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A Laser Flash Photolysis Study on the Reaction Mechanisms of Benzil with Various Amines

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Laser flash photolysis of benzil in the presence of various amines was investigated to determine absolute reaction quantum yield (ϕ_r) of benzil ketyl radicals produced from both free triplet benzil and ground state complex. The reaction quantum yields of benzil ketyl radical from free triplet benzil (ϕ_r^{free}) were 0.31, 0.17, 0.13, 0.08, and ca. 0 for triethylamine (TEA), *N*,*N*-diethylaniline, diethylamine, *N*-ethylaniline, and aniline, respectively. ϕ_r^{free} largely depends on the number of the hydrogen atoms that can be abstracted by benzil. The reaction quantum yield of the complex formed in the ground state (ϕ_r^{com}) was determined to be unity for all amines used. This large quantum yield ($\phi_r^{com} = 1$) was explained by a calculated conformation of the ground state complex.

Introduction

Hydrogen abstraction of excited carbonyl compounds from amines in solution is a typical photochemical reaction. Electron transfer followed by proton transfer has been proposed as a possible mechanism for the hydrogen abstraction reaction of triplet benzophenone (BP) from amines.[1−3] The quenching rate constant of triplet carbonyl by amines is well-known to be a function of oxidation potential of amines.[4] Quantum yields of ketyl radical formation are reported to be 0.7−0.8 for several anilines, triethylamine, and diphenylamine.[2] Photoreaction also takes place when a charge transfer (CT) complex formed in the ground state is excited, but its reaction in the excited state is different from that of free triplet BP. In the BP/*N*-methyldiphenylamine (MDPA) system, Miyasaka et al. reported that encounter complexes, both ^{1}BP*-MDPA and ^{3}BP*-MDPA, produced the benzophenone ketyl radical through electron transfer and proton transfer reaction, whereas photoreaction of CT complex gives only the ion-pair state, $^1(BP^-\text{-}MDPA^+)^*$ and $^3(BP^-\text{-}MDPA^+)^*$, these being deactivated without giving the ketyl radical.[5] The reactivity of the ion-pair state was explained by the difference in the structure of the ion pair. The encounter complex between free BP and MDPA is a nonactivated CT state in which the complex is able to undergo proton transfer, whereas the complexes in the ground state are considered to be a relaxed CT state in which proton transfer does not take place.

Benzil is one of typical α-dicarbonyl compounds. Upon excitation of benzil in the presence of amine, hydrogen abstraction reaction takes place. Encinas and Scaiano reported that the triplet encounter complex produced an ion pair state in aqueous acetonitrile solution.[6,7] Ketyl radical formation was reported by Mukai et al. in benzil/triethylamine (TEA) in 2-propanol.[8,9] It is notable that the chemically induced dynamic electron polarization (CIDEP) signal observed in this system showed dual spin polarization depending on the concentrations of quenchers. When the concentration of the quencher was higher than 10^{-1} M, absorptive spin polarization was observed, when the concentration of quencher was less than 10^{-3} M, an emissive signal was observed. Two mechanisms were proposed to explain this phenomenon. Mukai et al.[10] proposed that different electronic states give different polarized radicals. Our explanation is that the complex formed in the ground state gives the opposite spin polarized radical to free triplet benzil.[11] In our preliminary paper, we successfully demonstrated switching of the polarization change depending on the concentration of triethylamine, where we suppose that the quantum yield of ketyl radical from ground state complex is nearly unity, because considerably strong intensity of the CIDEP signal was observed. Interaction between ketyl radical produced from the ground state complex and triplet benzil generates emissive spin polarization by the radical−triplet pair mechanism (RTPM).[12,13] It means that the quantum yield of the reaction to produce benzil ketyl radical should be different between the triplet encounter complex and the ground state complex. In this study, the reaction mechanism of both complexes has been investigated by nanosecond laser photolysis experiment.

