A Brønsted plot of the dehydration rate constants is shown in Figure 11. The points for base catalysis by H₂O and OH⁻ define a line yielding a Brønsted β of 0.34. This is essentially the same value reported by Bruice and Bruice for the catalytic effect of oxyanion bases on enolization, but the dehydration rates are displaced to higher values by 1.1 log units. Therefore, in these "normal" buffers dehydration is likely to be always faster than enolization regardless of buffer concentration and no rate crossover will be observed.

Also, plotted in Figure 11 are the rate constants determined here for tertiary amine-catalyzed dehydration together with those taken from ref 9 which have been assigned to carbinolamine formation. It is seen that the two sets of constants are virtually identical, once again providing evidence that the rates of the same process have been measured in these two studies.

The rate constants found for triethylamine and quinuclidine catalysis are observed in Figure 11 to lie close to the line drawn through the points for H₂O and OH⁻, which appear to define an upper limit on catalysis. The other tertiary amines show sharply decreasing catalytic effectiveness as their basicity decreases. The dashed line drawn through the tertiary amine data points has a slope of 1.4. Although tertiary amine bases are excellent catalysts for tautomerization, unless they are strongly basic they are seen to be poor catalysts for the solvational processes. Thus, in tertiary amine buffers at low concentration, dehydration rates are faster than those for tautomerization, but as the tertiary amine con-

centration increases, the enolization velocities become markedly faster and eventually surpass the dehydration rates. It is this behavior which accounts for the change in slope noted by Bruice and Bruice.[9]

The difference in sensitivity to tertiary amines likely reflects the operation of two essentially different mechanisms. In enolization, the tertiary amine is required to approach the substrate closely in order to promote the removal of a proton from the carbon atom
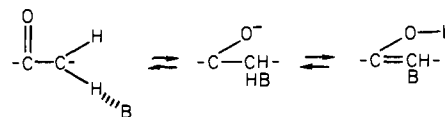
while in hydration an intervening H₂O molecule likely is required
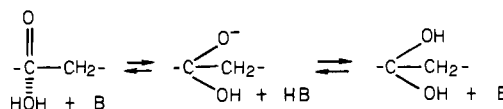
An OH⁻ ion could, of course, directly attack the carbon atom of the carbonyl group.

Exciplex Emissions of Intra- and Intermolecular Benzophenone and *N*,*N*-Dimethylaniline Systems

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Abstract: Emission spectra of intra- and intermolecular exciplex systems of benzophenone and *N*,*N*-dimethylaniline were studied in detail at low temperature. Two new emissions were observed for the first time in the present work in addition to the well-known phosphorescence of the CT complex formed in the ground state. The first emission has a lifetime of a few tens nanoseconds, which is common to intra- and intermolecular systems. The second emission with a longer lifetime than that of the first one is obtained only in the case of the intramolecular system. A possibility that these emissions are due to fluorescent products was examined. Considering solvent, temperature, and concentration dependences of these emissions, it is proposed that the first and the second emissions are due to the singlet and the triplet exciplexes, respectively. Dynamic behaviors and geometrical structures of these exciplexes are discussed.

Introduction

Hydrogen abstraction by the triplet benzophenone from amines is well-known as a typical organic photochemical reaction which proceeds with a large rate and a high quantum yield. With examination of the kinetic data, it has been concluded that this reaction occurs through the triplet exciplex state.[1] Namely, charge transfer (CT) from amines to the triplet ketone is induced at first, which is followed by proton transfer. More direct information on this CT intermediate state has been given by the following two types of studies. The first is flash-photolysis studies giving absorption spectra of transient species. The benzophenone anion and the amine cation dissociated from the exciplex were first observed in strongly polar solvents.[2] Detailed laser-photolysis studies confirmed the competing processes of ionic dissociation

and proton transfer in the CT state formed immediately after quenching reaction.[3] Rapid electron transfer was also demonstrated for the intramolecular benzophenone–*N*,*N*-dimethylaniline (DMA) system by a picosecond laser-photolysis method.[4] However, no distinct absorption spectra of the triplet exciplex have been reported at the present stage of investigation.

The other study on the CT intermediate is to observe emissions of the relevant CT complexes stable in the ground state. Arimitsu

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(1) S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, **73**, 1141 (1973). R. S. Davidson in "Molecular Association", Vol. 1, R. Foster, Ed., Academic Press, London, 1975.

(2) R. F. Bartholomew, R. S. Davidson, P. F. Lambeth, J. F. McKellar, and P. H. Turner, *J. Chem. Soc., Perkin Trans. 2*, **2**, 577 (1972).
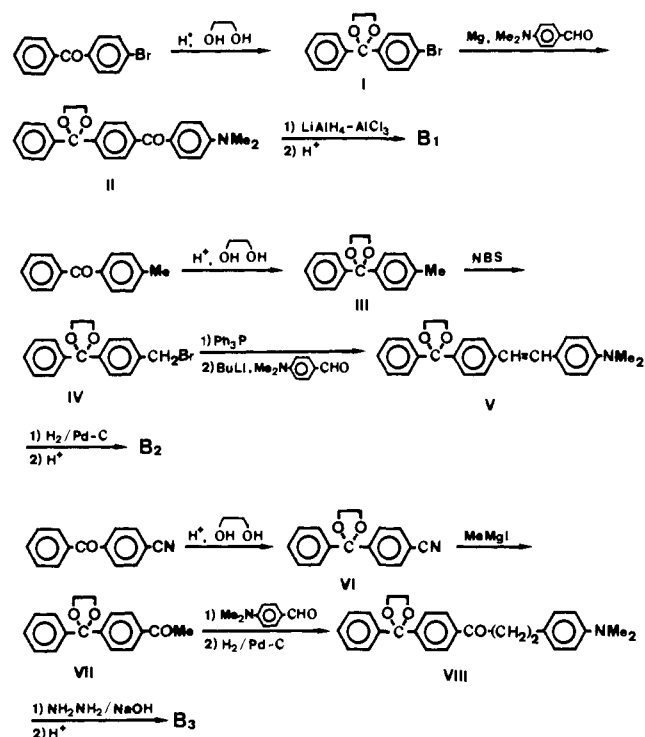
(3) S. Arimitsu and H. Masuhara, *Chem. Phys. Lett.*, **22**, 543 (1973); S. Arimitsu, H. Masuhara, N. Mataga, and H. Tsubomura, *J. Phys. Chem.*, **79**, 1255 (1975).

