Photochemistry of Benzophenone in Aliphatic Amines Studied by Laser Photolysis in the Temperature Range 300–77 K

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Laser photolysis studies of benzophenone in both *sec*-butylamine and triethylamine were carried out in the temperature range 300–77 K. For the *sec*-butylamine solution of benzophenone, the transients observed after laser pulsing are found to be the ketyl and anion radicals of benzophenone. The ratio of the yield for the formation of ketyl radical to that of the anion radical is markedly dependent on temperature: the ketyl radical is the major product at high temperatures while the anion radical becomes predominant at low temperatures. On the other hand, the triethylamine solution of benzophenone gives solely the ketyl radical as a photoproduct in the temperature range studied. The photochemical reaction of benzophenone in both *sec*-butylamine and triethylamine is markedly suppressed on going from high to low temperatures. These results are discussed in detail on the basis of the photochemical reaction mechanism involving the formation of the triplet charge-transfer complex (i.e., triplet exciplex) between triplet benzophenone and an amine molecule. The solvent effects on the photoreaction are also discussed.

Introduction

Photoreaction of aromatic ketones by amines has been extensively studied in order to elucidate the primary processes in the excited state.[1-8] For benzophenone, the photoreduction by amines was suggested to occur by rapid formation of a charge-transfer complex between the triplet benzophenone and an amine molecule, followed by internal proton transfer in the complex to produce the benzophenone ketyl and amine radicals.[2,9]

Nanosecond laser photolysis as well as microsecond flash photolysis studies of benzophenone in solutions containing aromatic amines have confirmed that the yields of the ketyl radical and the anion radical of benzophenone markedly depend on the dielectric constant of the solvent: an increase in the dielectric constant of the solvent results in an increase in the yield of the anion radical and a decrease in the yield of the ketyl radical.[10-12] Recently, Simon and Peters have carried out picosecond laser photolysis of benzophenone in acetonitrile solutions containing 1.0 M aromatic amines.[13] They observed that the solvent-separated ion pairs initially produced are transformed to the contact ion pairs, followed by internal proton transfer to yield the ketyl radicals. At 2 ns after pulsing, an equilibrium between the anion and ketyl radicals is found to be achieved. The equilibrium constant markedly depends on the dielectric constant of solvents: the ratio of the yield for the ketyl radical to that for the anion radical increases with a decrease in the dielectric constant of solvents. These findings support earlier postulation that the primary events in the photoreduction involve the electron transfer from amines to triplet benzophenone.

Photoreduction of benzophenone by aliphatic amines has also been subjected to extensive studies. Cohen's group has measured the quantum yields for the photoreduction of benzopheonone in neat amine solutions.[14] Subsequent laser photolysis studies[15] on the photoreduction of benzophenone in benzene solutions containing aliphatic amines have revealed that (1) triplet exciplex between triplet benzophenone and an aliphatic amine molecule is efficiently transformed to the ketyl radical with the quantum yield of almost unity independent of the nature of the amines and (2) hydrogen atoms of both –NH– and –CH– groups in amine molecules can be abstracted in the photoreaction.

The role of the exciplex in the photoreduction of benzophenone by triethylamine has been first observed by Shaefer and Peters.[16] They have carried out picosecond laser photolysis of benzophenone in acetonitrile solutions containing 3 M triethylamine. The transient spectrum of the exciplex observed at 10 ps has an absorption maximum at 610 nm and decays with a lifetime of 15 ps to produce the ketyl radical. From these results, the ketyl radical formation is interpreted in terms of the quenching of the exciplex by fast internal proton transfer.

In spite of a number of studies on the photoreduction of benzophenone, as mentioned above, the temperature effects on the photoreduction in amine solutions have not yet been reported. In the present study, we have carried out nanosecond laser photolysis of benzophenone in *sec*-butylamine and triethylamine solutions in the temperature range 300–77 K to elucidate the detailed mechanism for the photoreduction of benzophenone in aliphatic amines.

Experimental Section

Benzophenone was recrystallized from ethanol solution. Reagent grade *sec*-butylamine was stored over molecular sieves to remove the small amount of water and distilled for purification before use. Reagent grade triethylamine was purified by distillation and stored over Na–K alloy to remove traces of water. Concentrations of benzophenone were ca. 1.0×10^{-3} M.

