*N*-diethylaniline (DEA) system,[21] because DEA^+ and DEA neutral radical show practically no absorption in 600—700 nm region.

Summarizing the above discussions, we use here the following values of the extinction coefficients; 6500 $M^{-1}\,cm^{-1}$ at 525 nm for $^3BP^*$, 4600 $M^{-1}\,cm^{-1}$ at 545 nm for BPH, 18000 $M^{-1}\,cm^{-1}$ at 700 nm for the contact IP state, $^3(BP^- \cdots DPA^+)$, in isooctane, and 32000 $M^{-1}\,cm^{-1}$ at 675 nm for the IP state, $^3(BP^- \cdots DPA^+)$, in 2-propanol, and 31500 $M^{-1}\,cm^{-1}$ for the IP state, in acetonitrile and in ethyl acetate.

Results and Discussion

Photoreduction Process of BP-DPA System in Isooctane. Figure 1 shows the time-resolved transient absorption spectra of BP–DPA (0.13 M, 1 M=1 mol dm^{-3}) system in isooctane solution excited with a picosecond 355 nm laser pulse. A transient absorption spectrum with an absorption maximum at 525 nm observed at 40 ps after the excitation can be assigned to the $T_n \leftarrow T_1$ transition of BP.[20] With increase of the delay time, one can observe the increase of the absorbance at 545 nm, 700 nm, and 750 nm. On the basis of the wavelengths of the absorption maxima and the spectral band shapes, these absorption bands can be assigned to each species as follows: the 545 nm band to BPH,[5,25] the 700 nm band to the contact IP, $^3(BP^- \cdots DPA^+)$,[22,23] and the 750 nm band to the diphenyl nitrogen radical (DPN),[26] respectively. The transient absorption spectra in Fig. 1 indicate that the spectrum at the shortest delay time which is mainly due to $^3BP^*$ gradually evolves in the course of time into those of BPH and DPN formed by the hydrogen abstraction reaction, and of $^3(BP^- \cdots DPA^+)$ produced through the electron-transfer reaction.

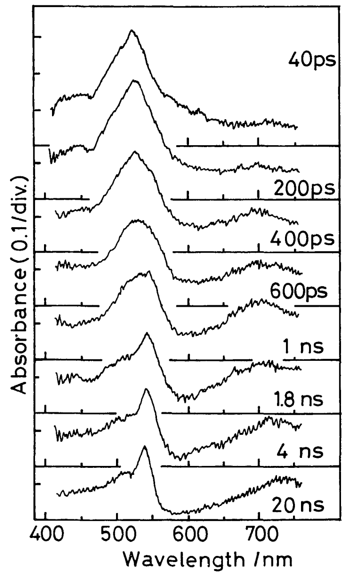

Fig. 1. Transient absorption spectra of benzophenone (BP) (0.01 M)-diphenylamine (DPA) (0.13 M) in isooctane, excited with a picosecond 355 nm laser pulse.

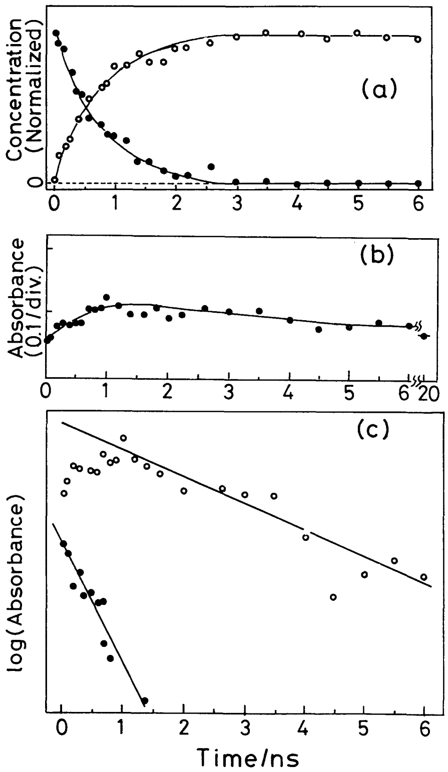

Fig. 2. (a) Time profiles of ^{3}BP* (●) and BPH radical (○) of BP (0.01 M)-DPA (0.13 M) in isooctane, excited with a picosecond 355 nm laser pulse (see text). (b) Time profiles of the transient absorbance at 700 nm of BP (0.01 M)-DPA (0.13 M) in isooctane, excited with a picosecond 355 nm laser pulse. (c) time profiles of ^{3}(BP$^-$···DPA$^+$) (○) of BP (0.01 M)-DPA (0.13 M) in isooctane, excited with a picosecond laser pulse (●: rise component) (see text).

