Photochemical reaction in the molecular clusters of benzophenone with hydrogen donors formed in a supersonic free jet expansion

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Abstract

Photochemical reactions in neutral molecular clusters of benzophenone with hydrogen donors formed in a supersonic free jet expansion have been studied. It has been found that intracluster hydrogen abstraction reaction takes place to form benzophenone ketyl radical in the benzophenone–1,4-cyclohexadiene mixed cluster. On the contrary, no ketyl radical has been detected when ethanol, 2-propanol, or several kinds of amine are used as a hydrogen donor. Excitation and emission spectra of the benzophenone–*N,N*-dimethylaniline cluster have suggested that benzophenone and *N,N*-dimethylaniline form a ground state charge transfer complex. The excitation of the benzophenone–tri-*n*-butylamine cluster promotes the transformation of the van der Waals complex to an exciplex. The reactivity of the clusters on hydrogen abstraction and charge transfer reactions has been discussed on the basis of the nature of hydrogen donors.

Keywords: Clusters; Benzophenone; Hydrogen donor; Supersonic jet

1. Introduction

Recently solute–solvent clusters generated in a supersonic free jet expansion have been extensively studied by laser spectroscopy [1–3]. The energetics and dynamics of the clusters have been investigated after electronic excitation or ionization. A wide range of clusters has been investigated: halogen molecules in rare gas clusters, large non-polar aromatic molecules in rare gas clusters, polar aromatic molecules in hydrogen-bonding solvents etc. Among the various properties of clusters, much attention has been paid to the reactions within microsolvent clusters [4–12]. It has been expected that the investigation of intermolecular reactions in collision-free microsolvent clusters will allow the study of liquid phase reactions at a molecular level free from the complicated effects of solvent environment.

The behaviour of carbonyl compounds in the excited triplet state has been one of the most fundamental and important subjects in photochemistry [13,14]. In particular, hydrogen abstraction reactions of benzophenone in the excited triplet state have been extensively studied [15–23]. Excited benzophenone can abstract a hydrogen atom from several classes of compounds including alkanes, alkenes, alcohols, and amines to form benzophenone ketyl (BPK) radical.

In particular, much attention has been paid to the reaction of benzophenone–amine systems owing to its high efficiency. It is widely known that the reaction rates of triplet benzophe-

none with various amines are close to the diffusion-controlled reaction rate and the yields of the reaction are very high [13,16,17,19]. Thus considerable interest has been paid to the reaction mechanism. It has been proposed that the hydrogen abstraction of benzophenone from amines proceeded by rapid formation of the charge transfer (CT) complex or ion pair state followed by proton transfer to generate BPK [16,17].

Although the mechanism for the photoreduction of benzophenone in the condensed phase has been extensively studied, many questions still remain unanswered. If proton transfer following electron transfer between benzophenone and amine is the dominant process of the reaction, can the proton transfer directly or is it necessary to form a long-lived ion pair? What is the role of surrounding solvent molecules? Is a specific orientation between benzophenone and hydrogen donor necessary for the reaction to progress?

Whereas the photoreduction process of benzophenone in the condensed phase has been extensively studied for several decades, very few studies have been reported on the gas phase reaction of triplet benzophenone [24]. In our previous investigation, it has been reported that the photoreduction of excited benzophenone proceeds to form BPK without contributions from surrounding solvent molecules in the gas phase [25]. We have also investigated the hydrogen abstraction reaction in molecular clusters of benzophenone and hydrogen donors formed in a supersonic free jet expansion [26].

In this investigation, the hydrogen abstraction and CT reactions in molecular clusters of benzophenone and hydrogen donors are reported. The exciplex and CT emission in the excitation of benzophenone–amine mixed clusters is also observed. The relation between the photochemical reactivity of the clusters and the nature of the hydrogen donors is discussed.

2. Experimental details

2.1. Molecular cluster source and vacuum chamber

Benzophenone was purified by repeated recrystallization from ethanol. The following compounds were used as hydrogen donors: 1,4-cyclohexadiene, ethanol, 2-propanol, triethylamine, tripropylamine, tri-n-butylamine, tri-iso-butylamine, and N,N-dimethylaniline. Amines were purified by repeated distillation under vacuum. It was confirmed that these compounds did not fluoresce following laser excitation (308 nm, 337 nm, 340–400 nm, and 465–575 nm).