The absorption and emission spectra were recorded on a Hitachi 330 spectrophotometer and a Hitachi MPF 4 spectrofluorimeter, respectively.

Laser photolysis was carried out by using the third harmonics (355 nm) of a Nd:YAG laser (HY 500 from JK Laser Ltd.). The energy and duration of a laser pulse were ca. 100 mJ and 20 ns, respectively. The detection system of the transient spectra was reported in an earlier paper.[17] A cryostat, DN 10200 from Oxford

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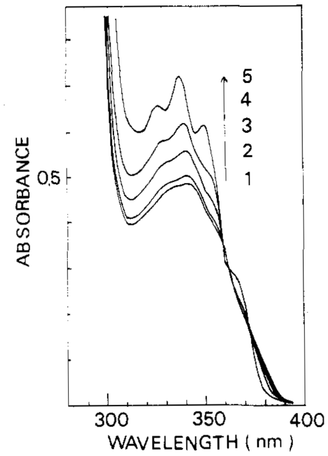

Figure 1. Optical absorption spectra observed for a *sec*-butylamine solution of benzophenone: (1) at 300 K; (2) at 250 K; (3) at 200 K; (4) at 160 K; (5) at 100 K.

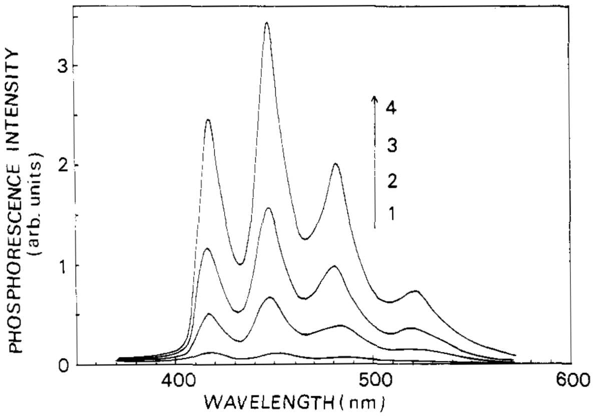

Figure 2. Phosphorescence spectra observed for a *sec*-butylamine solution of benzophenone: (1) at 120 K; (2) at 110 K; (3) at 100 K; (4) at 77 K.

Instruments, was used for controlling the sample temperature.

Results

Figure 1 shows the absorption spectra of benzophenone in a *sec*-butylamine solution measured in the temperature range 300–100 K. The n–π^* absorption band of benzophenone observed at 300 K has a peak around 340 nm. The vibrational structures of the band becomes clear with a decrease in temperature. No absorption ascribable to a charge-transfer compalex was observed even at 77 K.

Figure 2 shows the phosphorescence spectra of benzophenone in *sec*-butylamine in the temperature range 120–77 K. The phosphorescence was hardly observed at temperatures higher than 120 K. Since the vibrational structures and location of the phosphorescence spectrum are similar to those observed for benzophenone in other solvents such as alcohol or toluene at 77 K, we conclude that the charge-transfer complex is not formed between benzophenone and *sec*-butylamine in the ground state.

Figure 3 shows the transient absorption spectra observed for benzophenone in *sec*-butylamine at 50 ns after 355-nm laser pulsing at several temperatures. The spectrum measured at 291 K has two absorption maxima at 555 and 660 nm. The former peak is ascribed to the benzophenone ketyl radical and the latter to the benzophenone anion radical.[18] This result indicates that both anion and ketyl radicals are produced within a duration (20 ns) of a laser pulse. No transformation from the anion radical to the ketyl radical was observed with the lapse of time. At lower temperatures, the ratio of the yield for the ketyl radical to that for the anion radical was found to be diminished. The transient spectrum observed at 160 K indicates that the major product is ascribed to the benzophenone anion radical. The yield of the anion radical was found to decrease with a decrease in temperature from 240 to 120 K. Below 120 K, we can observe solely the triplet benzophenone after laser pulsing: the transient spectrum measured at 100 K has an absorption peak at 535 nm, in agreement with that of the triplet benzophenone.[19] The decay rate of triplet benzophenone in *sec*-butylamine at 100 K was determined as 2.2 × 10^5 s^{-1}. Neither the ketyl nor the anion radical formation was detected below 120 K.