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Scheme I

Figure 1. Absorption spectra of B_n and its reference compounds at room temperature: $B_1(—)$, $B_2(---)$, $B_3(-\cdot-)$, and the sum of 4-methylbenzophenone and *N,N*-dimethyl-4-methylaniline ($\cdots$). Solvents are (A) methylcyclohexane and (B) ethanol.

Figure 2. Emission spectra of B_n systems ($\cdots$) and 4-methylbenzophenone phosphorescence (—) at 77 K: (A) B_2 in methylcyclohexane (a), MTHF (b), and ethanol (c); (B) B_1 (a), B_2 (b), and B_3 (c) in *n*-butyronitrile.

and Tsubomura reported for the first time that excitation of CT complexes formed between benzophenone and aromatic amines such as DMA, *N,N*-diethylaniline, and *N*-methyldiphenylamine gives CT phosphorescence at 77 K.[5] Although similar results were also given by time-resolved emission spectroscopy,[6,7] an exciplex emission has never been reported until now.

In order to detect exciplex emissions, we have investigated intra- and intermolecular benzophenone–DMA systems at low temperature and found out two new emissions. Here we report these results, examine them from the viewpoint of an artifact, and discuss their dynamic behaviors.

Results

(A) Intramolecular Benzophenone–DMA System. Syntheses. The following intramolecular exciplex model compounds have been studied: 4-(*p*-(*N,N*-dimethylamino)benzyl)benzophenone, 4-[2-(*p*-(*N,N*-dimethylamino)phenyl)ethyl]benzophenone, and 4-[3-(*p*-(*N,N*-dimethylamino)phenyl)propyl]benzophenone. These compounds are abbreviated as B_n, where *n* represents the meth-

B_n
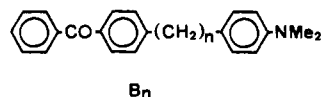
ylene number of the chain connecting benzophenone and DMA moieties. Syntheses of B_1–B_3 were carried out by the usual methods as shown in Scheme I. Condensation reaction of I with *p*-(dimethylamino)benzaldehyde was troublesome. It proceeded neither with magnesium in the usual conditions for Grignard reaction nor with phenyl- or butyllithium. With use of activated magnesium,[8] the reaction proceeded smoothly to give unexpected oxidation product II. Presumably the oxidation reaction occurred while the magnesium addition complex was decomposed.

Absorption Spectra. In Figure 1, absorption spectra of B_n compounds are compared with the sum of the bands of 4-
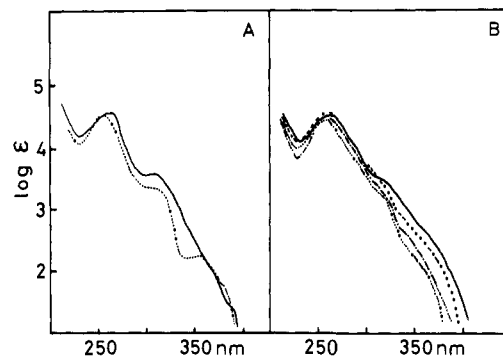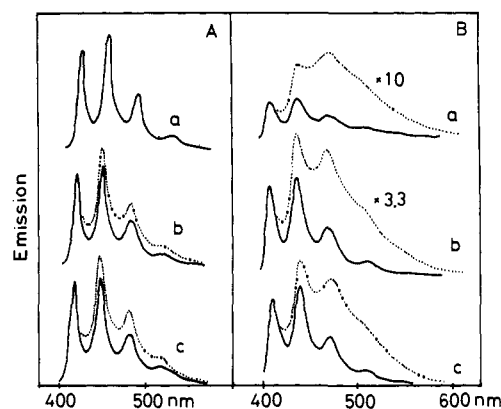
methylbenzophenone and 4-methyl-*N,N*-dimethylaniline. Observed spectra of intra- and intermolecular systems in methylcyclohexane are identical with each other except for B_1. The band intensity of the latter compound in the wavelength region of 320–350 nm is a little stronger compared with the case for the intermolecular system, although the position of the 0–0 band is unchanged. When ethanol is the solvent, the bands of B_n systems observed in the region of 300–400 nm show the red shift and its intensity is increased compared with the case for the intermolecular reference system. These differences decrease as *n* increases. These characteristics at room temperature hold also at 77 K, although vibrational structures are observed at low temperature.

Emission and Excitation Spectra at Low Temperature. Since no emission was observed with conventional spectrophotofluorometer at room temperature, the measurements were performed at low temperature. Rigid solvents used were methylcyclohexane, EPA (volume ratio of diethyl ether, isopentane, and ethanol is 5:5:2), MTHF, ethanol, and *n*-butyronitrile. With examination of the emission data of B_n compounds, these solvents are classified into two groups as shown in Figure 2. One includes methylcyclohexane and EPA in which benzophenone phosphorescence is the only emission observed. In other solvents measured spectra are different from those of monomer phosphorescence. The difference spectra obtained by normalizing the intensity at the 0–0 band of benzophenone phosphorescence are broad and structureless and independent of *n* except in *n*-butyronitrile. In the latter solvent the intensity of the new broad emission decreases as *n* increases. Excitation spectra of this broad band agree with absorption spectra of corresponding B_n compounds. As the temperature is increased in ethanol and *n*-butyronitrile, vibrational structure due to benzophenone monomer phosphorescence decreases and the new broad emission band shows an increase in intensity and a red shift to the wavelength region of $\sim$540 nm. The temperature at which monomer phosphorescence disappears is 110, 120, and 130 K for B_1, B_2, and B_3, respectively.