Benzophenone–hydrogen donor clusters were generated in a supersonic free jet expansion employing a magnetically operated pulsed valve (General Valve 9-279-900) with temporal pulse width of 400–500 μs. An electric heater was used to raise the temperature of the valve and a reservoir of benzophenone to 415 K. Benzophenone at a vapour pressure of 1.0–5.0 Torr, corresponding to a temperature of 380–415 K, was seeded into the hydrogen donor – He gas mixture. The vapour pressure of the hydrogen donors ranged from 1.0 to 50.0 Torr and the stagnation pressure was in the range from 0.8 to 2.0 atm.

It has been known that certain kinds of nozzle shapes effectively produce larger clusters at a constant flow rate. With this in mind, the mixed gas was expanded into a vacuum chamber through a conical nozzle (300 μm diameter, 9 mm length) or a straight nozzle (500 μm diameter, 5 mm length). The conical nozzle was made by using a laser machining technique to minimize the friction of the nozzle surface.

The vacuum chamber with a volume of about 30 l was made of stainless steel. The chamber was evacuated by a 6 inch water-baffled oil diffusion pump (1300 l s^{-1}) and a mechanical rotary pump (960 l s^{-1}). Under the above pumping conditions, the residual gas pressure in the vacuum chamber was 1×10^{-4} Torr and 1×10^{-6} Torr when the supersonic jet source was on and off respectively.

2.2. Lasers and detection methods

The $S_1 \leftarrow S_0$ excitation spectra of benzophenone and benzophenone–hydrogen donor clusters were recorded by the one-colour one-photon resonant three-photon ionization (1C3PI) method. A dye laser (Lumonics HyperDye-300, 0.06 cm^{-1} resolution) pumped by an XeCl laser (Lambda Physik EMG 52-MSC) was used as an ionization light source. The laser beam (355–382 nm) was focused with a lens of 50

cm focal length and crossed perpendicularly the free jet expansion at $X/D = 15$. Ions generated by multiphoton ionization (MPI) process were repelled by a positively charged plate electrode placed 2.5 cm from the focus of the laser beam and were detected with a channel electron multiplier (Murata Ceratron) positioned 4 cm from the ionization region. Signals from the channeltron were amplified by a current amplifier (Keithley 427).

A telescope system placed at a right-angled configuration to the free jet expansion and laser beams was used to detect the phosphorescence of benzophenone, fluorescence of BPK, and exciplex and CT complex fluorescence of benzophenone–amine systems. Benzophenone in the neutral clusters was excited by pulses from an N_2 laser (Molectron UV22), the XeCl laser, or the dye laser pumped by the XeCl laser at $X/D = 15$–25. The laser systems typically produce pulses of approximately 15 ns duration. BPK generated by the photoreduction of triplet benzophenone with hydrogen donor was subsequently excited with pulses from a dye laser (Molectron DL-14P, 0.3 cm^{-1} resolution) pumped by the N_2 laser at $X/D = 18$–30. The excitation and probe pulses were synchronized with a variable time delay from 100 ns to several microseconds.

The action spectrum of BPK formation was measured in the following way. The dye laser light in the wavelength region 355–382 nm was used to excite benzophenone in the neutral cluster. The excitation laser of benzophenone was scanned while the dye laser was fixed at 530 nm to probe BPK. Excitation and probe lasers were synchronized with a constant time delay (about 1 μs).

The emission signals were detected by a photomultiplier (Hamamatsu R-928) connected to an amplifier (EG&G model 115). The emission was detected through short-wavelength cut-off filters for the fluorescence and phosphorescence excitation spectra measurements. Dispersed emission spectra were measured on a grating monochromator (Nikon P-250) with a resolution of 2–5 nm. The signals were integrated with a gated integrator (Stanford SR-250) before being digitized by an analogue-to-digital converter (Standford SR-245).