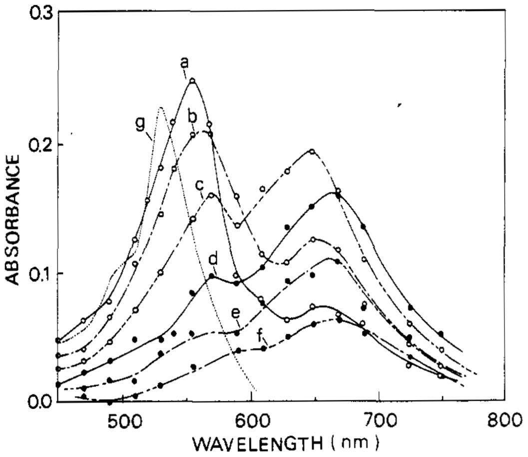

Figure 3. Transient absorption spectra observed for a *sec*-butylamine solution of benzophenone at 50 ns after 355-nm laser pulsing: (a) at 291 K; (b) at 260 K; (c) at 240 K; (d) at 200 K; (e) at 180 K; (f) at 160 K; (g) at 100 K.

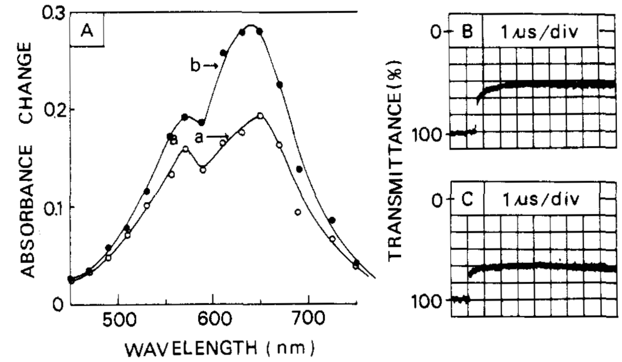

Figure 4. Transient absorption spectra (A) observed for a *sec*-butylamine solution of benzophenone at 50 ns (a) and at 5 μs (b) after laser pulsing at 240 K, and oscilloscope traces monitored at 650 (B) and 555 nm (C) after pulsing.

Part A of Figure 4 shows the transient spectra measured for benzophenone in *sec*-butylamine at 240 K after laser pulsing. The yields of the ketyl and the anion radicals increase with time after laser pulsing. The yields measured at 5 μs were as large as 1.5 times those obtained at 50 ns after laser pulsing. These results are interpreted in terms of the reduction of benzophenone by amine radicals, which are created by the hydrogen atom transfer and/or electron transfer from *sec*-butylamine to the triplet benzophenone.

Parts B and C show the oscilloscope traces monitored at 650 and 555 nm, respectively, at 240 K. These traces give evidence that benzophenone is reduced by amine radicals at 240 K as mentioned above. The reduction of benzophenone by amine radicals was observed in the temperature range 180–260 K.

Photochemistry of Benzophenone in Triethylamine. The absorption spectra of benzophenone in triethylamine exhibited the n–π^* absorption band around 345 nm. The vibrational structure of the absorption band became clear with a decrease in the tem-

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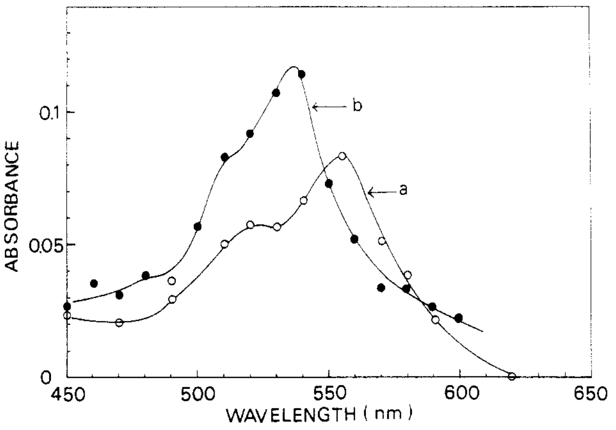

