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# Femtosecond–Picosecond Laser Photolysis Studies on Reduction Process of Excited Benzophenone with N-Methyldiphenylamine in Acetonitrile Solution

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Photoreduction processes of benzophenone (BP)-N-methyldiphenylamine (MDPA) system in acetonitrile solution were studied by means of femtosecond-picosecond laser photolysis and time-resolved transient absorption spectroscopy. The reaction processes including the formation of geminate ion pairs (IP) by electron transfer (ET) between BP\* and MDPA at encounter followed by intra-IP proton transfer giving the ketyl radical (BPH<sup>•</sup>) were clearly observed in both the triplet and singlet excited states, while the IP produced by excitation of the CT complex between BP and MDPA formed in the ground state did not give BPH<sup>\*</sup>. The reactivity of the IP depending on the mode of its production and on the energy gap for its formation and recombination reactions were discussed by integrating the present results with previous ones on BP-tertiary aromatic amines and with recent experimental and theoretical studies of the ET reactions.

#### Introduction

Electron transfer (ET) and related phenomena such as charge separation (CS), charge recombination (CR), ionic dissociation (ID), etc., play fundamental and important roles in many photochemical reactions occurring in the condensed phase, and a number of experimental and theoretical investigations have been performed from various viewpoints.<sup>1-4</sup> Hydrogen abstraction of excited benzophenone (BP\*) from aliphatic as well as aromatic amines (AH) in solution is one of the most typical photochemical reactions closely related to these fundamental processes and has been extensively studied for a long time.<sup>5-20</sup> On the basis of the experimental results that the yield of the reaction with AH is fairly large and that the rate constant is close to those of the diffusion-controlled reactions, the ET reaction producing the ion-pair (IP) state followed by proton transfer (PT) has been proposed as the possible mechanism for the hydrogen abstraction of triplet BP (<sup>3</sup>BP<sup>\*</sup>) from AH:

$${}^{3}BP^{*} + AH \xrightarrow{} {}^{3}(BP^{-} \cdots AH^{+}) \xrightarrow{} {}^{proton transfer}$$
  
(BPH<sup>•</sup> + A<sup>•</sup>)

where <sup>3</sup>(BP-...AH<sup>+</sup>) is the CT complex or ion pair, AH is an amine, and BPH<sup>•</sup> is a ketyl radical. It should be noted here that much attention has been paid for the reaction of <sup>3</sup>BP<sup>\*</sup> since the rate of the intersystem crossing (isc) from the lowest excited singlet state of BP (<sup>1</sup>BP<sup>\*</sup>) is very large (ca.  $10^{11} \text{ s}^{-1}$ ). Although a number of investigations by using time-resolved spectroscopic methods were performed in order to elucidate the reaction mechanism directly, clear conclusion on the role of the IP state or CT interaction in the hydrogen abstraction reaction was not obtained; the time

resolution of the nanosecond apparatus is not sufficient to directly detect the intermediate species and the measurement in picosecond time region usually requires a rather high concentration of AH, which causes the participation of the species other than <sup>3</sup>BP\* and makes it difficult to elucidate the reaction mechanism of <sup>3</sup>BP\*.

Actually, we have demonstrated that, in addition to the IP formed by the ET between <sup>3</sup>BP<sup>\*</sup> and AH, the IP produced by the ET between <sup>1</sup>BP\* and AH as well as that from the excited state of the CT complex formed between BP and AH in the ground state are efficiently produced in concentrated solutions of AH<sup>17,18,20</sup> (>ca.  $10^{-1}$  M). Moreover, we have revealed that the dynamic behaviors of IPs including the chemical reactivity are strongly dependent on their production pathways in the cases of BP-N,-N-dimethylaniline (DMA) and -N, N-diethylaniline (DEA) systems in acetonitrile.<sup>17,18,20</sup>

The elucidation of the different reactivity of the IP depending on the mode of its production provides very important information not only for the comprehensive understanding of the hydrogen abstraction mechanism of BP\* from AH but also for the elucidation of the mechanisms of the ET reaction and related processes in general,<sup>21</sup> since the intermolecular PT process is much more strongly dependent on the donor-acceptor mutual geometry such as intermolecular distance and orientation than the ET process and, hence, the information on the structure of the IP could be obtained from the PT dynamics.

In the present paper, we report the reduction process of BP\* with N-methyldiphenylamine (MDPA). The reactivity of IPs depending on the mode of their production will be discussed on the basis of the femtosecond and picosecond time-resolved transient absorption spectra. In addition, integrating the present experimental results with previous ones<sup>17,18,20</sup> obtained by using DMA, DEA, and N,N-diethyl-p-toluidine (DET) as hydrogen donors and with a number of accumulated data on photoinduced ET and

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Figure 1. (a) Time-resolved transient absorption spectra of the BP (0.5 M)-MDPA (0.6 M) system in acetonitrile excited with a picosecond 397-nm laser pulse. (b) Time profiles of transient absorbance at 645 nm of the BP (0.5 M)-MDPA (0.6 M) system in acetonitrile excited with a picosecond 397-nm laser pulse.

related processes,  $^{21,24,29-31}$  we will discuss the photoreduction process of the excited BP from the viewpoint of the structure of the transient IP which is determined by the mode of its production and by the energy gaps for its formation and recombination reactions.