3. Results and discussion

3.1. Cluster formation in the mixed expansion of benzophenone and hydrogen donors monitored by multiphoton ionization spectroscopy

Much attention has been paid to the nature and dynamics of the electronic excited state of benzophenone because of their importance in photochemistry. The electronic absorption spectrum of benzophenone exhibits a weak and broad $n\pi^*$ transition centred near 350 nm with faint vibrational structure even in the gas phase. Thus insufficient information had been available on the electronic and geometric structure of the first excited state of benzophenone. Recently Ito and
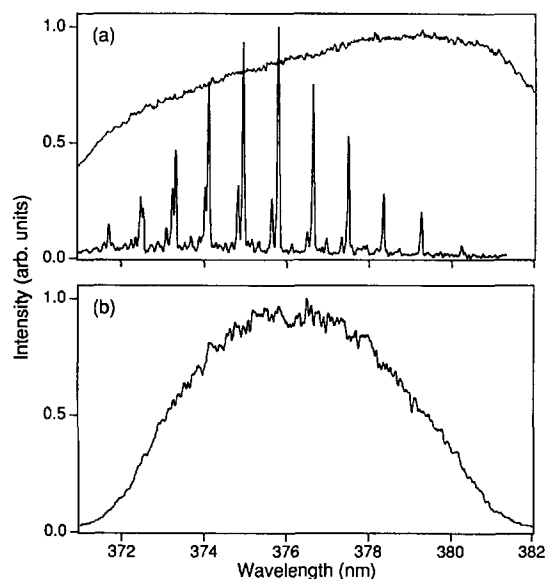
Fig. 1. MPI spectra of (a) benzophenone (1.0 Torr) and (b) benzophenone (1.0 Torr)-triethylamine (10.0 Torr) mixed system seeded in 1.0 atm of He obtained by the 1C3PI method. The intensities of these spectra are not normalized with respect to the laser power spectrum (· · ·).

coworkers [27] and Pratt and coworkers [28] reported the excitation spectra of benzophenone with well-resolved vibrational features under supersonic free jet conditions. These two groups measured the 0–0 band region at 382–370 nm and the vibronic bands involving the excited state C=O stretching mode at about 1230 cm^{-1} in the 364–355 nm region. Both spectral regions are characterized by long progressions of about 60 cm^{-1} which are assigned to the excited state totally symmetric torsional mode of the phenyl rings.

Fig. 1(a) shows a 1C3PI spectrum of benzophenone (1.0 Torr) seeded in 1.0 atm of He covering the $S_1 \leftarrow S_0$ origin region. The spectrum consists of several progressions with an interval of 60 cm^{-1} starting from different origins and is in good agreement with the spectra reported by Ito and coworkers and Pratt and coworkers.

Fig. 1(b) shows a 1C3PI spectrum obtained in benzophenone (1.0 Torr)-triethylamine (10.0 Torr) mixed expansion. The sharp peaks vanished completely and a broad and diffuse spectrum was observed. The observed spectral feature is similar to the envelope of the 60 cm^{-1} progressions of bare benzophenone in the corresponding region. Similar broadening of the MPI spectrum was observed when ethanol, 2-propanol, and 1,4-cyclohexadiene were used as hydrogen donors. The spectral shape did not change significantly when the pressure of hydrogen donors was varied from 1.0 to 50.0 Torr.

The broadening of the MPI spectrum in benzophenone–hydrogen donor mixed expansion probably arises from the generation of molecular clusters. Such a broad spectral feature must be produced by the spectral congestion caused by the combination of low frequency intermolecular modes of van der Waals (vdW) vibration and ring torsional mode of benzophenone, and the contribution from several kind of isomers.

3.2. Hydrogen abstraction in a neutral molecular cluster of benzophenone and hydrogen donor

In the condensed phase, BPK has an absorption band in the visible region with a maximum at around 545 nm and fluorescence of BPK characterized by a maximum near 575 nm is readily observable after the excitation into the D_1 state [29–33]. The hydrogen abstraction reaction of benzophenone in a supersonic free jet expansion is studied by monitoring the laser-induced fluorescence of BPK.