Figure 5. Transient absorption spectra observed for a triethylamine solution of benzophenone at 293 (a) and 90 K (b) after 355-nm laser pulsing. No transient absorption was detected in the wavelength region 650–900 nm.

perature. The phosphorescence of benzophenone can be observable below 110 K. The location of the phosphorescence spectrum in triethylamine was blue-shifted by ca. 3 nm in comparison with that in *sec*-butylamine. No marked differences in the phosphorescence spectra between triethylamine and *sec*-butylamine solutions of benzophenone were observed. We, therefore, consider that the ground state charge-transfer complex between benzophenone and triethylamine is not produced in the temperature range 300–77 K.

Figure 5 shows the transient absorption spectra observed for a triethylamine solution of benzophenone at 293 and 90 K, obtained by 355-nm laser photolysis. The spectrum measured at 293 K has a peak maximum at 555 nm, in agreement with the absorption spectrum of the ketyl radical.[18,20] The laser photolysis of the solution at 90 K gives a transient spectrum having a peak maximum at 535 nm. The decay of the transient follows the first-order kinetics with a rate constant of $2.8 \times 10^2\ \mathrm{s}^{-1}$. Since the rate constant is very close to the phosphorescence decay rate, $2.3 \times 10^2\ \mathrm{s}^{-1}$, the transient is undoubtedly attributed to the triplet benzophenone. Measurements of the transient spectra were carried out in the temperature range 293–77 K. The experimental results are summarized as (1) no benzophenone anion radical was detected in the temperature range studied, (2) the yield of the ketyl radical decreased with a decrease in the temperature, (3) only triplet benzophenone could be detected below 100 K, and (4) contrary to the case of *sec*-butylamine solutions, no reduction of benzophenone by amine radicals was observed.

Figure 6 shows the relative absorbance of the ketyl radical at 555 nm observed at 50 ns after laser pulsing, represented as a function of temperature. The ketyl radical is scarcely detected below 120 K. The phosphorescence intensities are also represented as a function of temperature as shown in Figure 6. The phosphorescence became detectable below 120 K. It should be noted that the ketyl radical, the triplet benzophenone, and the phosphorescence are hardly observed at 120 K.

The relative absorbance, R, of the ketyl radical at 555 nm measured at 20 ns after laser pulsing is well expressed as a function of temperature

$$R = \Phi_\infty/\Phi(T) = 1 + 3.0 \times 10^{-4} \exp(1.3 \times 10^3/T)$$

Here Φ_∞ and $\Phi(T)$ stand for the quantum yields for the formation of the ketyl radical at an infinite temperature and at T, respectively. The meaning of the above expression will be discussed later.

Discussion

Mechanism for Photoreduction of Benzophenone in sec-Butylamine. Photoproducts of benzophenone in aliphatic amine solutions have been well investigated. On the basis of the laser photolysis studies and quantum yield measurements at room temperature, the mechanism for the photoreduction of enzophenone by primary amines, $H_2N(CH_2R)$, has been proposed[2,15,16] as

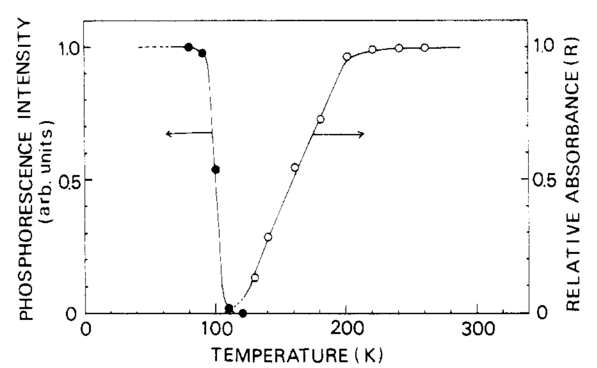

Figure 6. Relative absorbance, R, of the benzophenone ketyl radical measured at 555 nm for a triethylamine solution of benzophenone after laser pulsing, and the phosphorescence intensity of benzophenone, represented as a function of temperature.