Figure 2(a) shows the time profiles of ^{3}BP* and BPH, which were obtained by the analysis of the observed spectra in the 400—560 nm region into the two components of ^{3}BP* and BPH. In this wavelength region, the spectra are almost exclusively composed of the bands due to these two species. The decay time of ^{3}BP* (610 ps) coincides with the rise time of BPH. The bimolecular rate constant of the quenching reaction between ^{3}BP* and DPA was obtained to be 1.3×10^{10} M^{-1} s^{-1}, which was equal to the diffusion-controlled rate constant in isooctane (1.3×10^{10} M^{-1} s^{-1} at 25 °C).

On the other hand, dependence of the absorbance at the maximum of the ^{3}(BP$^-$···DPA$^+$) band (700 nm) is exhibited in Fig. 2(b). The absorbance increases until the delay times of 1—2 ns and decreases. Since the absorbance due to DPN radical extends to the 700 nm region, the contribution of this neutral radical was subtracted from the absorbance in Fig. 2(b) in such a way that the time profile of DPN radical is identical with that of BPH. The time profile of the absorbance due to ^{3}(BP$^-$···DPA$^+$) at 700 nm obtained in this way is shown in Fig. 2(c), of which the rise and decay times were 600 ps and ca. 3 ns, respectively. The rise time of ^{3}(BP$^-$···DPA$^+$) (600 ps) was identical with that of the decay of ^{3}BP* and with rise time of BPH within the experimental error, which means that the formation process of ^{3}(BP$^-$···DPA$^+$) is in competition with that of BPH radical. Furthermore, the decay of ^{3}(BP$^-$···DPA$^+$), of which the time constant is ca. 3 ns, is not accompanied by the production of BPH, as shown in Fig. 2(b). This figure indicates that almost all BPH formation is completed with the time constant of 610 ps which is identical with that of the decay of ^{3}BP*.

From the above results, it can be concluded that BPH is not produced by the proton transfer in the stable ^{3}(BP$^-$···DPA$^+$) state, but through the direct hydrogen abstraction process. This conclusion is supported also by the estimation of the yields of the BPH and ^{3}(BP$^-$···DPA$^+$) as follows. By using the values of the extinction coefficient given in the Experimental section, the yield of BPH from ^{3}BP* was estimated to be 0.7—0.8 and that of ^{3}(BP$^-$···DPA$^+$) 0.07—0.1. Even if the deactivation of ^{3}(BP$^-$···DPA$^+$) terminates in the BPH formation, this is a minor path. Almost all of BPH was confirmed, within the experimental accuracy, to be formed directly from ^{3}BP*. Summarizing above results, we can conclude the following reaction scheme for the photoreduction of ^{3}BP* by DPA in isooctane.

$$\begin{tikzcd}
{}^3\mathrm{BP}^* + \mathrm{DPA} \arrow[r, "k_{\mathrm{HT}}"] \arrow[d, "k_{\mathrm{ET}}"] & \mathrm{BPH} \cdots \mathrm{DPN} \arrow[r] & \mathrm{BPH} + \mathrm{DPN} \\
{}^3(\mathrm{BP}^- \cdots \mathrm{DPA}^+) & &
\end{tikzcd} \qquad (1)$$

where, $(k_{HT}+k_{ET})$ is the rate constant of the quenching reaction between ^{3}BP* and DPA.

Photoreduction Process of BP—DPA System in Acetonitrile and Other Polar Solvents. Figure 3 shows time-resolved transient absorption spectra of BP-DPA (0.044 M) system in acetonitrile. With increase of the delay time, ^{3}BP*, whose absorption maximum observed at 60 ps lies at 523 nm, decays and a new band at 675 nm which comprises contributions from DPA^{+} and BP^{-}, and that due to BPH at 545 nm appear. Time profiles of concentrations of ^{3}BP*, BPH, and ^{3}(BP^{-}…DPA^{+}) are displayed in Fig. 4, which were obtained by the analysis of the observed spectra into these species on the basis of their individual reference spectra. In this figure, the ordinate represents the concentration of the individual species calculated by using the extinction coefficient given in the Experimental section. In acetonitrile, the extinction coefficient of 31500 M^{-1} cm^{-1} was used for ^{3}(BP^{-}…DPA^{+}) at 675 nm. This value was obtained by the addition of the extinction coefficient of DPA^{+} and that of BP^{-} at 675 nm. From Fig. 4, the decay time of ^{3}BP* was obtained to be 2.85 ns and the rate constant of the quenching reaction between ^{3}BP* and DPA was obtained to be 0.80×10^{10} M^{-1} s^{-1}. Moreover, one can see clearly that the formation process of BPH corresponds very well to the decay process of ^{3}BP*. We have confirmed also that the rise profile of ^{3}(BP^{-}… DPA^{+}) is also in agreement with that of the ^{3}BP* decay. Solid lines in this figure are calculated on the basis of the reaction scheme similar to Eq. 1. From such analysis the reaction yield of BPH from ^{3}BP* was obtained to be 0.76±0.05, and that of ^{3}(BP^{-}…DPA^{+}) from ^{3}BP* 0.16±0.02.