Experimental Section

For transient absorption measurements, a Nd^{3+}:YAG laser (Quanta-Ray GCR-130 or Quantel YG-571, 355 nm) was used as an excitation light source. The samples were flowed through a quartz cell at a flow rate of ca. 30 mL min^{-1}. The transient signals were detected by a photomultiplier tube. The output signals were measured by a digital oscilloscope (Sony Tektronix

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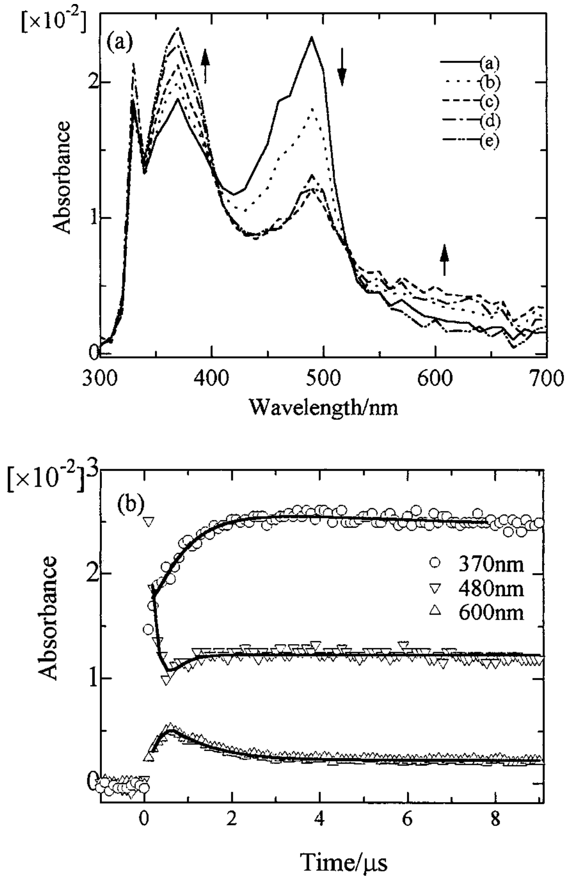

Figure 1. (a) Transient absorption spectra obtained by laser photolysis of benzil (2×10^{-2} M)/TEA (5×10^{-4} M) in benzene at (a) 200, (b) 400, (c) 800, (d) 1600, and (e) 3200 ns after the laser pulse. (b) Time profiles of the transient absorption of (a) 370 (○), (b) 480 (▽), and (c) 600 nm (△) obtained from benzil (2×10^{-2} M)/TEA (5×10^{-4} M) in benzene; solid lines indicate model fits.

TDS380P) and transferred to a personal computer. Steady state emission was recorded on a HITACHI M-850 fluorescence spectrometer and absorption spectrum was recorded on a HITACHI U3300 spectrophotometer.

All samples and solvents are guaranteed reagent grade. Benzil (Tokyo Kasei) was used for transient absorption experiments without further purification. Zone-refined benzil was used for fluorescence measurement. Triethylamine, *N*,*N*-diethylaniline, diethylamine, and *N*-ethylaniline were purchased from Tokyo Kasei and used without further purification. Aniline (Kishida Chemical) was purified by vacuum distillation under reduced pressure. Benzene (Kanto Kagaku) and 2-propanol (Kanto Kagaku) were used as solvents without further purification.

Results and Discussion

Transient absorption spectra of the benzil/TEA system in benzene solution are shown in Figure 1a. The spectrum obtained at 200 ns after the laser flash has peaks at 370 and 480 nm, and a broad absorption around 600 nm. The peak at 480 nm is attributed to the T−T absorption of benzil, because the transient absorption spectrum of benzil in the absence of TEA has a typical peak at 480 nm due to triplet benzil.[6] The peak at 370 nm is assigned to the benzil ketyl radical because the transient absorption spectrum of benzil in 2-propanol showed a peak at 370 nm, where the benzil ketyl radical is known to be produced.[10] The longer wavelength transient absorption around 600 nm was reported to be benzil anion radicals.[6] As the transient signals were not observed for the oxygen-saturated solution, the transient species were considered to be produced from triplet precursors.