#### **Experimental Section**

A picosecond laser photolysis system with a repetitive modelocked Nd<sup>3+</sup>:YAG laser was used for transient absorption spectral measurements in the 10 ps to a few nanosecond region.<sup>22,23</sup> The third harmonic pulse (355 nm) with 22 ps fwhm or Raman scattering light (397 nm) obtained by focusing the 355-nm pulse into cyclohexane liquid was used for exciting the sample. For the measurement of spectra in the shorter time region, a femtosecond photolysis system was used.<sup>4,24</sup> The second harmonic pulse (355 nm) of the pyridine 1 dye laser (710 nm) with 500-fs fwhm was used for the excitation.

BP (Wako, Special Guarantee) was purified by repeated recrystallization from ethanol and sublimation in a vacuum. MDPA (Tokyo Kasei, guaranteed reagent grade) was distilled under reduced pressure four times. Acetonitrile (Merck Uvasol) was used without further purification for the time-resolved transient absorption spectral measurements. All sample solutions were deaerated by repeated freeze-pump-thaw cycles. All measurements were performed at  $22 \pm 2$  °C.

The extinction coefficients used for the estimation of the reaction yields are as follows:  $6500 \text{ M}^{-1} \text{ cm}^{-1}$  at ca. 525 nm for  ${}^{3}\text{BP}^{*}$ ,  $3600 \text{ M}^{-1} \text{ cm}^{-1}$  at 575 nm for  ${}^{1}\text{BP}^{*}$ ,  $4600 \text{ M}^{-1} \text{ cm}^{-1}$  at 545 nm for BPH<sup>\*</sup>, 14 500 M<sup>-1</sup> cm<sup>-1</sup> at 645 nm for MDPA<sup>+</sup> and 10 000 M<sup>-1</sup> cm<sup>-1</sup> for BP<sup>-</sup> around 700 nm. Detailed discussion on the determination of the extinction coefficient of each species were presented in the previous papers.<sup>16,18</sup>

#### **Results and Discussion**

Excited-State Dynamics of a Weak CT Complex Formed in the Ground State. As stated in the previous papers,  $^{16-18,20}$  BP forms a weak CT complex with AH in the ground state. Also in the present case of BP-MDPA system, the increase of the absorbance due to formation of the weak CT complex was observed in the wavelength region 350-430 nm as the concentration of MDPA increased. The equilibrium constant for the complex formation was estimated to be ca. 0.1 M<sup>-1</sup>.

The dynamic behaviors of the excited state of the weak CT complex was investigated by measuring time-resolved transient absorption spectra of BP (0.5 M)-MDPA (0.6 M) system in acetonitrile solution excited with a picosecond laser pulse at 397 nm, where the CT band was selectively excited (Figure 1a). The absorption spectrum immediately after the excitation in Figure 1a shows a maximum at 645 nm ascribed to MDPA<sup>+20</sup> and a



Figure 2. Time-resolved transient absorption spectra of BP (0.05 M)– MDPA (0.6 M) system in acetonitrile, measured by exciting with a 500-fs 355-nm laser pulse. The dotted line in the first frame is the  $S_n \leftarrow S_1$  absorption spectra of BP in the amine-free condition.

broad band in the 700-800-nm region attributable to  $BP^{.25}$  The transient IP state produced by the CT complex excitation (<sup>1</sup>IP<sub>com</sub>) decreases with increase in the delay time after the excitation. No change of spectra was observed in the time region longer than 1 ns after the excitation. The absorption spectra due to  $BP^-$  and  $MDPA^+$  in this time region may be assigned to the dissociated free ions.

Time profiles of transient absorbance at 645 nm, absorption maximum of MDPA<sup>+</sup>, is shown in Figure 1b. Rapid appearance of the absorption of MDPA<sup>+</sup> due to the production of <sup>1</sup>IP<sub>com</sub> by the CT band excitation is followed by the decay with the time constant of  $310 \pm 25$  ps and reaches a plateau value due to the free ion produced by the ionic dissociation (ID) process. The formation yield of the free ions was  $0.18 \pm 0.02$ . It is rather difficult to precisely determine the formation yield of BPH radical due to the weak absorption signal at a longer delay time after the excitation. However, from the absorbance at 545 nm of the spectra at longer delay times, at which wavelength BPH radical has an absorption maximum, the formation yield of BPH radical from  $^{1}(BP - MDPA^{+})_{com}$  was estimated to be  $\ll 10\%$ . Accordingly, it may be concluded that more than 70% of <sup>1</sup>(BP-...MDPA<sup>+</sup>)<sub>com</sub> returns to the ground state by the charge-recombination (CR) process. On the basis of the lifetime of the IP and the yield of each reaction process, the rate constants of the CR, the ID, and the proton-transfer (PT) processes were obtained to be  $2.4 \times 10^9$  $s^{-1}$ , 5.8 × 10<sup>8</sup>  $s^{-1}$ , and  $\ll 3 × 10^8 s^{-1}$ , respectively.

