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Intermolecular Hydrogen Transfer Reactions in the Excited States of EDA-Complexes of Benzophenone with Aromatic Amines at Low Temperature

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Electronic absorption and emission spectra of the mixtures of benzophenone and aromatic amines have been studied in rigid solutions. From absorption spectral measurements, it has been concluded that benzophenone as an acceptor forms the molecular complexes with various aromatic amines as donors. Emission spectra different from those of the component molecules were observed at longer wavelengths in the same systems. The maxima of the anomalous emission spectra of these systems were found to shift slightly to lower frequencies with the decrease in the ionization potentials of donor molecules. On account of their decay times, the emissions may be ascribed to the phosphorescence of benzophenone-aromatic amine complexes. Photolysis of benzophenone-aromatic amine complexes in rigid matrices always resulted in the appearance of the visible absorption spectrum of benzoketyl radical, together with ESR spectra, the analysis of which indicated that there is an interacting pair of radicals which is in the combined triplet ($S=1$) state. From the evaluation of the zero field splitting constants, the average distances between the interacting radicals were estimated. These results suggest that intermolecular hydrogen atom transfer from aromatic amines to benzophenone occurs, yielding the ketyl and aromatic amine radicals which lie close to each other. The reaction was found to proceed by way of the lowest excited triplet state of benzophenone.

The photochemical reactions of aromatic ketones as correlated with the nature of their excited electronic structures have been an interesting subject in photochemistry. As the results of numerous investigations, it has been confirmed that ketones at the lowest $^3(n,\pi^*)$ state were photoreduced easily, while those at the lowest $^3(\pi,\pi^*)$ state were scarcely photoreduced.[1] The spectra of the photochemical reaction intermediates of these ketones, such as the triplet species and the ketyl radicals, have been obtained.[2-6]

Recently, Cohen and co-workers found that the yields of benzopinacol and related compounds from benzophenone and its derivatives get higher in aliphatic amines.[7] They proposed that the photoreduction may be facilitated by initial electron transfer from the amine to the excited ketones, leading to charge transfer complexes or pairs of ions, followed by proton transfer and electron redistribution. However, no evidence has been presented suggesting the formation of charge transfer complexes between aromatic ketones in the excited state and aliphatic amines in the ground state.

We have reported in a short communication that the photoreduction of benzophenone (BP) in *N,N*-dimethylaniline (DMA) and 2-methyltetrahydrofuran (2MTHF) mixed solvent occurs easily, producing ketyl radical at the temperature of liquid nitrogen.[8] Since no ketyl radical was found appreciably by the photolysis of BP in 2MTHF solution at 77°K, we pointed out that the charge transfer complex formation between BP and DMA, suggested by an electronic absorption measurement, is a prerequisite for the formation of ketyl radical.

In the present paper, more detailed studies on the BP-aromatic amine systems will be reported, and the photoreactivity and photoreaction mechanism of the charge transfer complexes of BP with aromatic amines will be discussed in relation with the electronic structure and the charge transfer interaction in the excited molecular complex.

Experimental

Materials. BP was purified by recrystallization from ethanol and sublimation twice in vacuum. Aromatic amines

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used were aniline (AN), *N*-methylaniline (NMA), *N,N*-dimethylaniline (DMA), *N,N*-diethylaniline (DEA), and *N*-methyldiphenylamine (NMDPA). Aniline and *N*-methylaniline were purified by distillation under reduced pressure. All other amines were refluxed with acetic anhydride for several hours, and purified by fractional distillation. The amines were kept in a deoxygenated condition. 2-Methyltetrahydrofuran (2MTHF) was dried with sodium and purified by distillation. The solvent used as a transparent organic matrix was a mixture of 2MTHF and aromatic amine (3: 1 by volume). The concentration of the solution of BP was about 5×10^{-3}M in most experiments. All samples studied were deaerated by the usual method with an evacuating system.