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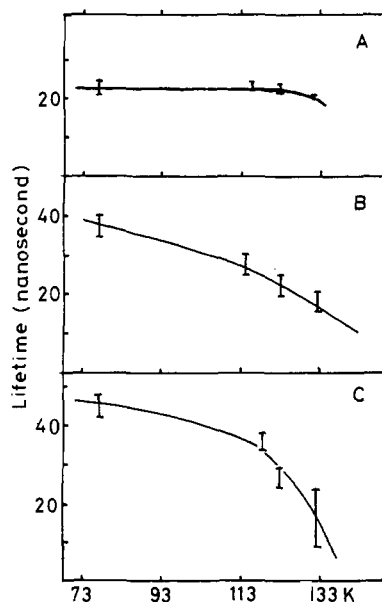(8) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974).

Figure 3. Temperature effect on emission decay time of B_n compounds in ethanol: (A) B_1 observed at 500 nm, (B) B_2 at 540 nm, and (C) B_3 at 540 nm.
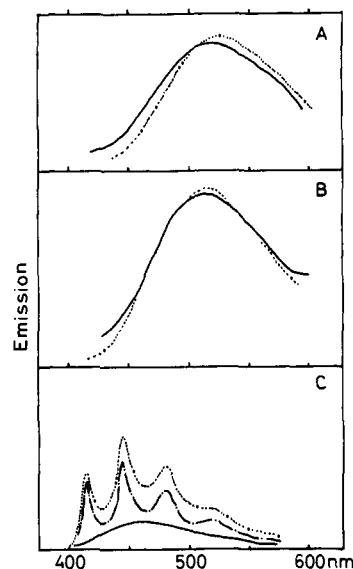

Figure 4. Temperature dependence of emission spectra of B_1 in ethanol: (A) 122—125 K, (B) 117—119 K, and (C) 77 K. Total emission (···), benzophenone monomer phosphorescence (-·-), and time-resolved spectra (—) obtained immediately after N_2 gas laser excitation.

Figure 5. Temperature dependence of emission spectra of B_2 in ethanol: (A) 127–128 K, (B) 120–122 K, and (C) 77 K. Notations are the same as given in Figure 4.

Figure 6. Temperature dependence of emission spectra of B_3 in ethanol: (A) 135 K, (B) 114 K, and (C) 77 K. Notations are the same as given in Figure 4.

Temperature Effect on Emission Lifetimes. Short emission lifetimes obtained by method I (see Experimental Section) are plotted against temperature, as given in Figure 3. The B_1 system shows a small change up to 133 K while the lifetimes of B_2 and B_3 decrease continuously as the temperature is raised. The temperature effect is more pronounced in the compounds with larger n. In order to detect a slow decay component, whose intensity may be weak, we applied method II by using output resistors with various values larger than 50 Ω. However, we could not detect any other components giving lifetimes longer than the above fast components except monomer phosphorescence ($\sim$5 ms).

Time-Resolved Emission Spectra. With use of rise and decay curves observed at various wavelengths, transient emission spectra with short lifetimes were obtained. In Figures 4–6, these spectra are shown and compared with total emission spectra which were obtained by using a 500-W Xe lamp under the same optical conditions. At 77 K, difference spectra between total emission and benzophenone monomer phosphorescence spectra are in agreement with transient emission, which holds for all B_n com-
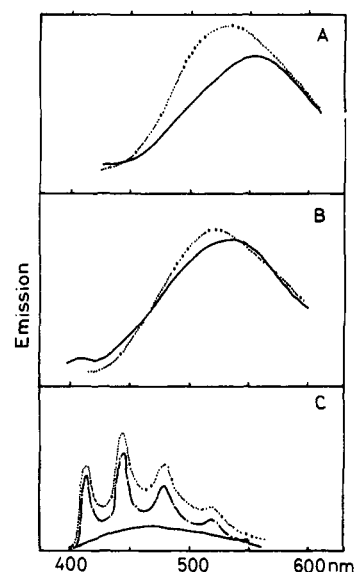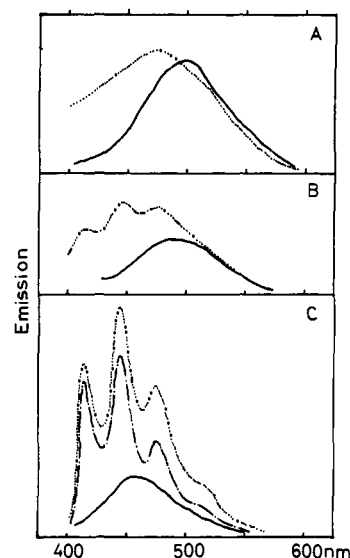
pounds. As the temperature is raised, benzophenone phosphorescence disappears and only broad and structureless emissions are observed. In the case of the B_1 system, the transient and difference spectra are almost identical with each other at 117–125 K. Similar results have been observed for the B_2 system at 120–122 K, while the transient spectra give a peak at longer wavelength compared to total emission spectra at 127–128 K. This indicates that the latter spectra consist of the above transient and new emissions. Either these new species have a slow rise or their lifetime is 1 order of magnitude longer than that reported above, since no decay except those of the transient and monomer phosphorescence spectra was observed by method II. Almost the same results have been obtained for the B_3 system.

Hydrogen Abstraction. With use of the 500-W Xe lamp, the n–π^* bands of the benzophenone component of B_n compounds were excited in ethanol at 77 K. However, no absorption spectral change due to ketyl radical formation was observed.