The fluorescence excitation and dispersed emission spectra were measured in the mixed expansion of benzophenone (1.0 Torr)-1,4-cyclohexadiene (50.0 Torr) seeded in 1.0 atm of He. The mixed expansion was subsequently excited with a dye laser in the wavelength region corresponding to the $D_1 \leftarrow D_0$ transition of BPK at 1.0 μs after 308 nm irradiation. The dye laser was tuned at 540 nm for the measurement of the dispersed emission spectrum (Fig. 2 (a)). The spectrum is very similar to that of BPK in the condensed phase. Recently, we have carried out a spectroscopic study of jet-cooled BPK formed by the photolysis of α-phenylbenzoin. The emission spectrum of the radical is also similar to the spectrum shown in Fig. 2(a). The good agreement of the spectral data indicates that the luminescent chemical species generated in the mixed expansion is BPK. In contrast, no ketyl radical fluorescence was detected by 540 nm excitation when 2-propanol, ethanol, or amines listed in the experimental section were used as a hydrogen donor.

Two possible mechanisms for BPK generation can be proposed from the above results: (i) collision-induced reaction in a supersonic free jet expansion and (ii) intracluster reaction in benzophenone and hydrogen donor neutral cluster. To reveal which mechanism is correct, the laser power dependance of the emission and the action spectrum of BPK formation were examined.

The dispersed emission spectrum for the mixed expansion measured for the one-colour excitation at 308 nm was similar to that obtained for the 540 nm excitation. The double-logarithmic plot of the fluorescence intensity vs. the light intensity of the XeCl laser has a slope of 1.9 ± 0.1, indicating that the fluorescence is generated by the two-photon excitation process. This fact implies that BPK generated by the 308 nm excitation absorbed one more photon within the time width of the laser pulse. That is to say, in contrast to the gas phase reaction initiated by collisions, the reaction rate is very fast in a supersonic free jet expansion.

The action spectrum of BPK formation was also measured. The excitation laser of benzophenone was scanned in the wavelength region of 382–355 nm while fixing the other dye laser at 540 nm to probe BPK. The action spectrum in the photoexcitation of benzophenone-1,4-cyclohexadiene mixed system was in good agreement with MPI spectrum of the cluster obtained by the 1C3PI method.

The results on the laser power dependence of BPK emission intensity and the action spectrum of BPK formation measurements strongly suggest that BPK observed in this
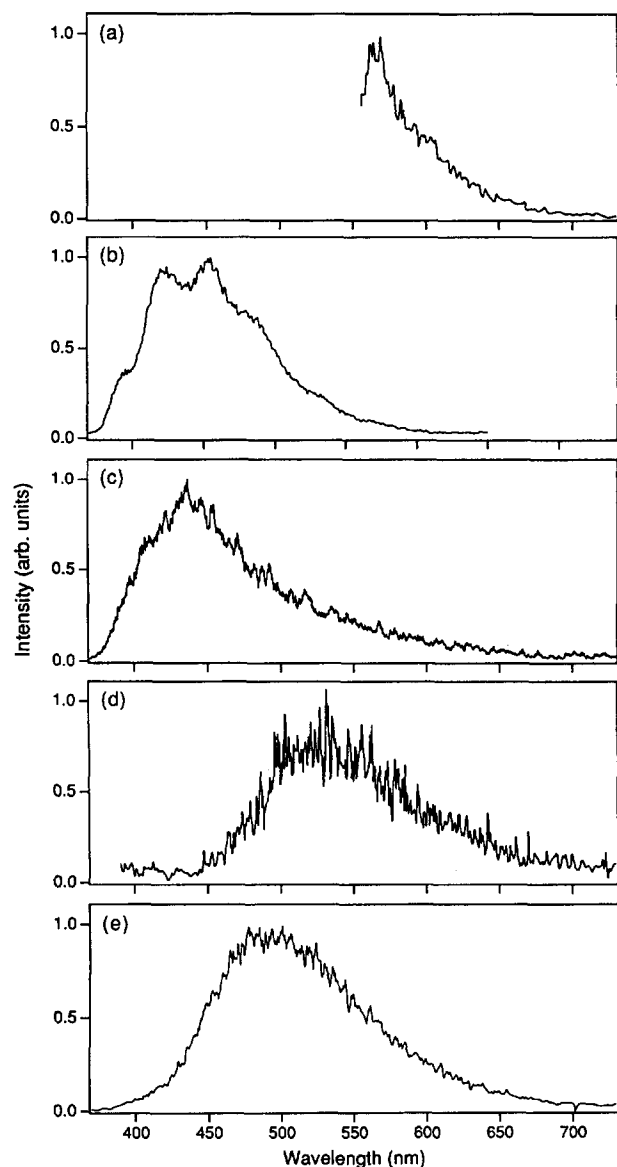
Fig. 2. (a) Dispersed emission spectrum obtained by 540 nm excitation at 1.0 μs after 308 nm irradiation for the benzophenone (1.0 Torr) and 1,4-cyclohexadiene (50.0 Torr) mixed expansion. The XeCl and dye lasers were positioned at $X/D = 15$ and 20 respectively. (b) Dispersed emission spectrum of benzophenone (1.0 Torr) in the gas phase excited with 337 nm laser light. (c) Dispersed emission spectrum for the benzophenone and triethylamine mixed cluster obtained by the excitation at 308 nm. (d) Dispersed emission spectrum for the benzophenone and N,N-dimethylaniline mixed cluster obtained by the excitation at 376 nm. (e) Dispersed emission spectrum for the benzophenone and tri-n-butylamine mixed cluster obtained by the excitation at 308 nm.