$$^3\Phi_2C{=}O^* + H_2N(CH_2R) \rightarrow [\Phi_2\dot{C}O^-\cdots\overset{+}{N}\dot{H}_2(CH_2R)]^* \quad (^3CTC^*)$$

$$^3CTC^* \rightarrow \Phi_2C{=}O + H_2N(CH_2R)$$

$$^3CTC^* \rightarrow \Phi_2\dot{C}OH + \text{amine radicals } (\dot{N}H(CH_2R) \text{ and/or } NH_2(\dot{C}HR))$$

$$2\Phi_2\dot{C}OH \rightarrow \text{benzpinacole}$$

The triplet benzophenone, $^3\Phi_2C{=}O^*$, reacts with primary amine, $H_2N(CH_2R)$, to form a triplet charge-transfer complex (i.e., triplet exciplex), $^3CTC^*$. The triplet complex undergoes the ketyl radical formation by internal proton transfer in the complex.

In the present work, we found that the triplet benzophenone in neat *sec*-butylamine solutions gives rise to the formation of both the ketyl and anion radicals of benzophenone. In particular, the major transient observed at low temperatures was confirmed as the anion radical. This fact indicates that the anion radical is also produced from the triplet charge-transfer complex in neat *sec*-butylamine

$$^3[\Phi_2\dot{C}O^-\cdots\overset{+}{N}\dot{H}_2CH(CH_3)(C_2H_5)]^* \quad (^3CTC^*)$$

It is frequently observed that both ketyl and anion radicals are produced simultaneously by photoreduction of benzophenone in solutions containing aromatic amines after laser pulsing at room temperature.[11,12] Arimitsu and his co-workers studied the photoreduction of benzophenone by ca. 10^{-3} M aromatic amines in various solvents with the use of a nanosecond lasers.[10,11] They suggested that the ketyl and the anion radicals are competitively formed from an encounter charge-transfer complex between triplet benzophenone and an aromatic amine molecule. On the other hand, Simons and Peters have investigated, by using a picosecond photolysis technique, the photoreduction of benzophenone by 1.0 M aromatic amines in aliphatic nitriles.[13] Their results imply that an initial process for the formation of the ketyl radical is an electron-transfer reaction from aromatic amines to triplet benzophenone.

In an earlier paper,[18] we reported the pulse radiolysis studies of benzophenone in aliphatic amine solutions in the temperature range 291–193 K. The benzophenone anion radical in primary aliphatic amines, $H_2N(CH_2R)$, was found to be in equilibrium with the ketyl radical

$$\Phi_2\dot{C}O^-\cdots H_2N(CH_2R) \rightleftarrows \Phi_2\dot{C}OH\cdots\bar{N}H(CH_2R)$$

Taking account of the facts that (1) the anion and ketyl radicals are produced immediately after laser pulsing and (2) no formation of the ketyl radical from the anion radical is observed, we consider

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[20] Beckett, A.; Porter G. *Trans. Faraday Soc.* **1963**, *59*, 2038–2050.

that the equilibrium between them establishes within a duration of the laser pulse. Presumably the anion radical initially produced from the triplet charge-transfer complex abstracts rapidly a proton from a *sec*-butylamine molecule in its nearest neighbor to yield the ketyl radical. The following mechanism is proposed for the photoreduction of benzophenone in *sec*-butylamine:

$$^3\Phi_2CO^* + H_2NCH(CH_3)(C_2H_5) \rightarrow {}^3CTC^*$$

$$^3CTC^* \rightarrow H_2{}^+\dot{N}CH(CH_3)(C_2H_5) + [\Phi_2\dot{C}O^-]$$

$$[\Phi_2\dot{C}O^-] + H_2NCH(CH_3)(C_2H_5) \rightarrow [\Phi_2\dot{C}O^-\cdots H_2NCH(CH_3)(C_2H_5)]$$

$$[\Phi_2\dot{C}O^-\cdots H_2NCH(CH_3)(C_2H_5)] \rightleftarrows \Phi_2\dot{C}OH\cdots H\overset{-}{N}CH(CH_3)(C_2H_5)$$