To elucidate the kinetics of the electron transfer and hydrogen abstraction reactions, time profiles of the transient absorption were measured. Figure 1b shows the time profiles monitored at 370, 480, and 600 nm. Decay at 480 nm is composed of triplet benzil and long-lived absorption of the benzil ketyl radical. The time profile at 600 nm is composed of rise and decay. The 600 nm absorption is ascribable to the contact ion pair between benzil anion and TEA cation, not to the benzil anion radical. The reasons are that in polar solvent such as acetonitrile slow rise is observed but the successive decay is not observed, and the decay time profile could be analyzed by the single-exponential decay function with the rate constant of 1.7×10^6 s^{-1} independent of the concentration of TEA. The time profile at 370 nm is composed of very fast rise that is faster than the decay of the triplet and slow rise continued up to 3 μs. The origin of the fast rise is discussed below. The reaction mechanism for the slow components is expressed as follows

$$^3\mathrm{B}^* \xrightarrow{k_0} {}^1\mathrm{B} \tag{1}$$

$$^3\mathrm{B}^* + \mathrm{TEA} \xrightarrow{k_{\mathrm{et}}} (\mathrm{B}^- \cdots \mathrm{TEA}^+)_{\mathrm{CIP}} \tag{2}$$

$$(\mathrm{B}^- \cdots \mathrm{TEA}^+)_{\mathrm{CIP}} \xrightarrow{k_{\mathrm{pt}}} \mathrm{BH}^\bullet + \mathrm{TEA}^\bullet \tag{3}$$

$$2\mathrm{BH}^\bullet \xrightarrow{k_{\mathrm{r}}} (\mathrm{Ph{-}COCOH{-}Ph})_2 \tag{4}$$

where $(\mathrm{B}^- \cdots \mathrm{TEA}^+)_{\mathrm{CIP}}$ is the contact ion pair (CIP), and $\mathrm{BH}^\bullet$ and $\mathrm{TEA}^\bullet$ are benzil ketyl radical and the counter radical, respectively. The rate equations of (1)−(4) are

$$\frac{\mathrm{d}[^3\mathrm{B}^*]}{\mathrm{d}t} = -(k_0 + k_{\mathrm{et}}[\mathrm{TEA}])[^3\mathrm{B}^*] \tag{5}$$

$$\frac{\mathrm{d}[\mathrm{TEA}]}{\mathrm{d}t} = -k_{\mathrm{et}}[\mathrm{TEA}][^3\mathrm{B}^*] \tag{6}$$

$$\frac{\mathrm{d}[\mathrm{B}^- \cdots \mathrm{TEA}^+]}{\mathrm{d}t} = k_{\mathrm{et}}[\mathrm{TEA}][^3\mathrm{B}^*] - k_{\mathrm{pt}}[\mathrm{B}^- \cdots \mathrm{TEA}^+] \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{BH}^\bullet]}{\mathrm{d}t} = k_{\mathrm{pt}}[\mathrm{B}^- \cdots \mathrm{TEA}^+] - k_{\mathrm{r}}[\mathrm{BH}^\bullet]^2 \tag{8}$$

where k_{r} is a recombination rate constant between benzil ketyl radicals. These equations are numerically solved using the rate constants of $k_0 = 2 \times 10^5$ s^{-1}, $k_{\mathrm{et}} = 6 \times 10^8$ M^{-1} s^{-1}, $k_{\mathrm{pt}} = 1.5 \times 10^6$ s^{-1}, and $k_{\mathrm{r}} = 2 \times 10^5$ M^{-1} s^{-1}.

Immediate formation suggests a reaction of the complex formed in the ground state. Benzil is reported to form complexes with several phenols, amines, and alcohols.[15] Figure 2a shows the absorption spectra in the benzil (1×10^{-2} M)/TEA system obtained at various concentrations of TEA from 0 to 10^{-1} M. Absorbance in the region of 350−450 nm increases with increasing in [TEA], which indicates complex formation. The slight absorbance change even in the presence of 10^{-1} M of TEA suggests that the complex is not a strong CT complex. More detailed discussion is given below.

The equilibrium constant was measured by the fluorescence quenching

$$\mathrm{B} + \mathrm{TEA} \overset{K}{\rightleftharpoons} \mathrm{B} \cdots \mathrm{TEA} \tag{9}$$