study is formed by the intracluster hydrogen abstraction reaction after photoexcitation of benzophenone.

3.3. Reactivity of hydrogen abstraction of benzophenone–hydrogen donor clusters

As described above, the hydrogen donors exhibit different reactivities in benzophenone–hydrogen donor clusters after photoexcitation. Formation of BPK was observed only in the benzophenone–1,4-cyclohexadiene mixed cluster, but no BPK fluorescence was observed when ethanol, 2-propanol, or amines were used as a hydrogen donor. Furthermore, 1,4-cyclohexadiene and amines quench the long-lived benzophenone phosphorescence, although ethanol and 2-propanol do not.

In our previous study [25], we measured the quenching rate constants of triplet benzophenone for several kinds of hydrogen donors in the gas phase and suggested that the rate constants in the gas phase exhibited a similar trend to those in the liquid phase. The quenching rate constants for amines are 30–500 times larger than that for 2-propanol in the gas phase, which is comparable with the effective reactivity of amines in the liquid phase, that is 1.5×10^2–10^3 times larger than 2-propanol. The quenching rate of 1,4-cyclohexadiene is also 50 times higher than that of 2-propanol in the gas phase. The reactivity of the clusters will be discussed on the basis of the nature of the hydrogen donors.

The results of the quenching rate study in the gas phase suggest that the small quenching rate constants of alcohols are one of the reasons why ketyl radical fluorescence was not observed in the mixed expansion of benzophenone and alcohols. In addition to this, the effect of the cluster structure on the reactivity should be considered. The most probable structure of the benzophenone–alcohol mixed cluster is the hydrogen-bonded structure, which is bound by a weak hydrogen bond between the hydroxylic group of the alcohol and the oxygen atom of benzophenone. It is also worth noting that the hydrogen-bonded structure of the benzophenone–alcohol mixed cluster is not suitable for hydrogen abstraction to take place because cleavage of the O–H bond in alcohols does not occur in the reaction. If the reaction proceeded in the mixed cluster, an α-hydrogen atom would be transferred. In contrast to the liquid and gas phase reactions, because of the restricted internal degrees of freedom, the hydrogen–bonded cluster may not be able to reorient to a geometry suitable for hydrogen abstraction.

The effective quenching of triplet benzophenone by 1,4-cyclohexadiene in the gas and liquid phases may be explained in terms of the fairly low bond energy of the C–H bond which is cleaved in the reaction. The bond dissociation energy has been reported to be 69.8 kcal mol^{-1} [34] while those of 2-propanol, ethanol, and triethylamine are 83 kcal mol^{-1}, 91 kcal mol^{-1}, and 94 kcal mol^{-1} respectively. In addition to this, it should be noted here that 1,4-cyclohexadiene has four equivalent hydrogen atoms. This fact probably makes it easy to take a specific structure which is suitable for the hydrogen abstraction to take place.

Although the amines react with benzophenone triplet in the gas phase rapidly, no ketyl radical fluorescence was observed in the photoexcitation of the benzophenone–amine mixed clusters. The reaction mechanism of the benzophenone–amine system is further discussed in the following section.