On the basis of the quantum yield measurements for the disappearance of benzophenone in *sec*-butylamine, it has been suggested that ground-state benzophenone is reduced by amine radicals.[2,9] The laser photolysis studies carried out in the temperature range 260–180 K have confirmed that the anion and ketyl radicals are produced according to two processes: (1) a fast formation process due to the excited-state reaction of benzophenone in *sec*-butylamine and (2) a slow formation process due to the thermal reaction of benzophenone with amine radicals. The ratio of the yield for the ketyl radical to that for the anion radical is independent of their formation process: the ratio estimated from the fast formation process is identical with that from the slow formation process. We, therefore, consider that an electron of the amine radical is transferred to benzophenone, resulting in the formation of hydrogen-bonded anion radical, which readily establishes the equilibrium with the ketyl radical as mentioned above.

The slow formation of the ketyl and anion radicals was not detected above 260 K and below 180 K in the present laser photolysis studies. These results suggest that (1) above 260 k, reduction of benzophenone by amine radicals occurs rapidly within the duration of laser pulse and (2) below 180 K, the rate for the reduction of benzophenone by amine radicals becomes very slow owing to an increase in the viscosity of the solvent.

The photoreduction mechanism of benzophenone in *sec*-butylamine solutions is complicated because of the participation of the thermal reduction of benzophenone by amine radicals as mentioned above. Thus, the temperature dependence of the yields for the ketyl radical and the anion radical formation from triplet benzophenone was not examined quantitatively. However, it is found that the yield for the photoreduction of benzophenone decreases on going from 300 to 120 K without detection of triplet benzophenone. This finding suggests that the ionic dissociation of ^{3}CTC*, which is produced from triplet benzophenone and *sec*-butylamine, is suppressed due to the high viscosity of the solvent at low temperatures. Presumably solvent reorientation suitable for the ionic dissociation is necessary for the formation of the anion radicals from ^{3}CTC*, and therefore, back electron transfer in ^{3}CTC* becomes predominant at low temperatures, resulting in a decrease in the yield for the formation of the ketyl and anion radicals.

Triplet benzophenone in *sec*-butylamine was observable below 120 K. The peak maximum of the triplet absorption is located around 530 nm. On the basis that the triplet lifetime becomes short on going from 77 to 120 K, we consider that a *sec*-butylamine molecule efficiently quenches triplet benzophenone, leading to the formation of ^{3}CTC*. Since the laser photolysis was carried out for benzophenone in neat *sec*-butylamine solution, a translational diffusion process is not necessary for the formation of ^{3}CTC*. Presumably, formation of ^{3}CTC* can be achieved by rotational diffusion of a *sec*-butylamine molecule around triplet benzophenone.

Mechanism for the Photoreduction of Benzophenone in Triethylamine. Photoreduction of benzophenone in triethylamine solutions has been investigated by steady light photolysis as well as laser photolysis.[2,15,16] The mechanism for the photoreduction has been proposed

$$^3\Phi_2C{=}O^* \xrightarrow{k_1} \Phi_2C{=}O \tag{1}$$

$$^3\Phi_2C{=}O^* + N(C_2H_5)_3 \xrightarrow{k_2} {}^3CTC^* \tag{2}$$

$$^3CTC^* \xrightarrow{k_3} \Phi_2\dot{C}OH + N(\dot{C}HCH_3)(C_2H_5)_2 \tag{3}$$

$$^3CTC^* \xrightarrow{k_4} \Phi_2C{=}O + N(C_2H_5)_3 \tag{4}$$

Spectroscopic observation of ^{3}CTC* has been made by a picosecond photolysis of benzophenone in acetonitrile containing 1.0 M triethylamine. The formation of the ketyl radical is interpreted in terms of internal proton transfer in ^{3}CTC*.

In the present study, we have carried out optical absorption and phosphorescence measurements for triethylamine solutions of benzophenone in the temperature range 300–77 K. Judging from the optical absorption and phosphorescence spectra of benzophenone at various temperatures, no formation of the ground-state complex between benzophenone and triethylamine was concluded.