(B) Intermolecular Benzophenone–DMA System. Under similar experimental conditions we have investigated the intermolecular systems, changing the DMA concentration. Volume ratio of DMA to solvent ethanol were adjusted to be 1:6, 1:9, 1:39, and 1:159,
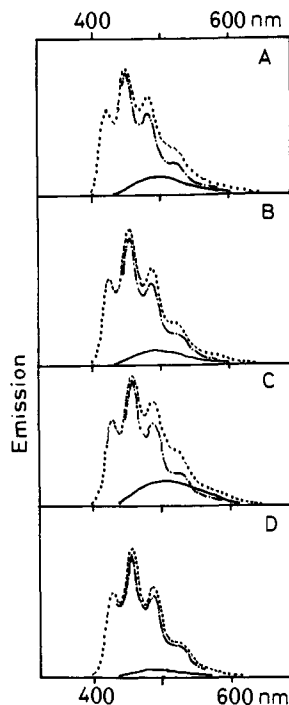
Benzophenone Exciplex Emissions

J. Am. Chem. Soc., Vol. 103, No. 3, 1981 637

Figure 7. Emission spectra of intermolecular benzophenone-*N,N*-dimethylaniline system at 77 K. Total emission (···), benzophenone monomer phosphorescence (−·−), and their difference spectra (—) obtained by normalizing their intensity at the 0–0 band: (A) 1D–6M, (B) 1D–6E, (C) 1D–39E, and (D) 1D–159E.

Table I. Emission Decay Time of the Intermolecular Benzophenone-*N, N*-Dimethylaniline System at 77 K

systems	fast decay compoenet,[a] ns 500 nm	slow decay component,[b] μs 480 nm
1D–6M	weak	11
1D–6E	weak	12
1D–9E	14	
1D–39E	20	8
1D–159E	18	7

[a] Method I, ±2 ns. [b] Method II.

and these samples are abbreviated as 1D–6E, 1D–9E, 1D–39E, and 1D–159E, respectively. When MTHF is used as a solvent, the notation is 1D–6M. The concentration of benzophenone is 10^{-3} M.

Absorption Spectra. The solutions show a new absorption band extending to ~450 nm in addition to the sum of bands of benzophenone and DMA. The intensity of this band decreases with decrease of DMA concentration; however, it is still observed in the case of the 1D–159E system. Since these results are identical with the ones published before,[5] it is concluded that the present band is due to the CT complex formed between benzophenone and DMA.

Emission Spectra. In Figure 7 emission spectra of 1D–6M, 1D–6E, 1D–39E, and 1D–159E systems are shown. Since the spectral shape is a little different from that of the monomer benzophenone phosphorescence, we normalized the intensity at the 0–0 band and subtracted the monomer phosphorescence from the observed spectra. The obtained difference spectra are broad and structureless and show a peak at 470–500 nm. This new emission is similar to the phosphorescence spectra of the CT complexes reported already.[5-7] This emission disappears with a little increase in temperature.

Lifetime Measurements. The rise and decay curves of the present emissions were measured by using a N_2 gas laser as an exciting light source and lifetimes obtained at 77 K are listed in Table I. The emissions show two-component decays. The slow process, observed by method II, occurs in about 10 μs, and the
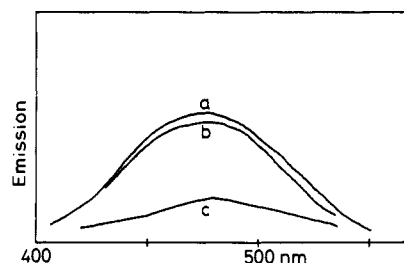

Figure 8. Time-resolved emission spectra of intermolecular benzophenone-*N,N*-dimethylaniline at 77 K, which is obtained at 60 ns after N_2 gas laser excitation. Systems are 1D–159E (a), 1D–39E (b), and 1D–9E (c).

value of its lifetime decreases with decrease of DMA concentration.[9] Since the value of the 1D–6M system agrees with that of the phosphorescence of CT complexes reported elsewhere,[5] the slow emissions are considered to be due to the triplet state of benzophenone–DMA complexes. The other decay process, which is 3 orders of magnitude faster than the above phosphorescence, was observed for the first time in the present work (method I). In the cases of 1D–9E, 1D–39E, and 1D–159E, lifetime of a few tens nanoseconds was observed, while it was hardly detected in the systems with high concentration of DMA. Namely, the intensity of the fast component becomes stronger as DMA concentration is decreased. Monomer phosphorescence of benzophenone was, of course, observed in addition to the above emissions and its lifetime was about 5 ms. On the basis of these lifetime data the difference spectra given in Figure 7 are considered to be the superposition of the phosphorescence of CT complexes and the new broad band with a short lifetime.

Time-Resolved Emission Spectra at 77 K. Using emission decay curves observed at various wavelengths, we have obtained time-resolved emission spectra at the 10-ns time range. In Figure 8 the spectra given at 60 ns after the beginning of laser oscillation are shown. In the cases of 1D–159E, 1D–39E, and 1D–9E systems, a broad band with a peak at 475 nm was obtained.

Hydrogen Abstraction. It is well-known that photoexcitation of benzophenone–DMA CT complexes leads to ketyl radical formation even at low temperature.[5] This is also confirmed in all of the present intermolecular systems.

Discussion

A Possibility That the Observed Emissions Are an Artifact. The primary photoprocesses of benzophenone have been extensively studied,[1-7,10] and effects of the unstable photoproduct are discussed in detail.[11] Steel et al. reported that irradiation of benzophenone in hydrogen-donor solvents leads to the formation of a light-absorbing transient which has an absorption band similar to that of the original molecule and decays in a few days.[12] This transient gives structureless emission with a lifetime of 10 ns.[13] Furthermore dynamic behaviors of intramolecular ketone–amine systems are sometimes affected by intermolecular interaction, which was demonstrated in the studies on the β-naphthyl-γ-(dimethylamino)propyl ketone system.[14] Similar reactions might occur in our systems, which leads to a possibility that the present new emissions are an artifact. However, this is excluded from the following viewpoints. (i) All the emissions reported here are

(9) A DMA concentration dependence of the lifetime is not considered here, since the purpose of this is to report and discuss new emissions.

(10) For example: J. H. Marshall, *J. Phys. Chem.*, **78**, 2225 (1974); M. A. Winnik, *Acc. Chem. Res.*, **10**, 173 (1977); R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **82**, 2064 (1978).