Summarizing the above results, it may be concluded that the main deactivation process of <sup>1</sup>IP<sub>com</sub> between BP and MDPA is the CR and the yield of BPH formation was much less than 10%. The result that the ion pair state produced via the excitation of the weak CT complex formed in the ground state does not yield BPH radical was observed also in cases of BP-DMA and -DEA systems in acetonitrile.<sup>17,18,20</sup>

ET Reaction between <sup>1</sup>BP<sup>+</sup> and MDPA. Figure 2 shows time-resolved transient absorption spectra of BP (0.05 M)-MDPA (0.6 M) in acetonitrile excited with a femtosecond 355-nm laser pulse. The absorption spectrum 1 ps after the excitation shows two absorption peaks at 575 and 645 nm. The former absorption maximum can be safely assigned to <sup>1</sup>BP<sup>+</sup> since the absorption peak is in accordance with the  $S_n \leftarrow S_1$  transition measured in the amine-free condition,<sup>17,18</sup> which is indicated by the dotted line in the first frame. The latter peak is due to MDPA<sup>+</sup> as shown in Figure 1a. The rapid appearance of MDPA<sup>+</sup> is due to the



Figure 3. Time profiles of the transient absorbance at 575 nm, (a), at 525 nm, (b), and at 645 nm, (c), of the BP (0.05 M)-MDPA (0.6 M) system in acetonitrile, measured by exciting with a 500-fs 355-nm laser pulse.

#### SCHEME I



transient IP formation (<sup>1</sup>IP<sub>com</sub>) by the excitation of the CT band overlapping on the absorption band of free BP. From the analysis of the spectrum immediately after the excitation into two species of <sup>1</sup>BP<sup>\*</sup> and <sup>1</sup>IP<sub>com</sub>, the initial yield of <sup>1</sup>BP<sup>\*</sup> and that of <sup>1</sup>IP<sub>com</sub> were obtained to be 0.75 and 0.25, respectively. It should be noted that the extinction coefficient at 355 nm of the weak CT complex formed in the ground state is several times larger than that of the free BP whose transition at 355 nm is due to the weak n  $\rightarrow \pi^*$ absorption. Hence, the portion of the excitation of the weak CT complex is larger than that estimated by the concentration ratio deduced from the equilibrium constant of the complex formation in the ground state. With an increase in the delay time after the excitation, the absorption due to <sup>1</sup>BP<sup>\*</sup> decreases together with the increase of that of MDPA<sup>+</sup> and that at 525 nm due to <sup>3</sup>BP<sup>\*,27,28</sup>

Time profiles of the transient absorbance at absorption maximum of each species, <sup>1</sup>BP<sup>\*</sup>, <sup>3</sup>BP<sup>\*</sup>, and MDPA<sup>+</sup>, are exhibited in Figure 3. The solid line in each frame is the calculated curve of the time dependence based on Scheme I and the extinction coefficient of each species at each wavelength.

The absorbance at 575 nm (an absorption peak of <sup>1</sup>BP<sup>\*</sup>) which shows a rapid rise identical with the response of the apparatus is followed by the fast decay in the first ~10-ps time region. The time constant,  $6.7 \pm 1.0$  ps, of the fast decay was obtained by averaging the time profiles of transient absorbance at several different wavelengths around 575 nm. This fast decay can be ascribed to the deactivation of <sup>1</sup>BP<sup>\*</sup> due to the ET from MDPA as indicated by the transient absorption spectra in Figure 2. Since the lifetime of S<sub>1</sub> state of BP in the acetonitrile solution without AH was 9.0 ps,<sup>17,18</sup> ca. 20–25% of <sup>1</sup>BP<sup>\*</sup> was quenched by MDPA.



Figure 4. Time-resolved transient absorption spectra of BP (0.01 M)-MDPA (0.6 M) system in acetonitrile solution, excited with a picosecond 355-nm laser pulse.

The time profile following the rapid decay may contain the contribution from the ET reaction between <sup>3</sup>BP<sup>\*</sup> and MDPA and also the decrease of <sup>1</sup>IP<sub>enc</sub> and <sup>1</sup>IP<sub>com</sub>.