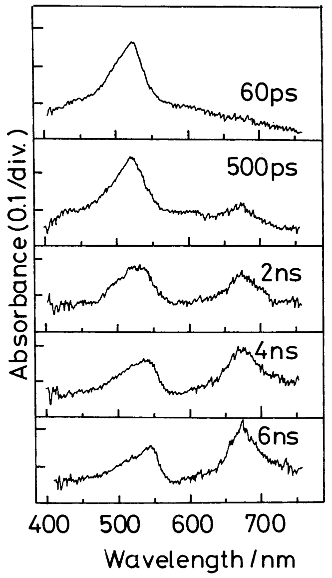

Fig. 3. Transient absorption spectra of BP (0.01 M)-DPA (0.044 M) in acetonitrile, excited with a picosecond 355 nm laser pulse.

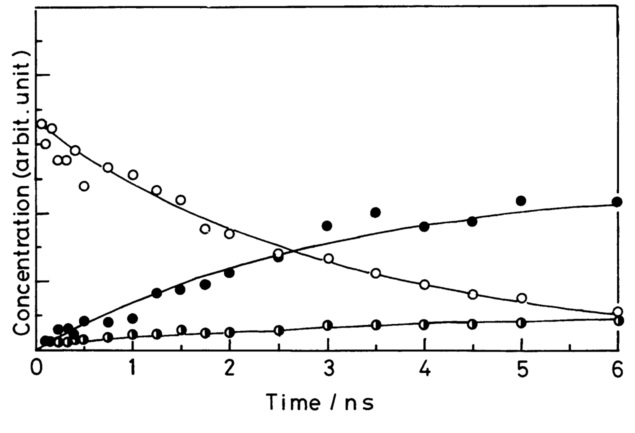

Fig. 4. Time profiles of ^{3}BP* (○), BPH (●), BP^{-} and DPA^{+} (◑) in BP (0.01 M)-DPA (0.044 M) in acetonitrile excited with a picosecond 355 nm laser pulse (see text).

In order to clarify the details of the reaction mechanism, we have photolyzed the solution containing higher concentrations of DPA. In Fig. 5, we show the transient absorption spectra of BP-DPA (0.42 M) system in acetonitrile, where the absorption due to DPA^{+} and BP^{-} was observed immediately after the excitation. The time profiles of the absorbance at 525 nm and 680 nm immediately after the excitation are plotted in Fig. 6, which indicates that the formation of the IP takes place almost simultaneously with the formation of ^{3}BP*. This rapid formation of the IP immediately after excitation is considered to be due to the electron transfer between benzophenone in its excited singlet state (^{1}BP*) and DPA in the vicinity of ^{1}BP*, and also due to the excitation of weak CT complex produced in the ground state. Such a rapid electron-transfer process between BP and amine has

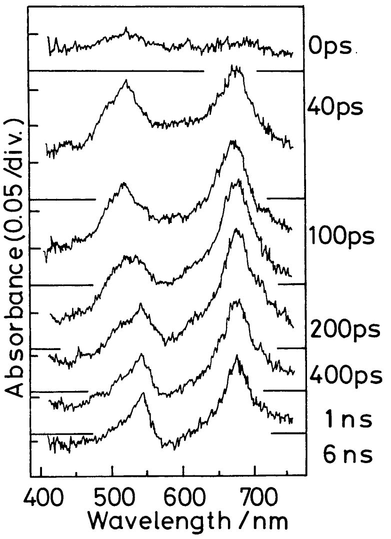

Fig. 5. Transient absorption spectra of BP (0.01 M)-DPA (0.42 M) in acetonitrile, excited with a picosecond 355 nm laser pulse.