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(12) J. Chilton, L. Giering, and C. Steel, *J. Am. Chem. Soc.*, **98**, 1865 (1976).

(13) M. A. Winnik, private communication. 1980.

observed only at low temperature, while the data on the above photoproducts[11-14] were obtained at room temperature. (ii) Emission lifetime measurements by method I do not show an accumulation effect caused by repetitive exciting pulse. (iii) Exposure of B_n compounds to light at low temperature leads to no irreversible change of absorption spectra. (iv) The emission of B_n compounds with short lifetime shows an interesting solvent dependence which is inconsistent with Steel's results.[12]

Another possible impurity emission may be due to benzophenone ketyl radical. As reported before,[5] this emission is observed by exciting the ketyl radical produced by photolyzing the present intermolecular benzophenone–DMA system at 77 K. This fluorescence peak is at about 570 nm, and a mirror-symmetry relation to the corresponding absorption band is observed.[15] However, the spectral shape, peak energy, and their temperature and solvent dependences of ketyl radical fluorescence are different from those of the present new emissions. Therefore we consider that the observed results are not an artifact.

Dynamic Behaviors of Intramolecular Benzophenone–DMA Systems. Since the broad and structureless spectra of new emissions are similar to those of the phosphorescence of the intermolecular benzophenone–DMA CT complexes, it is considered that the present emissions have CT character. This is supported also by the recent picosecond laser-photolysis studies on these B_n compounds[4] which confirmed rapid intramolecular electron transfer in acetonitrile. First we summarize the experimental results showing the nature of the emission at 77 K. (i) Although rigid solvents such as methylcyclohexane and EPA give only benzophenone monomer phosphorescence, a new emission was observed in the solvent with high micropolarity such as ethanol, n-butyronitrile, and MTHF. (ii) In n-butyronitrile the relative contribution of this emission increases with decrease of n. (iii) Excitation spectra of the new emission agree with absorption spectra of the corresponding B_n compounds. (iv) Their lifetimes are about a few tens nanoseconds. (v) Steady-light illumination does not give ketyl radicals. Results i, ii, and iii cannot be interpreted from the viewpoint of intramolecular ground-state complex formation. This is consistent with v, since the ketyl radical is observed by exciting the CT absorption band of intermolecular CT complexes. We consider that the present new emission is due to the exciplex state. Since electron transfer is induced by a weak interaction, photoexcitation of these compounds may lead to the formation of the CT state and it may fluoresce in the same geometrical structure. Here we call this state the 1st exciplex.

Characteristics of another new emission, which is observed at a little higher temperature than 77 K, are given as follows. (i) B_2 and B_3 give this emission. (ii) The lifetime is at least 1 order of magnitude longer than that of the first exciplex, or a slow formation process is expected. (iii) This is observed only when the solvents are a little softened and the benzophenone monomer phosphorescence has disappeared. The last result means that the molecular reorientation motion is required to form the new state. Electron transfer occurs after conformational change, and the formed CT state may take more stable structure. Therefore this state has a different geometrical structure from that of the above first one and is called the second exciplex. In what follows we discuss the spin states of these exciplexes.

(A) A possibility that both exciplexes are in the singlet state means that electron transfer is completed during the short fluorescent lifetime of 10^{-11} s.[16] However, it is difficult to assume this fast transfer, since the formation of the intramolecular triplet ion pair was directly confirmed in acetonitrile even at room temperature.[4] In general electron transfer under the latter condition is believed to be faster than that at the present low tem-
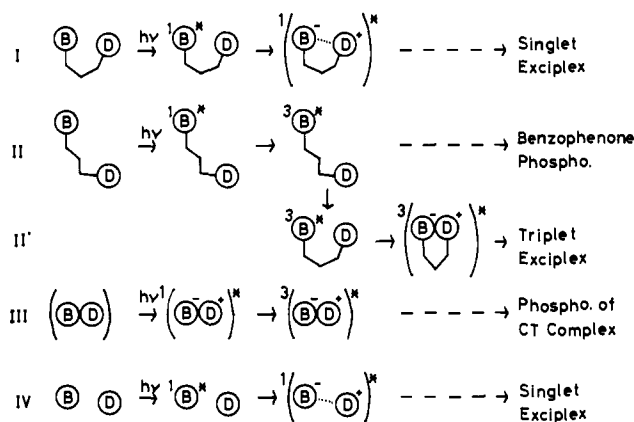
Figure 9. Schematic diagram showing dynamic behaviors of benzophenone-N,N-dimethylaniline systems. As an example B_2 and B_3 are given in I and II, respectively. Parentheses indicate that both component molecules interact with each other. See text.

perature. Therefore this possibility is excluded.

(B) The intersystem crossing of benzophenone occurs quite rapidly, and electron transfer might be possible only in the triplet state of benzophenone. The formed exciplexes are in the triplet spin state, and their difference is considered to be due to different geometrical structures. In this case it is difficult to explain the short lifetime of the first exciplex which is observed even at 77 K.

(C) Since fluorescence lifetime of 10 ns indicates in general that the luminescent state is in the singlet state, we propose that the first and second exciplexes are the singlet and triplet ones, respectively. Considered formation processes of both exciplexes are given schematically in Figure 9. In the case of B_2 and B_3, electron transfer may occur from DMA to the excited singlet benzophenone when a distance between both moieties is rather short (Figure 9,I). On the other hand intersystem crossing will overcome electron transfer in an extended form (Figure 9,II). Since the triplet state has a long lifetime, conformational change during the lifetime is possible at a little higher temperature. The structural change from an extended to a rather folded one induces electron transfer and formed CT triplet state takes the most stable conformation (Figure 9,II'). In the case of the B_1 system the emission spectra of the singlet exciplex may not be different from those of the triplet one, since the degree of conformation change is low.