The time profile at 525 nm in Figure 3b, where the absorption maximum of <sup>3</sup>BP<sup>\*</sup> is exhibited, shows the rise with the time constant of  $7.0 \pm 0.5$  ps following the rapid rise. The rapid rise of the absorbance identical with the response of the apparatus is due to the absorption tail of <sup>1</sup>BP<sup>\*</sup> and that of <sup>1</sup>IP<sub>com</sub>. The rise of the absorbance with the time constant of  $7.0 \pm 0.5$  ps can be ascribed to the production of <sup>3</sup>BP<sup>\*</sup> through the intersystem crossing from <sup>1</sup>BP<sup>\*</sup> on the basis of the coincidence of the time constants with that of the decay of <sup>1</sup>BP<sup>\*</sup> within the experimental error. After the rise due to the production of <sup>3</sup>BP<sup>\*</sup>, the decay of the absorbance with the time constant much longer than a few tens of picoseconds was observed, which is attributable mainly to the decay of <sup>3</sup>BP<sup>\*</sup> through the ET reaction with MDPA as is clearly shown in Figure 4.

Figure 3c exhibits the time profile at 645 nm, an absorption maximum of IPs. This figure indicates that the rapid rise of  ${}^{1}\text{IP}_{com}$  owing to the CT band excitation is followed by fast and slow increases of the absorbance. The fast increase can be ascribed to the ET reaction between  ${}^{1}\text{BP}^{*}$  and neighboring MDPA terminating in the production of  ${}^{1}\text{IP}_{enc}$ , since the time constant of the fast increase in the 0–20-ps time region,  $7.1 \pm 0.5$  ps, is in accordance with those of the decay of  ${}^{1}\text{BP}^{*}$  and the rise of  ${}^{3}\text{BP}^{*}$ . The following slow rise with the time constant much longer than a few tens of picoseconds is mainly attributed to the formation of  ${}^{3}\text{IP}_{enc}$  through the ET reaction between  ${}^{3}\text{BP}^{*}$  and MDPA at encounter collision.

Summarizing above results and discussion, it may be concluded that formation of  ${}^{1}IP_{enc}$  and  ${}^{3}BP^{*}$  take place competitively in the decay of  ${}^{1}BP^{*}$  as is shown in Scheme I. The  ${}^{1}IP_{enc}$ , denoted  ${}^{1}(BP^{-} - MDPA^{-})_{enc}$  in Scheme I, can be discriminated from the  ${}^{1}IP_{com}$ . The difference of the reactivity of the singlet ion pairs depending on the mode of their production will be discussed in following sections.

It should be noted here that the bimolecular rate constant of the ET between <sup>1</sup>BP\* and MDPA in the present condition, which was obtained to be  $5.3 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, is several times larger than that of the diffusion-controlled reaction rate in acetonitrile solution,  $1.7 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> at 20 °C. A similar fast ET reaction between <sup>1</sup>BP\* and AH was observed also in cases of BP-DMA and -DEA

TABLE I: Dependence of the Reaction Rate Constants of the Ion Pairs upon the Mode of Its Production<sup>a</sup>

	$-\Delta G^{\circ}_{IP}/cV$	$k_{\rm PT}/\rm s^{-1}$	$k_{\rm ID}/{\rm s}^{-1}$	$k_{\rm CR}/{ m s}^{-1}$	
<sup>3</sup> (BP <sup>-</sup> ···DEA <sup>+</sup> ) <sub>enc</sub>	2.53	7.3 × 10 <sup>8</sup>	2.1 × 10 <sup>9</sup>		
(BPDEA+)		$4.3 \times 10^{8}$	1.4 × 10 <sup>9</sup>	1.1 × 10 <sup>9</sup>	
(BPDEA+)		≪10 <sup>8</sup>	$1.4 \times 10^{9}$	9.3 × 10 <sup>9</sup>	
3(BPDMA+)	2.57	5.4 × 10 <sup>9</sup>	1.4 × 10 <sup>9</sup>		
1(BPDMA+)		$6.6 \times 10^{8}$	9.5 × 10 <sup>8</sup>	$5.8 \times 10^{8}$	
(BPDMA+)		≪10 <sup>8</sup>	$< 4 \times 10^{8}$	$1.1 \times 10^{10}$	
<sup>3</sup> (BP-···MDPA <sup>+</sup> )	2.67	8.2 × 10 <sup>9</sup>	$1.1 \times 10^{9}$		
1(BPMDPA+)		5.2 × 10 <sup>8</sup>	$5.6 \times 10^{8}$	$1.2 \times 10^{8}$	
<sup>1</sup> ( <b>BPMDP</b> A <sup>+</sup> ) <sub>com</sub>		$\ll 3 \times 10^{8}$	$5.8 \times 10^{8}$	$2.4 \times 10^{9}$	

 ${}^{a}-\Delta G^{o}{}_{1P}$  is calculated from eq 5 of ref 21. Results on BP-DMA and -DEA systems are taken from refs 17, 18 and ref 20, respectively.