3.4. Exciplex and charge transfer emission in the photoexcitation of benzophenone–amine clusters

It is widely known that the reaction rates of triplet benzophenone with various amines are close to the diffusion-controlled rate and the yields of the reaction are very high in the condensed phase. Cohen and coworkers [16,17] proposed the following reaction mechanism to explain the effective photoreduction of triplet benzophenone by amines yielding BPK. First, an electron is transferred from an amine to the triplet state of benzophenone, forming a CT or ion pair complex. This complex is then quenched either by proton transfer generating BPK and amine radicals or by spin inversion followed by back electron transfer, resulting in the ground state benzophenone and amines. In this generally accepted mechanism, the CT interaction plays an important role, and the mechanism is represented as follows:

(1)
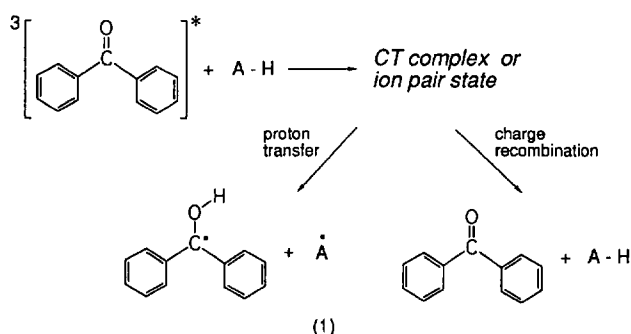
The quenching rate constant measurements presented in our previous investigation [25] have suggested that the CT interaction also plays a central role in the photoreduction process of benzophenone–amine systems in the gas phase.

Summarizing the above results, we can come to an idea that the CT interaction is also important in the decay process of photoexcited benzophenone–amine clusters. In recent years, CT reactions have been studied as one of the most important topics in the photochemistry of molecular clusters, where the absence of the complicated effect of the solvent environment may give us a better understanding of the factors involved in this reaction [35–38].

As mentioned in the previous section, jet-cooled bare benzophenone emitted long-lived phosphorescence by the excitation to the S_1 state and the phosphorescence was quenched in the benzophenone–1,4-cyclohexadiene mixed cluster. The phosphorescence intensity did not, however, alter with respect to that of bare benzophenone when ethanol or 2-propanol was used as a hydrogen donor.

Very different spectral features were observed when amines were used as a hydrogen donor. Fig. 2(c) shows the dispersed emission spectrum of benzophenone–triethylamine mixed cluster excited with 308 nm laser light. A broad and diffuse spectrum was observed. It is well known that benzophenone emits phosphorescence in the 380–600 nm region with a 1500 cm^{-1} C=O stretching progression in low temperature matrix or gas phase (Fig. 2(b)). The observed spec-
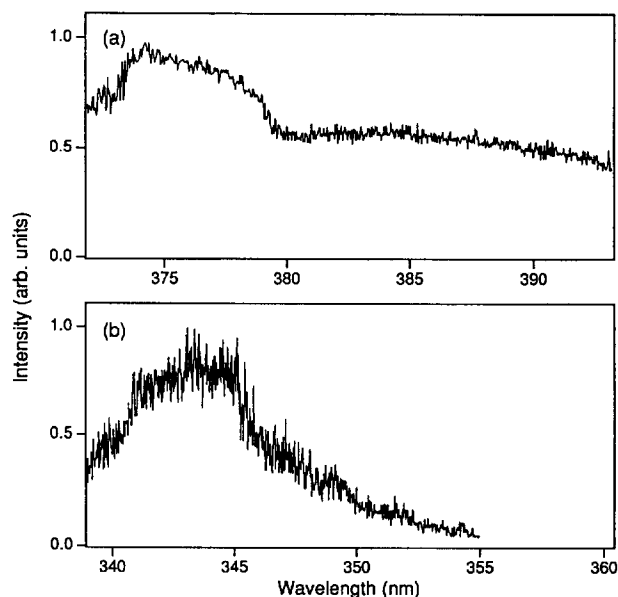

Fig. 3. (a) Excitation spectrum of benzophenone-N,N-dimethylaniline mixed cluster monitored at 430–700 nm. (b) Excitation spectrum of benzophenone-tri-n-butylamine mixed cluster monitored at 430–700 nm.

tral feature in the benzophenone–triethylamine system is similar to the envelope of the progression in the corresponding region.