An Intermolecular Benzophenone–DMA Exciplex. Characteristics of the new emission of the intermolecular system at 77 K are summarized as follows. (i) This emission is observed when the CT complex is depressed by lowering the DMA concentration. (ii) Their lifetimes are a few tens nanoseconds. These results suggest that the emission corresponds to the singlet exciplex of B_n compounds. There may be a number of benzophenone–DMA pairs whose distance is a little longer than that of the CT complex, and their relative orientation is random. Photoexcitation induces CT interaction, and fluorescene is emitted in the same geometrical structure (Figure 9,IV). It is considered that this emission is usually masked by the phosphorescence of the CT complexes (Figure 9,III) and can be observed only under the present condition of DMA concentration. At a little higher temperature than 77 K reorientational motion may lead to radiationless transition involving some reactions and gives no emission corresponding to the triplet exciplex of B_n compounds. The methylene chains of the latter compound restrict the molecular motion, which makes it possible to observe the triplet exciplex emission.

Summary. We have described dynamic behaviors of intra- and intermolecular benzophenone–DMA systems at low temperature and proposed the singlet and triplet exciplexes in addition to the phosphorescence of CT complexes. Although these emisions show similar broad and structureless spectra, their lieftimes and dependences upon temperature, solvent, and the number of methylene chain are different from each other. These indicate that geo-

(14) P. J. Wagner and D. A. Ersfeld, *J. Am. Chem. Soc.*, **98**, 4515 (1976).

(15) B. W. Hodgson, J. P. Keene, E. J. Land, and A. J. Swallow, *J. Chem. Phys.*, **63**, 3671 (1975); K. R. Naqvi and U. P. Wild, *Chem. Phys. Lett.*, **41**, 570 (1976).

(16) R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162 (1974); R. W. Anderson, Jr., R. M. Hochstrasser, H. Lutz, and G. W. Scott, *ibid.*, **28**, 153 (1974); B. I. Greene, R. M. Hochstrasser, and R. B. Weissman, *J. Chem. Phys.*, **70**, 1247 (1979).

metrical conformation and solvation condition determine their CT nature.

Experimental Section

Materials. All melting points are not corrected. The IR, NMR, and mass spectra were recorded with Hitachi EPI-G2, Hitachi R-20 (60 MHz), and Hitachi RMU-7 spectrometers, respectively. Liquid chromatography was performed with a Nihonbunsekikogyo LC-08 of GPC type.

4-Bromobenzophenone Ethylene Acetal (I). A stirred solution of 4-bromobenzophenone[17] (11 g, 42.1 mmol), ethylene glycol (20 mL, 354 mmol), and a catalytic amount of *p*-toluenesulfonic acid in benzene (200 mL) was refluxed for 54 h. During the reflux the resulting water was removed by azeotropic distillation. The reaction mixture was washed with aqueous NaOH and water. After removal of the dried (MgSO$_4$) solvent, the crude product was recrystallized from ethanol to give colorless scales of I (11.5 g, 89.5%), mp 55.5–56.0 °C. Anal. (C$_{15}$H$_{13}$O$_2$Br): C, H, Br.

4-(*p*-(*N*,*N*-Dimethylamino)benzoyl)benzophenone Ethylene Acetal (II). A solution of bromide II (2.0 g, 6.55 mmol) in THF (10 mL) was dropwise added over 30 min to a stirred suspension of activated magnesium in dry THF (10 mL), which was prepared by the procedure of Rieke and Bales[8] from anhydrous MgCl$_2$ (1.25 g, 13.1 mmol), KI (1.1 g, 6.56 mmol), and potassium (0.92 g, 23.5 mmol). The mixture was stirred further for 1 h. To the reaction mixture was added a solution of *p*-(*N*,*N*-dimethylamino)benzaldehyde (980 mg, 6.56 mmol) in THF (15 mL), and the mixture was allowed to stand at 50 °C for 20 h. After treatment with saturated aqueous NH$_4$Cl at 0 °C, the reaction mixture was extracted with benzene. After removal of the dried solvent, crude product was purified by means of column chromatography on silica gel with benzene–ether (99:1) and then recrystallization from methanol. II: colorless scales, 1.50 g (50.1%), mp 130.0–130.5 °C; IR (Nujol mull) 1642 cm^{-1} (C=O); MS, *m/e* 373 (M$^+$), 119 (base peak). Anal. (C$_{24}$H$_{23}$NO$_3$): C, H, N.

4-(*p*-(*N*,*N*-Dimethylamino)benzyl)benzophenone (B$_1$). A mixture of ketone II (115 mg, 0.308 mmol) and AlCl$_3$ (420 mg, 3.16 mmol) in dry THF (5 mL) was added over 10 min to a stirred suspension of LiAlH$_4$ (120 mg, 3.16 mmol) and AlCl$_3$ (410 mg, 3.08 mmol) in dry THF. Additional stirring was continued for 1 h at room temperature. The reaction mixture was treated with a saturated aqueous solution of Rochelle salt and extracted with benzene. The dried (MgSO$_4$) solvent was removed and the residue was chromatographed on silica gel with CCl$_4$. Without further purification the product was heated with 6 N HCl at 60 °C for 3 h with stirring. After the mixture was cooled, aqueous NaOH was added until the solution became alkaline and the mixture was extracted with benzene. After removal of the dried (MgSO$_4$) solvent, the residue was chromatographed on alumina with benzene to give crude B$_1$ in a yield of 78%. B$_1$: yellow scales from benzene–hexane; mp 80.5–81.0 °C; IR (Nujol mull) 1655 cm^{-1} (C=O); MS, *m/e* 315 (M$^+$, base peak); ^{1}H NMR (CDCl$_3$) δ 2.90 (s, 6 H, CH$_3$), 3.96 (s, 2 H, CH$_2$), 6.68 (dd, J_1 = 8, J_2 = 2 Hz, 2 H, ArH ortho to NMe$_2$ group), 7.08 (dd, J_1 = 8, J_2 = 2 Hz, 2 H, ArH meta to NMe$_2$ group), 7.2–8.0 (m, 9 H, ArH). Anal. (C$_{22}$H$_{21}$NO): C, H, N.