systems.<sup>17,18,20</sup> Such a large rate constant for the ET reaction is attributable to the nonstationary quenching process taking place between <sup>1</sup>BP<sup>\*</sup> and neighboring MDPA which is inside the reaction radius. Hence, the "rate constant" of the ET reaction between <sup>1</sup>BP\* and MDPA is time dependent. In the calculated curves presented in Figure 3, however, it was set constant since the determination of the parameters reproducing the nonstationary process from the present results was rather difficult. The rate constant obtained here is an approximate one averaged for the ET process between <sup>1</sup>BP\* and MDPA. At any rate, the calculated curves in Figure 3, which were obtained by the curve-fitting procedure of the three time profiles at the same time, reproduced the experimental results fairly well. From the results of this simulation, the initial yields of the 'BP\* and 'IP<sub>com</sub> were obtained to be 0.74 and 0.26, respectively. These values were in agreement with those obtained by the analysis of the spectra immediately after the excitation into the two species of <sup>1</sup>BP<sup>\*</sup> and <sup>1</sup>IP<sub>com</sub> (0.75 and 0.25). In addition, the yields of the formation of  ${}^{3}BP^{*}$  and <sup>1</sup>IP<sub>enc</sub> from <sup>1</sup>BP<sup>\*</sup> were 0.77 and 0.23, respectively. In other words, almost half of the absorbed light energy resulted in the production of singlet ion pairs in the present condition.

**Dynamic Behaviors of**  $^{1}\mathbf{P}_{exc}$  between BP and MDPA. Figure 4 shows time-resolved transient absorption spectra of the BP (0.01 M)-MDPA (0.6 M) system in acetonitrile excited with a picosecond 355-nm laser pulse. In the absorption spectrum immediately after the excitation, the maximum of MDPA<sup>+</sup> at ca. 645 nm due to <sup>1</sup>IPs and that of <sup>3</sup>BP<sup>\*</sup> at 525 nm are observed. With increase in the delay time after the excitation, the absorbance due to <sup>3</sup>BP<sup>\*</sup> decreases together with the increase of that due to MDPA<sup>+</sup> and BP<sup>-</sup>. The absorption due to IPs decreases in the nanoseconds time region and reaches a plateau value ascribable to the free ions. The increase of the absorption due to BPH radical at 545 nm were also observed.

In Figure 5 are exhibited time profiles of these three species, <sup>3</sup>BP\*, BPH, and IPs, obtained by the analysis of the observed spectra into these species. The ordinate of this figure is the concentration. The extinction coefficient of each species is presented in the Experimental Section. As described in the legends to Figures 2 and 3, the initial yields of <sup>1</sup>IP<sub>com</sub>, <sup>1</sup>IP<sub>enc</sub>, and <sup>3</sup>BP\* have been determined. In addition, the reactivity of <sup>1</sup>IP<sub>com</sub> was also elucidated as shown in Figure 1. The reaction profile of <sup>3</sup>IP<sub>enc</sub> between BP and MDPA has been already revealed;<sup>20</sup> the lifetime, the yield of the ID, and the yield of the PT of <sup>3</sup>IP<sub>enc</sub> are 90 ps, 0.08, and 0.74, respectively. Hence, in principle, information on the reactions of <sup>1</sup>IP<sub>enc</sub> can be obtained by subtracting from the observed results the contributions from the reaction between <sup>3</sup>BP\* and MDPA and that of <sup>1</sup>IP<sub>com</sub> on the basis of their initial yields and time dependences. In the actual analysis of the time profiles



Figure 5. Time profiles of  ${}^{3}BP^{*}(O)$ , BPH<sup>•</sup>( $\bullet$ ), and BP<sup>-</sup> and MDPA<sup>+</sup>( $\bullet$ ) of BP (0.01 M)-MDPA (0.6 M) system in acetonitrile solution excited with a picosecond 355-nm laser pulse.

of <sup>1</sup>IP<sub>enc</sub>, we employed the curve-fitting procedure where the lifetime and the reaction yields were varied as parameters. The solid lines in Figure 5 were calculated curves by assuming that the lifetime and the yields of the PT, ID, and CR processes of <sup>1</sup>IP<sub>enc</sub> were 900 ps, 0.45, 0.10, and 0.44, respectively. The solid lines for IPs and BPH in Figure 5 include the contributions from three IPs. The experimental results are fairly well reproduced by the calculated time dependence, and further, parameters for <sup>1</sup>IP<sub>enc</sub> were almost independent of the MDPA concentration. The averaged lifetime and the yields of the PT, ID, and CR reactions of <sup>1</sup>IP<sub>enc</sub> were 850 ps, 0.43, 0.10, and 0.43, respectively.