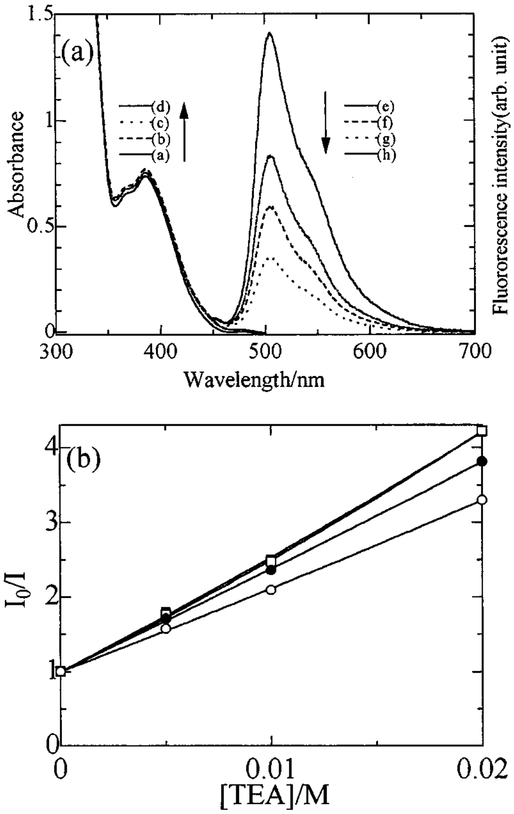

Figure 2. (a) Concentration dependence on TEA of absorption and fluorescence spectra of benzil (1×10^{-2} M)/TEA. TEA concentrations are (a) 0, (b) 1.25×10^{-1}, (c) 2.5×10^{-1}, and (d) 5×10^{-1} M for absorption measurements, and (e) 0, (f) 5×10^{-2}, (g) 1×10^{-1}, and (h) 2×10^{-1} M for fluorescence measurements. (b) Stern−Volmer plots of the fluorescence intensity vs concentration of TEA depending on the concentration of benzil. Concentrations of benzil are 5×10^{-3} (○), 1×10^{-2} (●), 2×10^{-2} (□), and 4×10^{-2} M (■).

In Figure 2a, fluorescence spectra are also shown at various TEA concentrations. Fluorescence was efficiently quenched by addition of TEA. Relatively high concentration of benzil (4×10^{-2} M) might give rise to fluorescence quenching by reabsorption or self-quenching process. The quenching caused by reabsorption can be neglected because of the small absorbance (<0.05) in the wavelength where absorption and fluorescence overlap each other. The self-quenching process could also be neglected because the fluorescence intensity was confirmed to be proportional to the concentration of benzil under our experimental condition. The Stern−Volmer plots are shown in Figure 2b at four different benzil concentrations. If the quenching is caused by only a diffusion-controlled process, the Stern−Volmer plots should follow a common straight line and slope of the plot should be independent of the benzil concentration. Our results show, however, that the plot does not give a straight line and fluorescence is more efficiently quenched at high concentration of benzil. This indicates that quenching is caused by not only a diffusion-controlled process but also complex formation in the ground state. The complex is considered to be non-fluorescent because no emission was observed at high concentration of TEA. The concentration of the complexes is written as follows:

$$[\mathrm{B\cdots TEA}] = \frac{(a_0K + b_0K + 1) - \sqrt{(a_0K + b_0K + 1)^2 - 4a_0b_0K^2}}{2K} \tag{10}$$

where K is the equilibrium constant, and a_0 and b_0 are the initial concentration of TEA and benzil, respectively.

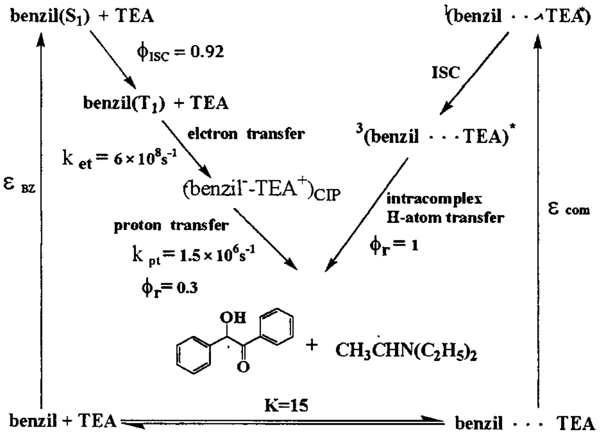

Figure 3. Reaction scheme to product benzil ketyl radical.