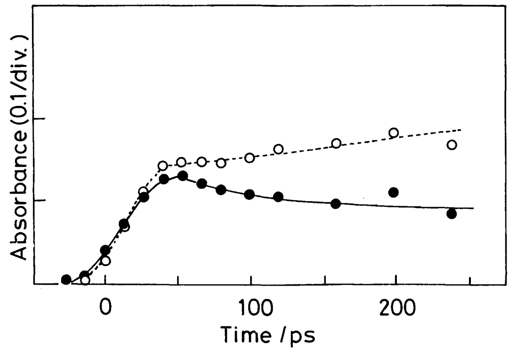

Fig. 6. Time profiles of transient absorbance at 525 nm (^{3}BP*) (●) and 680 nm (BP$^-$···DPA$^+$) (○) of BP (0.01 M)–DPA (0.42 M) in acetonitrile, excited with a picosecond 355 nm laser pulse.

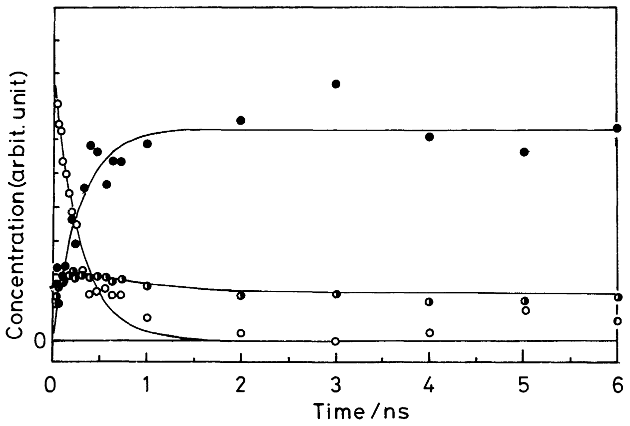

Fig. 7. Time profiles of ^{3}BP (○), BPH (●), BP$^-$ and DPA$^+$ (◑) in BP (0.01 M)–DPA (0.42 M) in acetonitrile excited with a picosecond 355 nm laser pulse (see text).

been recently observed by means of femtosecond laser photolysis[27] and also by means of picosecond laser photolysis.[28]

Time profiles of ^{3}BP*, BPH, and the IP are displayed in Fig. 7, which were obtained by the analysis of the observed spectra into these species on the basis of their individual reference spectra. From this figure, the decay time of ^{3}BP* was obtained to be 290 ps and the quenching rate constant of ^{3}BP* was obtained to be 0.82×10^{10} M^{-1} s^{-1}, which was identical with that obtained in the dilute solution. Moreover, it is clear from Fig. 7 that the rise time of BPH is in a fair agreement with the decay time of ^{3}BP*. On the other hand, the time profile of the IP state is complicated, since the decrease of the IP produced in the excited singlet state and that produced by the excitation of the weak CT complex formed in the ground state overlap the increase of ^{3}(BP$^-$···DPA$^+$) produced through the electron transfer between ^{3}BP* and DPA. In any way, the time profile of the IP state shows a rapid rise due to the ^{1}(BP$^-$···DPA$^+$) formation and decay with the time constant of 590 ps. The solid line for the time profile of the IP is the calculated curve, where the decay time of the ^{1}(BP$^-$···DPA$^+$) state is taken to be 590 ps and the rise time of the ^{3}(BP$^-$···DPA$^+$) state is taken to be identical with the decay time of ^{3}BP*. Moreover, it is assumed that the ionic dissociation from the ^{1}(BP$^-$···DPA$^+$) state is negligible, while ^{3}(BP$^-$···DPA$^+$) terminates almost exclusively in the production of the free ion. In addition, the yield of ^{3}(BP$^-$···DPA$^+$) from ^{3}BP* is taken to be 0.16 which is identical with the yield in the dilute solution in Fig. 4. The calculated curve and the experimental points are in fair agreement with each other. Accordingly, the ionic dissociation yield from ^{1}(BP$^-$···DPA$^+$) is considered to be very small and that of ^{3}(BP$^-$···DPA$^+$) is almost 1.0.

Table 1. Solvent Dependence of the Reaction Yields of ^{3}BP* and DPA

Solvent	Dielectric constant	ϕ_{BPH}	ϕ_{IP}
Isooctane	1.94	0.75	0.07
Ethyl acetate	6.09	0.73	0.12
2-Propanol	17.5	0.72	0.17
Acetonitrile	37.5	0.76	0.16

In Table 1, we summarize the ^{3}IP yield due to the ET reaction and the BPH yield due to the hydrogen abstraction reaction, not only for the acetonitrile solution but also for isooctane, 2-propanol, and ethyl acetate solutions. In the latter two solutions, the direct hydrogen abstraction process competing with the ET reaction was also observed. The yield of the ^{3}IP in solvents less polar than acetonitrile was obtained by considering the decay of the ion pair. For example, in 2-propanol solution, ^{3}IP showed decay with the time constant of 7.5 ns and the yield of the ionic dissociation from the ^{3}IP was about 50%. In Table 1, we give the yields of the ^{3}IP prior to the recombination and the dissociation.