Apparatus. Photolysis was carried out by use of a 500-W super high-pressure mercury lamp, combined with Toshiba UV-D25 and UV-35 glass filters transparent in the wavelengths from 350 to 400 nm. The absorption spectra were measured with a Cary 15 spectrophotometer. The emission spectra were measured with an Amino-Bowman spectrophotofluorimeter equipped with a photomultiplier of RCA Type R213. The emission decay time was measured by using a Xe-flash lamp and the discharge from a tungsten air gap having duration times of *ca.* 10 μsec and 100 nsec, respectively. ESR spectra were measured at 77°K by a JES-3BX spectrometer of Japan Electron Optics using X-band with 100 kHz field modulation.

Results and Discussion

Absorption Spectra of Benzophenone - Aromatic Amines. The electronic absorption spectrum of BP in the near ultraviolet region shows vibrational structures at low temperature, assigned to the (n,π^*) transition (Fig. 1a). On the other hand, the spectrum of BP in *N,N*-diethylaniline (DEA) shows a quite different shape in the same region at 77°K as shown by spectrum b in Fig. 1, which was obtained by subtracting the absorption of DEA. The difference between these two spectra is obviously much greater than to be explained by the solvent effects, but seems to suggest a molecular complex formation between BP and DEA. The spectrum of Fig. 1b then may be interpreted as an (n,π^*) band of BP broadened by the coupling with the intermolecular vibration within the complex. From the electronic nature of benzophenone, it seems most probable that BP acts as an electron acceptor and *N,N*-diethylaniline (DEA) acts as a donor. Similar spectra, which suggest the formation of complex, have been observed for BP in various mixed solutions of 2MTHF and aromatic amines at 77°K. As the electronic absorption spectrum of BP in triethylamine solution does not change appreciably from that of BP in 2MTHF at 77°K, the interaction in this case seems to be very weak.

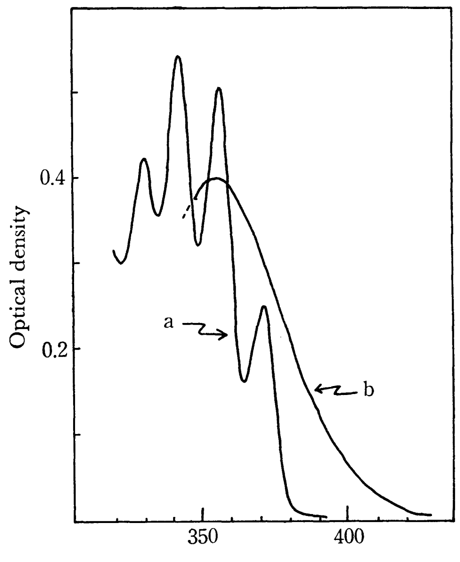

Fig. 1. Electronic absorption spectra of benzophenone in solvents at 77°K.
a: in 2-methyltetrahydrofuran, b: in *N,N*-diethylaniline

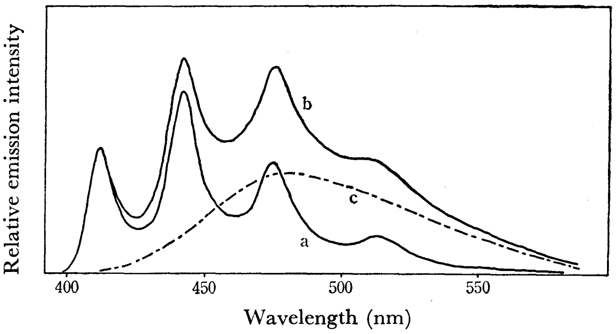

Fig. 2. Emission spectra of benzophenone and its complex with *N,N*-dimethylaniline at 77°K.
a: benzophenone in 2-methyltetrahydrofuran, b: benzophenone in 1 vol. *N,N*-dimethylaniline and 3 vol. 2-methyltetrahydrofuran, c: Emission of benzophenone-*N,N*-dimethylaniline complex obtained by subtracting spectrum a from b.