The laser photolysis studies of benzophenone in triethylamine have shown that the transients observed for the solution were the ketyl radical and triplet benzophenone. Transient absorption ascribable to ^{3}CTC* could not be detected in the temperature range 300–77 K. Furthermore, no emission from ^{3}CTC* was observed. It, therefore, is likely that ^{3}CTC* has an extremely short lifetime in neat triethylamine solutions.

Contrary to the case of *sec*-butylamine solutions, we could not detect benzophenone anion radicals in triethylamine solutions after laser pulsing. This result suggests that ^{3}CTC* can undergo ionic dissociation in polar solvents having an N–H group in the solvent molecule while it does not in less polar solvent such as triethylamine. The dielectric constant of triethylamine is reported as 2.4 at 25 °C, and that of *sec*-butylamine is assumed to be ca. 4–5 from the values of other primary amines.[21]

Relative quantum yields for the formation of the ketyl radical were measured in the temperature range 300–77 K in order to elucidate the detailed mechanism for the hydrogen abstraction by triplet benzophenone in triethylamine. From reactions 1–4, we can derive the following equation:

$$\Phi(T) = \Phi_{ST}k_2(k_1 + k_2)^{-1}k_3(k_3 + k_4)^{-1} \tag{I}$$

Here $\Phi(T)$ and Φ_{ST} stand for the quantum yield for the formation of the ketyl radical at a temperature, T, and the triplet yield of benzophenone, respectively. Since the photolysis was carried out in neat triethylamine, we safely assume $k_2 \gg k_1$ under the experimental condition. Equation I, therefore, is transformed to

$$\Phi(T) = \Phi_{ST}k_3(k_3 + k_4)^{-1} \tag{II}$$

On the assumption that (1) $\Phi_{ST} = 1$ for benzophenone[22-25] in triethylamine and (2) k_3 and k_4 are expressed by usual Arrhenius expression

$$k_3 = k_3{}^0 \exp(-\Delta E_3/RT) \tag{III}$$

$$k_4 = k_4{}^0 \exp(-\Delta E_4/RT) \tag{IV}$$

Equation II, therefore, is transformed to

$$\Phi(T) = (1 + k_4{}^0/k_3{}^0 \exp(\Delta E_{3,4}/RT))^{-1} \tag{V}$$

where $\Delta E_{3,4} = \Delta E_3 - \Delta E_4$. The quantum yield, $\Phi(\infty)$, at an infinite temperature is represented as

$$\Phi(\infty) = (1 + k_4{}^0/k_3{}^0)^{-1} \tag{VI}$$

The quantum yield for the photoreduction of benzophenone by

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triethylamine at room temperature has been determined as unity.[15] This fact implies that (1) $\Phi(T)$ shows a leveling off around room temperature and, therefore, (2) $k_4{}^0/k_3{}^0 \sim 0$. With eq V and VI and $k_4{}^0/k_3{}^0 \sim 0$, the following equation is derived:

$$\Phi(\infty)/\Phi(T) = 1 + k_4{}^0/k_3{}^0 \exp(\Delta E_{3,4}/RT) \qquad \text{(VII)}$$

As described previously, we have measured the relative quantum yields for the formation of the ketyl radical at various temperatures by laser photolysis. The values of $\Phi(\infty)/\Phi(T)$ determined experimentally are well explained with the use of $k_4{}^0/k_3{}^0 = 3.0 \times 10^{-4}$ and $\Delta E_{3,4}/R = 1.3 \times 10^3$ deg.

Picosecond spectroscopy for benzophenone in an acetonitrile solution containing 3.0 M triethylamine has confirmed that ^{3}CTC* decays with a first-order rate constant of $(1.4 \pm 0.7) \times 10^{10}$ s^{-1} at room temperature.[16] Subsequent picosecond studies of benzophenone showed that ^{3}CTC* is not detected in neat triethylamine, presumably owing to ultrafast decay of ^{3}CTC* at room temperature.[26] From these results, the decay rate constant, $k_3 + k_4$, of ^{3}CTC* in neat triethylamine at room temperature is estimated as $k_3 + k_4 \gg 1.4 \times 10^{10}$ s^{-1}. On the assumption that the activation energy is very small for the deactivation process of ^{3}CTC*, i.e., $k_4 = k_4{}^0$, $\Delta E_4 = 0$, and $\Delta E_{3,4} = \Delta E_3$, we obtain

$$k_3 = k_3{}^0 \exp(-1.3 \times 10^3/T) \qquad \text{(VIII)}$$

This result implies that the activation energy for intracomplex proton transfer in ^{3}CTC* is estimated as 2.6 kcal mol^{-1} on the assumption of $\Delta E_4 = 0$. The value of 2.6 kcal mol^{-1} is similar to the activation energies for hydrogen abstraction of triplet benzophenone from various alcohols.[27]