4-Methylbenzophenone Ethylene Acetal (III). Acetal III was prepared from 4-methylbenzophenone[18] in the similar manner as described for I. After recrystallization from benzene–ethanol, III was obtained as colorless needles in a yield of 68%: mp 40.5–40.7 °C; MS, *m/e* 240 (M$^+$, base peak). Anal. (C$_{16}$H$_{16}$O$_2$): C, H.

4-(Bromomethyl)benzophenone Ethylene Acetal (IV). A mixture of III (510 mg, 2.13 mmol), NBS (420 mg, 2.36 mmol), and a small amount of benzoyl peroxide in CCl$_4$ (10 mL) was refluxed for 1 h. After the mixture was cooled, the resulted imide was filtered off and the filtrate was washed with water and dried. Crude product was recrystallized from ether to give colorless needles of IV (482 mg, 71%), mp 78.5–79.0 °C. Anal. (C$_{16}$H$_{15}$O$_2$Br): C, H, Br.

4-(*p*-(*N*,*N*-Dimethylamino)styryl)benzophenone Ethylene Acetal (V). A mixture of bromide IV (1.45 g, 4.55 mmol) and triphenylphosphine (1.33 g, 5.08 mmol) in dry benzene (10 mL) was refluxed for 6 h. After the mixture was cooled, precipitated phosphonium salt was filtered, washed with benzene, and dried in vacuo. To a stirred suspension of the phosphonium salt in dry benzene (10 mL) was added BuLi (4.2 mmol) in hexane, and stirring was continued for 4 h at room temperature. To this mixture was added *p*-(*N*,*N*-dimethylamino)benzaldehyde (624 mg, 4.21 mmol) at once, and the mixture was refluxed for 24 h. The reaction mixture was diluted with water and extracted with benzene. The dried

extract was evaporated, and the residue was chromatographed on silica gel with benzene–hexane to give V (425 mg, 31%) as a mixture of cis and trans isomers. Anal. (C$_{25}$H$_{25}$NO$_2$): C, H, N.

4-[2-(*p*-(*N*,*N*-Dimethylamino)phenyl)ethyl]benzophenone (B$_2$). Catalytic hydrogenation of V (250 mg, 0.673 mmol) in AcOEt (10 mL) was carried out by stirring with 5% Pd–C (100 mg) for 16 h. The mixture was filtered, and the solvent was removed. To the crude product was added 6 N HCl, and the solution was heated at 60 °C for 5 h with stirring. After the mixture was cooled, aqueous NaOH was added until the solution became alkaline and, then, the reaction mixture was extracted with benzene. The organic layer was washed with saturated aqueous NaCl and dried (MgSO$_4$). The solvent was evaporated in vacuo, and the residue was chromatographed on alumina (activity I) with CCl$_4$ to give a pale yellow solid of B$_2$ (183 mg, 72%), which was recrystallized from benzene–hexane to yield pure B$_2$, pale yellow plates: mp 121.0–121.5 °C; IR (Nujol mull) 1650 cm^{-1} (C=O); MS, *m/e* 329 (M$^+$), 134 (base peak); ^{1}H NMR (CDCl$_3$) δ 2.88 (s, 6 H, CH$_3$), 2.8–3.0 (m, 4 H, CH$_2$), 6.55 (dd, J_1 = 8, J_2 = 2 Hz, 2 H, ArH ortho to NMe$_2$ group), 6.92 (dd, J_1 = 8, J_2 = 2 Hz, 2 H, ArH meta to NMe$_2$ group), 7.1–7.9 (m, 9 H, ArH). Anal. (C$_{23}$H$_{23}$NO): C, H, N.

4-Cyanobenzophenone Ethylene Acetal (VI). Acetal VII was prepared for 4-cyanobenzophenone[19] in the similar manner as described for I. Crude product was purified by column chromatography on silica gel with benzene to give 390 mg (76%) of VI, which was recrystallized from methanol. VI: colorless prisms, mp 99.5–100.0 °C. Anal. (C$_{16}$H$_{13}$NO$_2$): C, H, N.

4-Acetylbenzophenone Ethylene Acetal (VII). To a methylmagnesium iodide solution (from 0.484 g, 20 mmol Mg) in dry ether (5 mL) was added cyanide VI (1.0 g, 4.0 mmol) in benzene (5 mL) at once, and the mixture was heated at 60 °C for 5 h. Aqueous NH$_4$Cl was added to the solution, and the mixture was heated at 80 °C for 1 h to accomplish hydrolysis. Then, it was extracted with benzene. After removal of the solvent, the residue was chromatographed on alumina (activity I) with benzene–hexane to give VII (722 mg, 77%). Recrystallization from methanol afforded pure VII as colorless prisms, mp 65.5–66.0 °C. Anal. (C$_{17}$H$_{16}$O$_3$): C, H.

4-[3-(4-(*N*,*N*-Dimethylamino)phenyl)-1-oxopropyl]benzophenone Ethylene Acetal (VIII). A mixture of acetyl derivative VII (1.22 g, 4.55 mmol), *p*-(*N*,*N*-dimethylamino)benzaldehyde (0.72 g, 4.8 mmol), and NaOH (2.0 g, 50 mmol) in ethanol–water (1:1) was stirred at room temperature for 40 h. The resulting yellow-brown solid was filtered and washed with cold ethanol and cold water, successively. The solid was recrystallized from benzene to give 1.1 g of unsaturated ketone as yellow needles. The filtrate was evaporated and the residue was chromatographed on silica gel with benzene to give an additional part of the ketone (350 mg). Total yield of the product was 1.45 g (80%). Without further purification the unsaturated ketone (1.16 g, 2.9 mmol) was hydrogenated in dioxane over 5% Pd–C (200 mg). Crude product was chromatographed on alumina (activity I) with benzene to give VIII in a yield of 70.5% (822 mg). Recrystallization from benzene–hexane afforded pure IX as pale yellow crystals, mp 86.0–86.5 °C; IR (Nujol mull) 1684 cm^{-1} (C=O); MS, *m/e* 401 (M$^+$). Anal. (C$_{26}$H$_{27}$NO$_3$): C, H, N.