Emission Spectra of Benzophenone - Aromatic Amines. The phosphorescence spectrum of BP observed in 2MTHF solution at 77°K, having characteristic vibrational structures, is shown by spectrum a in Fig. 2. The emission spectrum of BP in a mixed solution (1 vol. DMA–3 vol. 2MTHF) at 77°K is shown by spectrum b in Fig. 2. From the comparison between these spectra, it may be seen that spectrum b is composed of spectrum a plus an additional emission lying at the longer wavelengths. Spectrum c is obtained by subtracting spectrum a from b. The emission spectrum c thus obtained is undoubtedly due to neither BP nor DMA. Moreover, the excitation spectrum obtained for the emission at 495 nm, where the emission is mostly composed of spectrum c, is fairly similar to that of the absorption of charge transfer complex of BP with DMA, while that observed for the emission at 412 nm is in good agreement with that of the absorption of BP at 77°K. Therefore, it may safely be concluded that the emission corresponding to curve c is due to BP–DMA complex.

The emission spectra of BP complexes with DMA, DEA, and NMDPA are shown in Fig. 3. The emission maxima show a tendency to shift to the longer wavelength with decreasing the ionization potentials of donor molecules. These results, together with the finding that these emission spectra shift to longer wavelengths with increase in the dielectric constant of the solvent indicate that the excited state of the BP complexes has the charge transfer nature.

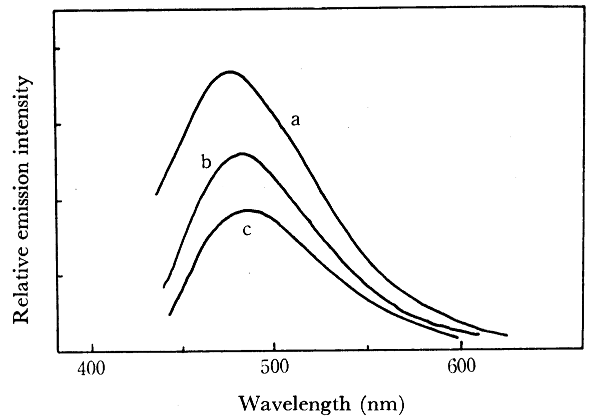

Fig. 3. Emission spectra of benzophenone complexes with various aromatic amines at 77°K.
a: *N,N*-dimethylaniline, b: *N,N*-diethylaniline, c: *N*-methyldiphenylamine

It was also found that the emission of the BP–DMA complex is quenched remarkably by ethanol used as a solvent instead of 2MTHF.

In order to get further information on the emission of the complexes, we also measured the emission decay-time. The phosphorescence of BP in 2MTHF decays exponentially with a decay time of 5 msec at 77°K. In the presence of aromatic amines at 77°K, the emission decay curve revealed that there are two components, one with a decay constant of 2.6 msec and another with a decay constant of *ca.* 10 μsec. The former may be assigned to an emission due to free BP, and the latter may be assigned to complexed BP, corresponding to the emission spectrum of Fig. 2c. It may be appropriate to conclude that the emission is due to the CT phosphorescence of the BP complex with the aromatic amine. The phosphorescent state of the complex may be mainly the locally excited $^3(n,\pi^*)$ configuration of BP mixed with the charge transfer configuration, since the peak positions of the phosphorescence spectra of complexes shift only slightly by changing the ionization potentials of donor molecules. The remarkable change of the phosphorescence life-time of BP-aromatic amine complex compared with that of free BP may be caused by the configuration interaction and spin-orbit coupling between the charge transfer and locally excited configurations. This problem is discussed in some detail by Iwata, *et al.*[9]

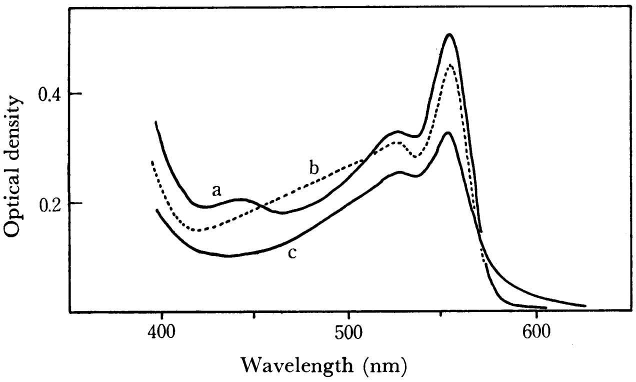

Fig. 4. Electronic absorption spectra of benzophenone complexes with aromatic amines irradiated at 77°K: a: benzophenone in *N*-methylaniline and 2-methyltetrahydrofuran, b: benzophenone in *N,N*-diethylaniline and 2-methyltetrahydrofuran, c: benzophenone in *N*-methyldiphenylamine and 2-methyltetahydrofuran