Fluorescence intensity quenched in the presence of TEA by the dynamic process of S_1 and complex formation is expressed as follows:

$$I = \left(1 - \frac{k_q\tau_f[\mathrm{TEA}]}{1 + k_q\tau_f[\mathrm{TEA}]} - \frac{(a_0K - b_0K + 1) + \sqrt{(a_0K + b_0K + 1)^2 - 4a_0b_0K^2}}{2b_0K}\right) I_0 \tag{11}$$

and the Stern−Volmer plot can be expressed as follows:

$$\frac{I_0}{I} = \left(1 - \frac{k_q\tau_f[\mathrm{TEA}]}{1 + k_q\tau_f[\mathrm{TEA}]} - \frac{(a_0K - b_0K + 1) + \sqrt{(a_0K + b_0K + 1)^2 - 4a_0b_0K^2}}{2b_0K}\right)^{-1} \tag{12}$$

The equilibrium constant K is determined to be ca. 15 M^{-1} by least-squares fitting when the dynamic fluorescence quenching rate constant of TEA $k_q = 7 \times 10^9$ M^{-1} s^{-1} and $\tau_f = 2 \times 10^{-9}$ s are used.[13]

The molar extinction coefficient of the complex between benzil and TEA was determined from the following equation:[15]

$$\frac{1 - \dfrac{\mathrm{OD}_0}{\mathrm{OD}}}{[\mathrm{TEA}]} = -K + \left(\frac{\epsilon_{\mathrm{com}}}{\epsilon_{\mathrm{B}}}\right) K \left(\frac{\mathrm{OD}_0}{\mathrm{OD}}\right) \tag{13}$$

where ϵ_B and ϵ_{com} are molar extinction coefficient of free benzil and complex, respectively. OD_0 and OD represents optical density of the solutions in the absence and presence of TEA. By using the obtained equilibrium constant K, ϵ_{com} was determined to be 490 M^{-1} cm^{-1}. The reaction scheme is shown in Figure 3.

To obtain the absolute quantum yield of the ketyl radical, ϕ_r, the concentration of the triplet and concentration of the benzil ketyl radical should be estimated. The former one could be obtained by use of the chemical actinometry method comparing with the optical density of the T−T absorption of benzophenone whose ϵ_{T-T} at 545 nm is known to be 4600 M^{-1} cm^{-1}.[16] To obtain the latter, the molar extinction coefficient of the benzil ketyl radical should be measured. This was estimated by using the transient absorption spectrum of the benzil/*N*,*N*-diphenylamine system. Photolysis of this system leads to hydrogen abstraction and produces both benzil ketyl and *N*,*N*-diphenyl-

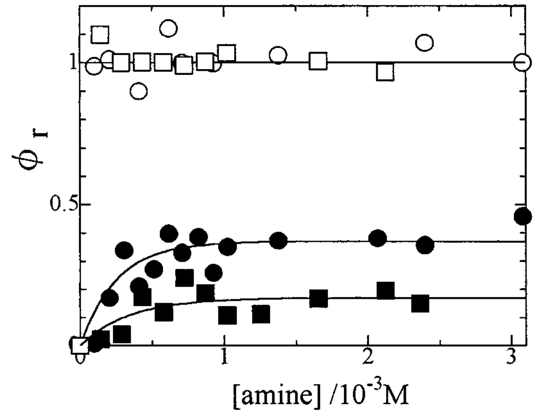

Figure 4. Plots of ketyl radical formation quantum yield from free benzil and from complex: (○, ●) ϕ_r^{com} and ϕ_r^{free} of benzil−TEA system, and (□, ■) ϕ_r^{com} and ϕ_r^{free} of benzil−DEA system, respectively.

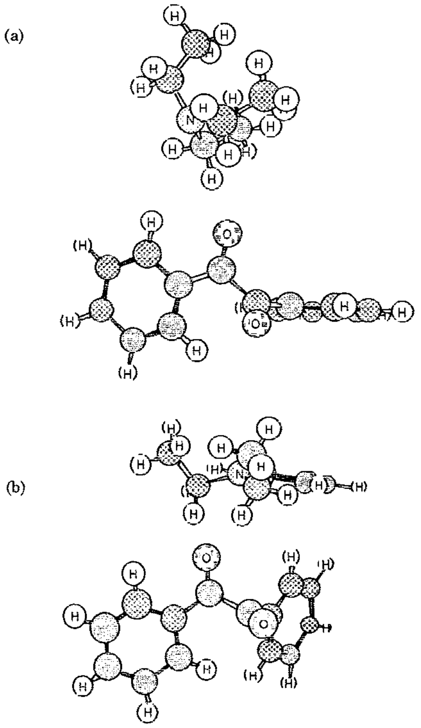

Figure 5. Calculated structure of the ground state complex of (a) benzil−TEA and (b) benzil−DEA by the MNDO/PM3 method.