Results in Table 1 show that the yield of BPH is almost independent of the solvent. Though the quenching rate constant of ^{3}BP* by DPA shows solvent dependence, it is rather close to the diffusion-controlled value in those solvents examined here. In addition, the yields of the ^{3}IP state in those solvents are 0.1—0.2. Summarizing above results, it may be concluded that the reaction mechanism between ^{3}BP* and DPA and the yields of the ^{3}IP and the BPH radical are almost independent of the nature of the solvent.

This relation between the yield of BPH and that of ^{3}IP from ^{3}BP* also seems to support the mechanism that the hydrogen abstraction competes with the production of the stable ^{3}IP state. Usually, such ^{3}IP state formation is followed by the recombination and the dissociation into the free ions. Especially, in polar solvent such as acetonitrile, the dissociation process is so effective that its rate constant is usually 0.5—

$2.0\times10^9\ s^{-1}$.[29] Therefore, almost all ionic species observed at a few nanoseconds after the excitation in acetonitrile solution may be the dissociated free ions. In less polar and nonpolar solvent, this dissociation process is not so effective as in acetonitrile, and the recombination process plays a dominant role. In any way, the properties of the ^{3}IP and its decay process may depend upon the nature of the solvent. In spite of such solvent dependence of the behaviors of the ^{3}IP state relaxed with respect to solvation the yields of BPH and the ^{3}IP state is almost independent of the nature of the solvent. This result supports the reaction mechanism that the hydrogen abstraction takes place directly at the encounter between ^{3}BP* and DPA.

The Mechanism of Hydrogen Abstraction Reaction between ^{3}BP* and DPA. The above described reaction mechanism of the hydrogen abstraction (the direct abstraction mechanisms) is different from that proposed by Cohen et al.[7] and seems in conflict with the experimental results presented by Peters and coworkers.[10—13] The hydrogen abstraction mechanisms presented by Cohen et al. was as follows,

$$^3\mathrm{BP} + \mathrm{AH} \longrightarrow {}^3(\mathrm{BP}^- \cdots \mathrm{AH}^+) \longrightarrow (\mathrm{BPH} + \mathrm{A})$$

where proton was transferred between the relaxed ions in the IP state, $^3(\mathrm{BP}^- \cdots \mathrm{H}^+)$. This mechanism was assumed in order to explain the experimental result that the photoreduction of ^{3}BP* by amines leading to BPH formation was very efficient, with rate constants of about 10^3 times larger compared with the case of other hydrogen donors. In view of this result, it is quite plausible that the CT interaction plays an important role in the hydrogen abstraction reaction of ^{3}BP*-amine systems, as suggested by Cohen et al. Their results that the yield of BPH was very high and the quenching rate constant was rather close to the diffusion-controlled one in the ^{3}BP*–DPA system are in a good agreement with our present results. However, our picosecond laser photolysis studies have demonstrated clearly that the relaxed ^{3}IP state does not contribute to the BPH formation in this system. Moreover, the deactivation of the relaxed ^{3}CT state or the contact ^{3}IP state in isooctane, where strong solvation may not take place, is not accompanied by the BPH formation. These results suggest strongly that the very short-lived CT state at encounter between ^{3}BP* and DPA will play the crucial role in this reaction. Namely, the mutual orientation of ^{3}BP* and DPA in this very short-lived CT state at encounter will determine the successive process, the formation of the ketyl radical or relaxed IP state. Peters and coworkers[10—13] concluded that the electron-transfer reaction leading to the formation of the solvent-separated IP was followed by the change of the structure to the contact IP where BPH formation by proton transfer took place. Their conclusion was based on the experimental results that the absorption maximum of BP$^-$ was blue-shifted with increase of the delay time after the excitation. In the present results, however, such a long-lived IP state does not participate in ketyl radical formation. This difference might be due to the fact that the secondary amine is used in the present works while Peters et al. used the tertiary amine. Hence, the direct comparison between the mutual results seems difficult. Moreover, the amine concentration in the solution used by Peters et al. for the photolysis was extremely high (ca. 1—5 M). In such a case, the ET reaction evidently occurred very rapidly in the excited singlet state, leading to no ^{3}BP* formation. Therefore, Peters et al. investigated the reaction of the quite different system from that formed by encounter between ^{3}BP* and amine. Results of detailed investigations on this problem will be discussed in the forthcoming paper, including those of our femtosecond laser photolysis studies.

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