Difference of the Reactivity of the IP Depending on the Mode of Its Production and the Energy Gaps for Its Formation and Recombination Reactions. In Table I, the dependence of the reactivity of each IP on the mode of its production is listed, together with the energy gap between the IP and the ground states. For comparison, the results on the BP–DMA and –DEA systems<sup>17,18,20</sup> are listed. The CR rate constant of <sup>3</sup>IP<sub>enc</sub> was not listed since the contribution from the CR process of <sup>3</sup>IP<sub>enc</sub> to its decay is too small to quantitatively determine the rate constant. This table clearly shows that each reaction rate constant is strongly dependent on the mode of the IP production and that the structure of the IP which is determined at the ET interaction strongly affects the subsequent PT process. In addition, it is indicated that the averaged structure of each IP is maintained approximately during the lifetime of the IP.

First, we concentrate ourselves on the difference of the reactivity between <sup>1</sup>IPs. As Table I shows, for both <sup>1</sup>IP<sub>enc</sub> and <sup>1</sup>IP<sub>com</sub>,  $k_{PT}$ does not show appreciable dependence on  $\Delta G^{\circ}_{IP}$ ;  $k_{PT}$  of <sup>1</sup>IP<sub>com</sub> is  $\ll 10^8 \text{ s}^{-1}$  and those of <sup>1</sup>IP<sub>enc</sub> are  $(5 \pm 1) \times 10^8 \text{ s}^{-1}$ . On the other hand, the CR rate constants are strongly dependent on  $\Delta G^{\circ}_{IP}$ . The difference of the reactivity including the CR rates between <sup>1</sup>IP<sub>enc</sub> and <sup>1</sup>IP<sub>com</sub> is closely related to our recent investigation on the CR rates and its dependence on the production mode of IP of various donor (D) and acceptor (A) systems.<sup>21</sup> According to these investigations, it was revealed that the CR rates of <sup>1</sup>IP<sub>com</sub> which is produced by the excitation of the CT complex formed in the ground state were quite different from those of <sup>1</sup>IP<sub>enc</sub> produced by the ET reaction at encounter collision in the fluorescence quenching reaction.

In Figure 6, we exhibit the dependence of the CR rates on  $-\Delta G^{\circ}_{IP}$ , obtained for various organic D and A pairs in acetonitrile,<sup>21</sup> together with those obtained for BP-aromatic tertiary

TABLE II: Dependence of the Reaction Rate Constants of Triplet Ion Pairs between BP and Tertiary Aromatic Amines upon the Oxidation Potential of the Amine in Acetonitrile

	oxid potential vs SCE/V	lifetime/ps	$k_{\rm PT}/{\rm s}^{-1}$	$k_{\rm ID}/{\rm s}^{-1}$
<sup>3</sup> (BP <sup>-</sup> ···MDPA <sup>+</sup> ) <sub>enc</sub>	0.86	90	$8.2 \times 10^{9}$	$1.1 \times 10^{9}$
3(BPDMA+)	0.76	140	5.4 × 10 <sup>9</sup>	$1.4 \times 10^{9}$
<sup>3</sup> (BP-···DEA <sup>+</sup> ) <sub>enc</sub>	0.72	290	$7.3 \times 10^{8}$	$2.1 \times 10^{9}$
<sup>3</sup> (BPDET <sup>+</sup> ) <sub>enc</sub>	0.69	>500	$\ll 2 \times 10^8$	$(2 \times 10^{9})$



Figure 6. Energy gap dependence of CR rate constant of  ${}^{1}IP_{com}$  ( $\bullet$ ) and that of <sup>1</sup>IP<sub>enc</sub> (O) in acetonitrile solution. 1, BP-DEA; 2, BP-DMA; 3, BP-MDPA. Results of various DA systems are taken from ref 21. Those on BP-DMA and -DEA systems are from refs 17, 18 and ref 20, respectively.

AHs. As indicated in this figure, the energy gap dependences of the CR rates of <sup>1</sup>IPenc and of <sup>1</sup>IPcom between BP and AH are respectively in agreement with the experimental results on various other D-A pairs. According to the interpretation made on the difference between the CR rate of  ${}^{1}IP_{com}$  and that of  ${}^{1}IP_{enc}$ ,<sup>21</sup> the structure of <sup>1</sup>IP<sub>com</sub> was supposed to be rather compact or contact one (CIP) with no intervening solvent between two oppositely charged ions. On the other hand, <sup>1</sup>IP<sub>enc</sub> may have rather loose structure (loose ion pair, LIP) probably with intervening solvents.

The fact that  $k_{\rm PT}$  of <sup>1</sup>IP<sub>com</sub> is much smaller compared to those of the other IPs indicates strongly that the most important factor for the production of BPH is the mutual orientation between BPand  $AH^+$  in the IP. Although the interionic distance in <sup>1</sup>IP<sub>com</sub> is shorter than that in <sup>1</sup>IP<sub>enc</sub>, its CIP structure, presumably close to the plane-parallel one, will not be favorable to PT and change of its structure during the lifetime will be difficult owing to its rigid structure. In the case of <sup>1</sup>IPene, BPH formation by PT during its lifetime may be possible to some extent because of the freedom to take a favorable configuration for PT owing to its structure.