From eq VIII, $k_4{}^0/k_3{}^0 = 3.0 \times 10^{-4}$, $k_4 = k_4{}^0$, and $k_3 + k_4 \gg 1.4 \times 10^{10}$ s^{-1} at 300 K, the value of $k_4{}^0$ is estimated as $k_4{}^0 \gg 3 \times 10^9$ s^{-1}. The laser photolysis studies of benzophenone in neat triethylamine have shown that no transient was detected at 120 K, indicating that triplet benzophenone is efficiently quenched by triethylamine without forming the ketyl radical. This result may be interpreted in terms of (1) the short lifetime of ^{3}CTC*, $\tau \ll 3$ ns, as evaluated from $(k_3 + k_4{}^0)$ and (2) $\Phi(T)/\Phi(\infty) \sim 0$ at 120 K.

Origins of Difference in Photochemistry between sec-Butylamine and Triethylamine Solutions of Benzophenone. The present studies revealed a marked difference in photochemistry between *sec*-butylamine and triethylamine solutions of benzophenone: the benzophenone anion radicals are produced in the *sec*-butylamine solution, while they are not in the triethylamine solution.

In a previous study,[18] it has been established that the benzophenone anion radicals in *sec*-butylamine produced by γ-radiolysis at 77 K has a peak maximum at 780 nm. When the γ-irradiated solution is warmed, the peak shifts irreversibly toward blue to give a new peak at 680 nm. Since the solvent reorientation occurs easily at higher temperatures, we consider that the peak shift of the benzophenone anion radical is caused by solvation associated with a hydrogen bond formation between the anion radical and a *sec*-butylamine molecule

$$\Phi_2\dot{C}\text{–}O^- + n\mathrm{H_2NCH(CH_3)(C_2H_5)} \rightarrow (\Phi_2\dot{C}O^{-}\cdots\mathrm{H_2NCH(CH_3)(C_2H_5)})_{\mathrm{solv}}$$

The benzophenone anion radical in *sec*-butylamine observed by laser photolysis exhibits an absorption band around 670 nm in the temperature range 293–120 K. At 120–160 K, triplet benzophenone is found to be efficiently quenched. However, the benzophenone anion radical having a peak maximum at 780 nm could not be detected. These results suggest that the solvation associated with a hydrogen bond formation between the anion radical and a *sec*-butylamine molecule is necessary for the ionic dissociation of the triplet charge-transfer complex, ^{3}CTC*, formed between triplet benzophenone and a *sec*-butylamine molecule.

Earlier pulse radiolysis studies have confirmed that the benzophenone anion radical in triethylamine at 183 K has an absorption peak at 760 nm.[18] No anion radical having a peak maximum around 680 nm was detected. It, therefore, is concluded that solvation of the anion radical by triethylamine does not give rise to a large shift of the absorption band, presumably owing to a small solvation energy of triethylamine.

Contrary to the *sec*-butylamine solution, laser photolysis of the triethylamine solution of benzophenone does not give rise to the formation of the benzophenone anion radical as a transient in the temperature range 300–77 K. It is likely that the solvation energy of triethylamine is too small to cause the ionic dissociation of the triplet charge-transfer complex (i.e., triplet exciplex) between triplet benzophenone and triethylamine, and therefore, intracomplex proton transfer in ^{3}CTC* becomes predominant in the triethylamine solution, resulting in the facile formation of the ketyl radicals.

Registry No. Benzophenone, 119-61-9; *sec*-butylamine, 13952-84-6; triethylamine, 121-44-8; benzophenone ketyl radical, 4971-41-9; benzophenone anion radical, 16592-08-8.

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