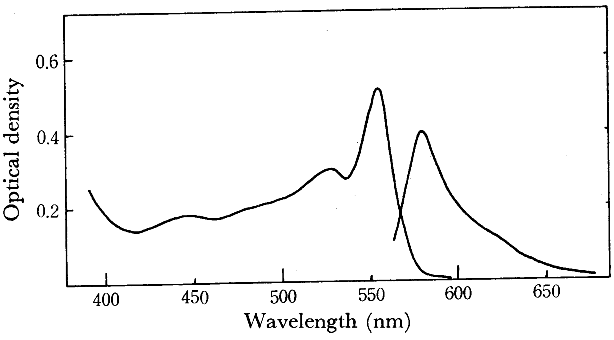

Fig. 5. Absorption and emission spectra of ketyl radical obtained by the photolysis of benzophenone-*N,N*-dimethylaniline complex at 77°K.

Hydrogen Abstraction of Benzophenone in Low Temperature Matrices. When the ternary solution of BP-aromatic amine-2MTHF was irradiated at the temperature of liquid nitrogen, the matrices colored red. The electronic absorption spectra after the photolysis of the solutions of BP–NMA, BP–DMA, BP–DEA, and BP–NMDPA in 2MTHF at 77°K are shown in Figs. 4 and 5. These absorption spectra disappeared after warming.

At a glance, these electronic absorption spectra are very similar to that of the ketyl radical obtained by flash photolysis of BP in ethanol or iso-pentane at room temperature.[5,6] Therefore, we may safely conclude that the main product is the ketyl radical. By more careful inspection of the spectra obtained, it is noticed that there is at least one more component, for instance, at about 445 nm in the case of DMA.

In the case of BP in a mixed solution of aniline and 2MTHF, the yield of ketyl radical was found to be about one tenth that for DMA and other aromatic amines mentioned above. It seems, therefore, that the presence of the alkyl group at the nitrogen atom is necessary for facilitating the hydrogen abstraction reaction.

The ketyl radical was also produced by the photolysis of BP in the solution of DMA and trichloro-trifluoroethane, the latter of which has no hydrogen atom to abstract. This result definitely indicates that the ketyl radical is produced as a result of hydrogen atom transfer from DMA to BP. The comparison of the absorption spectra shown in Figs. 4 and 5 with the absorption spectrum of ketyl radical obtained before[5] indicates that there are some components having absorptions in the region from 400 to 500 nm. In the case of the BP–DMA system, a clear peak is observed at 450 nm. In the present circumstances, these absorptions might be tentatively attributed to the radicals formed by the hydrogen abstraction from the alkyl group of the methylanilines; for example, $\phi\text{–N}\langle^{\text{CH}_3}_{\dot{\text{C}}\text{H}_2}$, in the case of BP–DMA.

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Since no ketyl radical was found noticeably by the photolysis of BP in the aniline-trichlorotrifluoroethane solution, it seems reasonable to assume that the hydrogen atom of the solvent is abstracted in the photoreduction of BP-aniline system.

These conclusions are confirmed by the measurement of ESR spectra and the excitation spectrum of the ketyl radical emission, which will be described in the following section.

When the solution of BP in a mixture of aliphatic amine, such as triethylamine, and ether was irradiated at 77°K, no ketyl radical was found appreciably. This result is in harmony with our observation of the absorption spectrum of the same system, which suggests no complex formation between BP and triethylamine in the ground state. It has also been found that photoreduction of BP proceeds only slightly in a solution of DMA and ethanol, contrary to the solution of DMA and 2MTHF.

Emission Spectrum of Ketyl Radical. We have tried to measure the luminescence spectrum of the ketyl radical using the photolysis products of BP complexes with aromatic amines. The emission spectrum observed in the case of the BP–DMA complex is shown in Fig. 5. The mirror symmetry relation between absorption and emission spectra can be seen. The excitation spectrum for the ketyl radical emission is in good agreement with the absorption spectrum of ketyl radical formed by the photolysis of BP–DMA complex, except that the absorption band with peak at 445 nm attributed to DMA radical was not found in the excitation spectrum.