The benzophenone-N,N-dimethylaniline system also gave a broad and structureless emission as shown in Fig. 2(d), which was red shifted relative to that of benzophenone or benzophenone–triethylamine systems. The excitation spectrum of benzophenone-N,N-dimethylaniline cluster obtained by monitoring the red-shifted emission is also indicated in Fig. 3(a). The cluster exhibits a new absorption band extending to longer than 390 nm in addition to that of the benzophenone–triethylamine system (Fig. 1(b)).

It has long been known that benzophenone and aromatic amines form CT complexes in a low temperature rigid matrix. Arimitsu et al. [39] studied the photochemistry of the benzophenone-N,N-dimethylaniline system at 77 K and observed ground state complex formation. They reported that the absorption band of the complex around the S_1 origin region broadened to the lower energy region with respect to that of bare benzophenone and the complex exhibited broad phosphorescence with a peak maximum around 490 nm. They also suggested that, since the peak wavelength tended to shift slightly toward the red as the ionization potential of the amine decreased, the phosphorescence state of the complex would be attributed to a CT state of the complex mixed with a locally excited (LE) state. As the spectral feature of the benzophenone–triethylamine system did not change appreciably from that of bare benzophenone, they concluded that the interaction in this case seemed to be very weak.

The observed spectral features of the benzophenone-N,N-dimethylaniline mixed cluster are in agreement with the results of the above investigation. The long-wavelength emission and broadened excitation spectrum of the benzophenone-N,N-dimethylaniline cluster are very similar to those
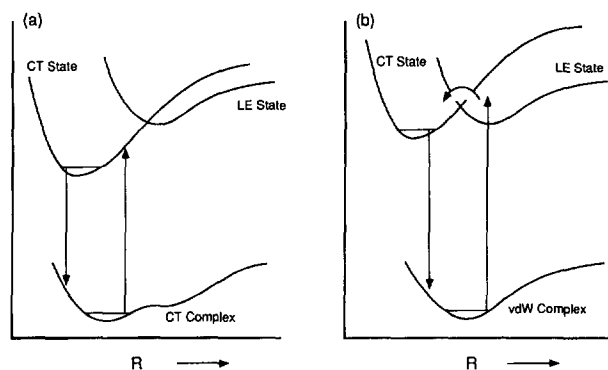
Fig. 4. Schematic diagrams showing the potential surfaces of (a) benzophenone-N,N-dimethylaniline and (b) benzophenone-tri-n-butylamine along the intermolecular coordinate.

of the CT complex observed in the rigid matrix at 77 K. From the above consideration, we can conclude that the benzophenone-N,N-dimethylaniline mixed cluster exhibits emission from a CT excited state of the CT complex formed in the ground state. Since the donor–accepter distance is shortened by the coulombic interaction in the CT state, the excited CT pair displays a structureless and red-shifted emission to reach the repulsive part of the ground state surface (Fig. 4(a)).

Fig. 2(e) indicates the dispersed emission spectrum of the benzophenone–tri-n-butylamine mixed cluster excited with 308 nm laser light. A similar red-shifted emission was observed when tripropylamine or tri-iso-butylamine was used as a hydrogen donor and its lifetime was a few tens of nanoseconds. In contrast to the benzophenone-N,N-dimethylaniline system, the benzophenone–tri-n-butylamine cluster did not fluoresce in the excitation of the origin region of bare benzophenone. As the excitation energy was increased from 355 nm, a gradual increase in emission intensity was observed (Fig. 3(b)).

The remarkable excess energy dependence of the intensity of the emission with large Stokes shift suggests the occurrence of transformation of the vdW complex to exciplex. Although the Franck-Condon state of the complex may be ascribed to the LE state rather than the CT state, rapid level crossing of the LE state to the CT state would take place followed by exciplex fluorescence (Fig. 4(b)). Although extensive studies have been carried out on the photochemical reaction of benzophenone–amine systems in the condensed phase, the exciplex emission of the benzophenone–aliphatic amine system has never been reported. The results of lifetime measurement suggest that the emission corresponds to that from the singlet exciplex.