4-[3-(4-(*N*,*N*-Dimethylamino)phenyl)propyl]benzophenone (B$_3$). A mixture of ketone VIII (822 mg, 2.04 mmol), hydrazine hydrate (10 mL), and NaOH (400 mg, 7.13 mmol) in diethylene glycol (20 mL) was refluxed for 1 h. After hydrazine and water were distilled off, the temperature of the reaction mixture was raised to 220 °C and held at that temperature for 4 h. To the solution was added 2 N HCl (100 mL), and the mixture was stirred for 1 h. Then, the mixture was extracted with benzene. After removal of the dried (MgSO$_4$) solvent, the residue was chromatographed on silica gel with benzene–ether to give B$_3$ as a yellow oil (450 mg, 67%). Further purification was carried out by liquid chromatography and molecular distillation (200–210 °C (10^{-4} mmHg)): IR (neat) 1654 cm^{-1} (C=O); MS, *m/e* 343 (M$^+$, base peak); NMR (CDCl$_3$) δ 2.90 (s, 6 H, CH$_3$), 2.05 (t, J = 7 Hz, 4 H, CH$_2$–Ar), 2.57 (q, J = 7 Hz, 2 H, CH$_2$–CH$_2$–CH$_2$), 6.58 (d, J = 8 Hz, 2 H, ArH ortho to NMe$_2$ group), 7.03 (d, J = 8 Hz, 2 H, ArH meta to NMe$_2$ group), 7.1–8.0 (m, 9 H, ArH). Anal. (C$_{24}$H$_{25}$NO): C, H, N.

Spectroscopic Measurements. Emission spectra were observed with an Aminco–Bowman and a Hitachi MPF spectrophotofluoremeters. Emission decay curves were obtained by using a home-made pulsed N$_2$ gas laser with 1-kW peak power as an exciting light source and a Bausch&Lomb high-intensity monochromator. The following two detection methods were applied. A HTV 1P28 photomultiplier with a 50-Ω resistor and a Tektronix 661 sampling oscilloscope was used for a fast decay in a 10-ns time range (method I). In this case the time constant is 2.5 ns. For a longer decay with low-emission intensity a value of the output resistor of a HTV 1P28 photomultiplier is varied and a Tektronix

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475 oscilloscope was used (method II). Temperature effects were investigated by placing the sample curvettes in a metal Dewar with quartz windows, and the temperature was controlled by a constant flow of cold nitrogen gas.

Photosensitized Dissociation of Di-*tert*-butyl Peroxide. Energy Transfer to a Repulsive Excited State

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Abstract: Energy transfer from a variety of aromatic hydrocarbons and ketones to di-*tert*-butyl peroxide has been examined by using nanosecond laser flash photolysis techniques. Triplet energy transfer to the peroxide leads to its efficient cleavage into two *tert*-butoxy radicals. Representative rate constants for triplet quenching in benzene at 25 °C are 7.9×10^6, 3.4×10^6, and 7.0×10^4 M^{-1} s^{-1} for *p*-methoxypropiophenone, benzophenone, and benz[*a*]anthracene, respectively. The rate of transfer for *p*-methoxypropiophenone ($E_T \approx 72.5$ kcal/mol) is approximately temperature independent; for lower energy sensitizers ca. 0.17 kcal/mol activation energy is required for each kilocalorie per mole decrease in triplet energy. No evidence indicating exciplex intermediacy was found. A model for energy transfer to a repulsive state of the peroxide is proposed in which no activation energy is required if the sensitizer meets the energy requirements at the O–O equilibrium distance. For sensitizers of lower triplet energy, energy transfer to a repulsive state is proposed to occur from a thermally activated ground state having a greater than equilibrium oxygen–oxygen bond length. The same mechanism may apply in other systems where the acceptor lacks low-lying excited states. A few rate constants for the quenching of singlet sensitizers have also been determined by using fluorescence techniques.

Introduction

Investigations of electronic energy transfer by the electron-exchange mechanism[2-4] have dealt with a variety of effects including those of separation[5] and orientation[6] of donor and acceptor, steric hindrance,[7] the energy change accompanying transfer,[8] and the influence of medium viscosity.[9] In most studies the acceptors have been molecules having energetically accessible, bound excited states. Few quenchers possessing energetically accessible repulsive excited states have been studied. Photosensitized dissociation of a quencher is, of course, not rare, but the process often involves a bound excited state which requires thermal activation for dissociation.[10] Several studies concerned with the photosensitized dissociation of peroxides have been published.[11-17] Among studies

Table I. Kinetics of Triplet Quenching by Di-*tert*-butyl Peroxide

sensitizer	solvent	k_q^a	τ_T (perox)^b	γ^c
propiophenone	benzene	9.6×10^6		
p-methoxypropio-phenone	benzene	7.9×10^6	23	0.57
benzophenone	benzene	3.4×10^6	60	0.72
benzophenone	acetonitrile	3.7×10^6		
phenanthrene	benzene	1.8×10^6	98	0.85
phenanthrene	acetonitrile	3.0×10^6		
naphthalene	benzene	1.1×10^6	150	0.62
benzil	benzene	2.8×10^4	3000	
fluorenone	benzene	2.4×10^5	680	
benz[*a*]anthracene	benzene	7.0×10^4	2200	
anthracene	benzene	9.7×10^4	1500	

^{a} Units of M^{-1} s^{-1}, at 25 °C. ^{b} In nanoseconds, in neat peroxide. ^{c} Efficiency of *tert*-butoxy radical generation (see text below), neglecting any differences in cage recombination between direct and sensitized photodecompositions.

of energy transfer to dissociative states of other molecules,[11,18,19] the kinetic study by Wallace, Van Duyne, and Lewis[18] on singlet and triplet quenching by dialkyl disulfides is the most extensive, but a general model for energy transfer to a dissociative state remains to be described.

In this paper we report a study of the quenching of several sensitizers by di-*tert*-butyl peroxide. We have obtained absolute

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