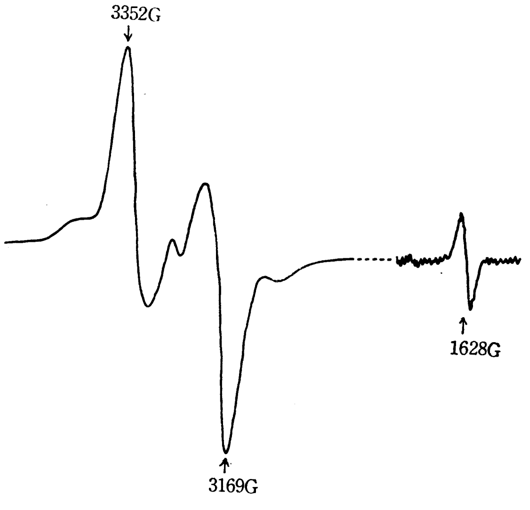

Fig. 6. ESR spectrum of benzophenone in *N*-methyldiphenylamine-2-methyltetrahydrofuran irradiated at 77°K: (ν=9143 MHz).

ESR Spectra of Irradiated BP-Aromatic Amine Complexes. Figure 6 shows a typical ESR spectrum obtained after the photolysis of BP in NMDPA–2MTHF rigid glass at 77°K. This spectrum can be interpreted clearly on the basis of randomly oriented radical pairs in the triplet state ($S=1$).[10] In some cases, the absorption due to a free radical was observed slightly at the region of $g=2$ in addition to the spectrum as shown in Fig. 6. Photolysis of BP complexes with NMA, DMA, and DEA in 2MTHF also showed the similar ESR spectra. In case where the fine structure constant E is assumed to be zero, the ESR spectrum of a triplet radical pair is predicted to consist of a band due to the forbidden $\Delta m=\pm 2$ transitions at magnetic field strength $H=h\nu/2g\beta$, and two pairs of bands due to the allowed $\Delta m=\pm 1$ transitions having separations D and $2D$ with the center at the magnetic field strength $H=h\nu/g\beta$. D represents here the zero field splitting constant and ν the resonance microwave frequency.

Table 1. Zero-field splitting constant (D) and average distance of the radical pairs between ketyl and aromatic amine radicals, calculated from observed ESR spectra of the irradiation products of benzophenone-aromatic amine complexes

Aromatic Amine	D (gauss)	R (Å)
Aniline	<95	<6.64
N-methylaniline	162	5.55
N, *N*-dimethylaniline	154	5.64
N, *N*-diethylaniline	128	6.00
N-methyldiphenylamine	166	5.48

The ESR spectra obtained in the present work unambiguously lead to the conclusion that radical pairs in the triplet state are obtained. Although there have been some investigations on the ESR spectra of radical pairs made of equal radicals,[11] the studies on radical pairs composed of different species are rather scarce.[12] Table 1 shows the D values obtained from the experimentally observed separation corresponding to $2D$. One can see from Table 1 that the zero field splitting constants change from one to another. This result suports our previous conclusion that the ketyl radical is produced as a result of intermolecular hydrogen atom transfer from aromatic amine to BP, because, if the hydrogen atom is abstracted from the solvent molecule, the D values should be the same in all systems.

The ESR spectrum observed for photolyzed BP-aniline complex is somewhat different from that of BP–NMDPA complex at 77°K as shown in Fig. 7, the zero-field splitting constant being about 95 gauss, at most, which is fairly small compared with other values obtained in the present work. This small separation, together with the apparent absence of the weak absorption bands corresponding to the $2D$ separation, might arouse the suspicion that the spectrum is not due to the triplet species. However, it seems unlikely that this spectrum is due to separated free radicals ($S=1/2$), because a splitting of about 95 gauss is inadequately large for an ESR spectrum of any aromatic free radicals. Moreover, it was also confirmed that the spectrum is not ascribed to the solvent radicals produced by a