The results in Table I indicate also that  $k_{\rm PT}$  values of <sup>1</sup>IP<sub>enc</sub> are considerably smaller than those of <sup>3</sup>IPency which may be understood on the basis of the circumstances similar to that described above. Namely, the ET between <sup>1</sup>BP<sup>\*</sup> and the amine will be restricted rather severely to the pairs in the short range and with mutual <sup>1</sup>BP\*-amine orientations favorable for ET reaction owing to the very short lifetime of <sup>1</sup>BP\*, which may lead to the formation of <sup>1</sup>IP<sub>enc</sub> with a more rigid and specific structure different from the loose structure of <sup>3</sup>IP<sub>enc</sub> formed via stationary diffusion process. Although the detailed mechanism is not very clear at the present stage of the investigation, the specific structure of <sup>1</sup>IP<sub>enc</sub> determined by the donor-acceptor configuration favorable for the rapid ET may not be suitable for PT and some configuration rearrangement will be necessary. The loose structure of <sup>3</sup>IP<sub>enc</sub> will be favorable for PT immediately after ET as well as for the rearrangement of structure to the one more favorable for PT.

In addition to the difference of the reactivity between <sup>1</sup>IPs depending on the mode of the production as well as that between <sup>1</sup>IP<sub>enc</sub> and <sup>3</sup>IP<sub>enc</sub>, a large difference of the reactivity of <sup>3</sup>IP<sub>enc</sub>, especially  $k_{\rm PT}$ , depending on  $-\Delta G^{\circ}_{\rm IP}$  was observed (Table II). With the decrease of  $-\Delta G^{\circ}_{IP}$  the rate constant,  $k_{PT}$ , decreases. The rate constant of the PT process of  ${}^{3}(BP-...DET^{+})_{enc}$  whose  $-\Delta G^{\circ}_{IP}$  is smaller than that of (BP····DEA<sup>+</sup>), 2.50 eV, was  $\ll 2 \times 10^8 \text{ s}^{-1,20}$  This dependence of  $k_{PT}$  on  $-\Delta G^{\circ}_{IP}$  seems to indicate the different structure of the IP depending on  $-\Delta G^{\circ}_{IP}$  and seems to be closely related to the problems of the energy gap dependence of the ET reaction. From recent experimental and theoretical studies on the energy gap dependence of the CS rate constant,  $k_{\rm CS}$ , at encounter in the luminescence quenching reaction,<sup>29-31</sup> it is predicted that the ET distance depends on the change of  $-\Delta G^{\circ}_{CS}$ value between the initial locally excited state and the final IP state. That is, for larger  $-\Delta G^{\circ}_{CS}$  value, CS at a little larger distance is favorable because the solvent reorganization energy,  $\lambda$ , becomes

larger at larger D-A distances.

Along these theoretical treatments, it is expected, for the PT process following the ET reaction, that the PT rate should be drastically slowed down with the increase of  $-\Delta G^{\circ}_{CS}$  due to the increase of the interionic distance in the geminate IP since the rate of the PT process is much more severely dependent on the mutual distance and orientation than ET. The present result of the dependence of  $k_{\rm PT}$  of  ${}^{3}\rm{IP}_{enc}$  on  $-\Delta G^{\circ}{}_{\rm IP}$ , that is, on  $-\Delta G^{\circ}{}_{\rm CS}$ , is in accord with these considerations.

The effect of  $-\Delta G^{\circ}_{CS}$  on the PT rate of the produced IP, which is attributable to the difference in the interionic distance may be expected also in the case of the <sup>1</sup>IP<sub>enc</sub>. However, as we have discussed already, because the ET between <sup>1</sup>BP\* and the amine is restricted severely to the pairs with orientations favorable for ET and in the short range owing to the very short life of <sup>1</sup>BP\*, which will diminish such effect of  $-\Delta G^{\circ}_{CS}$  on  $k_{PT}$ . Actually,  $k_{PT}$ in the <sup>1</sup>IP<sub>enc</sub> does not show such energy gap dependence; rather, they are rather similar to each other for the series of <sup>1</sup>BP\*-DEA, -DMA, and -MDPA systems.

#### **Concluding Remarks**

The results of the present femtosecond-picosecond laser photolysis studies together with those of our previous investigations on BP-tertiary aromatic amine systems in acetonitrile solutions demonstrate clearly that the recognition of the quite different behaviors of various kinds of IPs is of crucial importance for understanding the photochemical reaction mechanisms of BPamine systems.

It has been confirmed that the energy gap dependence of charge recombination of <sup>1</sup>LIP and that of <sup>1</sup>CIP of these BP-amine systems in acetonitrile solutions are in accordance with the results obtained by femtosecond-picosecond laser photolysis investigations on various electron donor and acceptor systems which do not undergo such chemical reactions as hydrogen abstraction associated with photoinduced ET. This result indicates clearly that the reaction mechanism of these BP-amine systems can be discussed on the basis of the experimental and theoretical results of the photoinduced ET reactions in general.