3.5. Photochemical reactivity of benzophenone–amine clusters

Recently Miyasaka et al. [40] have studied the photoreduction process of excited benzophenone with several kinds of amines by means of picosecond–femtosecond laser photolysis and time-resolved transient absorption spectroscopy. According to their results in the benzophenone-N,N-dime-

thylaniline system, the charge recombination rate of the ion pair produced by the excitation of the CT complex formed in the ground state is much higher than that of the ion pair formed by the electron transfer between excited benzophenone and N,N-dimethylaniline at the encounter between excited benzophenone and N,N-dimethylaniline in solution. From the experimental results, they concluded that the benzophenone-N,N-dimethylaniline ion pair formed by the excitation of the ground state complex has a rather rigid structure that cannot reorient to adopt a suitable structure for the proton transfer before the recombination, while the ion pair formed by the encounter of excited benzophenone and N,N-dimethylaniline has a rather loose structure and a long enough lifetime to form a suitable geometry for the proton transfer. Although it is rather difficult to compare the structure and dynamics of ground state complexes formed in a supersonic free jet expansion and the liquid phase directly, we can expect that the quenching mechanism of triplet benzophenone in the liquid phase is applicable for the mixed cluster.

The vertical ionization potentials of N,N-dimethylaniline and tri-n-butylamine are reported to be 7.37 eV and 7.88 eV respectively. Since the ionization potential of tri-n-butylamine is higher than that of N,N-dimethylaniline, the CT interaction in the benzophenone–tri-n-butylamine system may not be strong enough to form the ground state CT complex. The reason why BPK formation after the excited state CT was not observed may be explained as follows. The geometric requirement for the charge transfer seems to be looser than that for the proton transfer. The spread of the electronic molecular orbital promotes the charge transfer, while sites suitable for the proton transfer are limited within a rather narrow region. The CT pairs not having suitable orientation and distance for the reaction to take place cannot reorient in the low temperature molecular cluster.

There is another acceptable explanation for the absence of BPK fluorescence in the benzophenone–triethylamine system. Recently Kajii et al. [41] have observed the hydrogen-bonded 1:1 complex of BPK and triethylamine in non-polar solvents by means of transient absorption spectroscopy. They found that the equilibrium constants for complex formation were $99 \pm 6 \, \text{M}^{-1}$ in cyclohexane and $37 \pm 4 \, \text{M}^{-1}$ in benzene, and that BPK in the complex was non-fluorescent while bare BPK had a relatively high fluorescence quantum yield under the same experimental conditions. According to their results, even if BPK is formed in the benzophenone–triethylamine mixed cluster, it may easily form a complex with the amine and excited BPK is quenched in the complex.

4. Summary

It has been expected that the study of chemical reaction in solute–solvent clusters enables us to obtain information on the mechanism of liquid phase reaction at a microscopic level without the complicated effects of the solvent environment. In this investigation, we have studied the photochemical reac-

tion of the molecular clusters of benzophenone and hydrogen donors formed in a supersonic free jet expansion.

It is found that photoreduction of benzophenone yields BPK in the benzophenone–1,4-cyclohexadiene mixed cluster. It has been confirmed that BPK is formed by the intracluster reaction after photoexcitation of benzophenone from the following features: (i) excited BPK is generated within the time width of the 308 nm laser pulse through two-photon process, which suggests that the reaction rate is very fast in a supersonic free jet expansion, and (ii) the action spectrum of BPK formation is in good agreement with the MPI spectrum of benzophenone–1,4-cyclohexadiene mixed clusters in the low energy portion of the $S_1 \leftarrow S_0$ transition of benzophenone.

Photoexcited benzophenone–N,N-dimethylaniline and benzophenone–tri-n-butylamine clusters exhibit structureless emission red-shifted with respect to phosphorescence of bare benzophenone. The excitation spectrum of benzophenone–N,N-dimethylaniline cluster obtained by monitoring the red-shifted emission suggests CT complex formation in the ground state. The remarkable excess energy dependence of the intensity of red-shifted emission in benzophenone–tri-n-butylamine cluster indicates the transformation of the vdW complex to exciplex.

Acknowledgements

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