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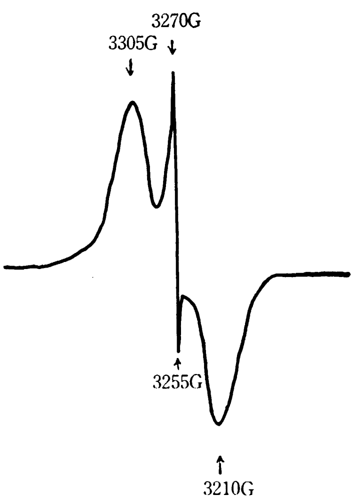

Fig. 7. ESR spectrum of benzophenone in aniline-2-methyltetrahydrofuran irradiated at 77°K: (ν=9135 MHz). The sharp ESR signal shown by arrows at 3270 G and 3255 G seems to be a radical species formed by dark reaction, because it was obtained for the BP-aniline-2MTHF mixture before irradiation.

photosensitization reaction. The most plausible interpretation for this spectrum is that the ketyl radical formed by direct hydrogen abstraction of BP from 2MTHF intracts with a 2MTHF radical. This is consistent with our experimental result described before that BP–AN complex in trichlorotrifluoroethane does not yield ketyl radical detectably.

The average distance R(Å) between radicals can be calculated using a point-spin-density approximation discussed by Kurita[13] as follows:

$$R^3(\text{Å}) = \frac{27800}{D(\text{gauss})}$$

The R values thus obtained are summarized in Table 1. In the case of BP–NMDPA complex, the average distance is the shortest of all cases. This might, however, be due to the theoretical approximation applied to a radical pair, because the unpaired electrons are distributed over the molecular framework of the component radicals, resulting in a slight underestimation of the average distance between radicals as the radicals get larger.

It seems curious that two radicals coexist stably at the temperature of liquid nitrogen within a short distance from each other as concluded in the present work. The reason for this may be attributed to a large resonance stabilization of these radicals owing to the delocalization of the unpaired electrons preventing a chemical bond formation or back transfer of hydrogen atom.

Photochemical Reaction Mechanism and Reactivity of BP Complexes. As is described in previous sections, we found that the photoreduction of BP undergoes easily in the solution of aniline derivatives and 2MTHF at 77°K. But the use of ethanol as the solvent instead of 2MTHF retards it to a great extent. Correspondingly, it has been found that the phosphorescence of BP complexes with aromatic amines is quenched remarkably by ethanol. This further gives support to the conclusion that photoreduction of the ketone in BP complexes undergoes through the triplet state of BP–aromatic amine complex.

In the case of BP–aniline complex, it has been concluded that hydrogen atom is abstracted from the solvent instead of aniline. As the yield of ketyl radical in this case is only about one tenth that in other cases, the hydrogen abstraction from solvent to BP is thought to be very slow. It seems plausible to attribute the difference in the photo-reactivity between aniline and other donors, to the presence of the *N*-methyl group. Although the reason for this effect of methyl group is not quite clear, it may be attributable to a steric circumstance for *N*-methylanilines, bringing a hydrogen atom at a closer position to the oxygen atom of BP in the complex.

The last question we have to answer is why photoreactivity of BP is much more enhanced in the molecular complex than in free BP. As mentioned before, the photoreduction of BP complexes undergoes most probably *via* the lowest triplet state, which is mainly of the locally excited $^3(n,\pi^*)$ character, with inclusion of a slight charge transfer character. That $^3(n,\pi^*)$ state is the state which undergoes hydrogen abstraction was demostrated by a paper by Porter and Suppan.[14] Our subsequent paper will give evidences for the necessary character of excited states for systems more directly related with the present problem. Therefore, the hydrogen abstraction reaction must essentially be a radical reaction and such a process as the electron transfer followed by proton jump from the aniline derivative to BP is unlikely. The reason why the hydrogen transfer is fascilitated by a comlpex formation between the anilines and BP may be as follows: 1) The binding of the complex may realize a geometric configuration where the hydrogen of the aniline derivative is situated at a position better for the abstraction reaction. 2) A slight mixing of the charge transfer character in the $^3(n,\pi^*)$ state may cause a change in the electron distribution, for example, a change in the orbital exponent of the oxygen n-orbital, which decreases the activation barrier for the hydrogen abstraction reaction.

The authors wish to thank Professor Koichi Ito for discussions on the interpretations of the ESR spectra.

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