Moreover, it has been demonstrated that  $k_{PT}$  of BP-tertiary aromatic amine <sup>3</sup>LIP significantly decreases with increase of  $-\Delta G^{\circ}_{CS}$  for the <sup>3</sup>LIP formation, indicating the increase of the interionic distance in <sup>3</sup>LIP in this order. This  $-\Delta G^{\circ}_{CS}$  dependence of the interionic distance in the geminate LIP is predicted by simple ET theory. However, its direct experimental confirmation in the photoinduced ET reaction in solution is difficult. The present results on the  $-\Delta G^{\circ}_{CS}$  dependence of  $k_{PT}$  in <sup>3</sup>LIP on BP-amine support strongly this mechanism contributing profoundly to the elucidation of the mechanisms of the solution photochemical reactions.

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# Theoretical Study of the Hydration Reaction of Ketene

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The addition of monomeric and dimeric  $H_2O$  to ketene has been studied by ab initio molecular orbital calculations using a 6-31G\* basis set and energy calculations up to MP4(SDTQ). Complete geometry optimizations relaxing all internal coordinates were performed. Our calculations indicate that a concerted addition of dimeric H<sub>2</sub>O to the carbon-oxygen double bond, yielding an enediol, is energetically slightly preferred to a similar addition to the carbon-carbon double bond, yielding acetic acid. The energy barriers obtained at the highest level of calculation, MP4(SDTQ)/6-31G\*//RHF/6-31G\*, were 17.4 and 19.4 kcal/mol for the two additions, respectively. After a zero-point energy (ZPE) correction was introduced, the energies were 19.9 and 21.8 kcal/mol, respectively. The potential barriers to addition of monomeric H<sub>2</sub>O were found to be substantially higher at the same calculational level, the values being 37.8 and 41.4 kcal/mol for the addition to the carbon-oxygen double bond and to the carbon-carbon double bond, respectively. The ZPE correction modified these values to 39.7 and 41.0 kcal/mol, respectively. The conversion of enediol to acetic acid through intramolecular hydrogen migration has an activation energy of 45.7 kcal/mol relative to the diol, calculated at the highest level and corrected for ZPE. A systematic search for stationary points representing noncyclic transient species for the system ketene and monomeric H<sub>2</sub>O revealed only a weakly bound complex with a  $C_{\alpha}$ -O(water) distance of 3.02 Å.

Recently there has been a revival of the chemistry of ketenes.<sup>1</sup> Their ability to undergo concerted [2 + 2] cycloaddition reactions<sup>2</sup> has renewed the theoretical interest in the mechanism and kinetics of their reactions. Theoretical calculations related to cycloadditions, including dimerization of ketene have very recently been published,3 and in some cases the relevance of a concerted mechanism has been questioned.3b,e

Additions, both electrophilic and nucleophilic, constitute an important class of ketene reactions.<sup>1b</sup> Nucleophilic additions, using a variety of nucleophiles, have been invoked in synthetic work. Among these additions the hydration reactions still present some intriguing questions regarding reaction mechanism. Hydration reactivities of ketene itself and of a series of substituted ketenes have been measured in aqueous and other solvents containing varying concentrations of water.<sup>5,6</sup> The observed reaction rates in neutral solutions have been interpreted in terms of a mechanism involving an interaction between a lone pair in H<sub>2</sub>O and the ketene LUMO.<sup>6</sup> In ketene the LUMO is extended in the molecular plane and has a large contribution from  $C_{\alpha}$ . This atom is thus assumed to be a likely site for nucleophilic attack. The reaction mechanism is complicated by the possible role of both monomeric and dimeric water as active reagents in the process.

The base-induced reaction is claimed to occur via a mechanism that is analogous to the one in neutral solution, the OH<sup>-</sup> ion playing the role of water.<sup>6</sup> Acid-catalyzed reactions are assumed to involve a rate-limiting proton transfer to  $C_{\beta}$  of ketene. Observed moderate steric effects from bulky substituents have led to the conclusion that the protonation occurs perpendicular to the molecular plane.<sup>6</sup>

Theoretical studies of hydration reactions of ketene and ketene derivatives in the gas phase have previously been published.<sup>7</sup> In one of the published studies<sup>7a</sup> only dimeric H<sub>2</sub>O was considered as attacking agent. Furthermore, the geometry optimizations were



made using a minimum basis, and correlation energies were not included in the estimates of energy differences. In addition, optimizations appeared to have been made without relaxation of all internal coordinates. In a later refined calculation<sup>7b</sup> it was confirmed that one of the stationary points previously claimed to be a transition state had two imaginary vibrational frequencies. More recent calculations<sup>7c,d</sup> have made use of double-5 basis sets augmented with polarization functions, but energy differences were estimated without inclusion of electronic correlation. Furthermore, transition structures were not characterized by using analytically