amine radicals whose molar extinction coefficient is 2300 M^{-1} cm^{-1} at 745 nm. The molar extinction coefficient of benzil ketyl could be obtained as 8680 M^{-1} cm^{-1} at 485 nm. The quantum yield from the complex, ϕ_r^{com}, is expressed as ϕ_r^{com} = (concentration of the radical from the ground state complex)/(concentration of the excited state complex). The concentration of the excited state complex is determined by

$$c^*_{com} = \frac{1000}{N_A V}\frac{\epsilon_{com}c_{com}l}{\epsilon_{free}c_{free}l + \epsilon_{com}c_{com}l} I_0 \times 10^{-\epsilon_{com}c_{com}l} \qquad (14)$$

where N_A is Avogadro's number. Under our experimental conditions with [benzil] = [TEA] = 2 × 10^{-3} M and $K = 15$, the concentration of the ground state complex, c_{com}, was estimated to be 5.7 × 10^{-5} M. By use of molar extinction coefficient of the complex, $\epsilon_{com} = 490$ M^{-1} cm^{-1}, $I_0 = 4.4 \times 10^{16}$ photon/pulse (25 mJ/pulse at 355 nm), and volume of the cell, $V_{cell} = 0.7$ mL^3, the concentration of the excited state complex, c^*_{com}, was estimated to be 3.3 × 10^{-6} M. On the other hand, the concentration of the ketyl radical derived from transient absorption spectrum was estimated to be 3.4 × 10^{-6} M, which is essentially the same as that of the precursor. The ϕ_r^{com} at the several concentrations of TEA are plotted in Figure 4. ϕ_r^{com} is found to be unity at any concentrations of TEA.

The quantum yields of the radical from the free triplet benzil, ϕ_r^{free}, are determined by estimating the concentration of the radical from the slow rise part of the transient absorption spectrum at the absorption wavelength of the benzil ketyl radical. The concentration of the radical should be estimated by subtracting the contribution of triplet benzil at this wavelength. ϕ_r^{free} is expressed as $\phi_r^{free} = [\text{ketyl}^{slow}]_{t=\infty}/[^3\text{benzil}]_{t=0}$. The concentration of quenched triplet is given by $k_q[\text{TEA}]/(k_0 + k_q[\text{TEA}])[^3\text{benzil}]_{t=0}$. The concentration of the triplet is estimated by the chemical actinometry using transient absorption of the triplet benzophenone. The concentration of triplet benzil was calculated by $[^3\text{benzophenone}]_{t=0}\phi_{ISC}(0.93)$ under the same experimental conditions. The calculated ϕ_r^{free} are plotted against [TEA] in the Figure 4. The resulting quantity of the radical is calculated by solving the following rate equations numerically, where ϕ_r^{free} was used as a fitting parameter.

$$\frac{d[^3B^*]}{dt} = -(k_0 + k_q[\text{TEA}])[^3B^*] \qquad (15)$$

$$\frac{d[\text{TEA}]}{dt} = -\phi_r^{free}k_q[^3B^*][\text{TEA}] \qquad (16)$$

$$\frac{d[\text{ketyl}]}{dt} = \phi_r^{free}\, k_q[^3B^*][\text{TEA}] \qquad (17)$$

Thus, the ϕ_r^{free} is estimated to be 0.31, which is smaller than that for the complex ($\phi_r^{com} = 1$). This fact strongly suggests that the geometry of encounter complex (between free triplet benzil and TEA) and the ground state complex are different from each other. To clarify the high efficiency of the ground state complex, MNDO-PM3 calculations were carried out, and the resulting conformations of the ground complex of benzil−TEA and benzil−*N*,*N*-diethylaniline are shown in Figure 5. β-Hydrogen is preferable to α-hydrogen in the abstraction by carbonyl O atom.[17] Both structures have a configuration in which the carbonyl O atom of benzil and H atom at β position of TEA or *N*,*N*-diethylaniline are close to each other. The distance and bond order between O and H atom for the benzil−TEA complex are 1.90 Å and 0.02, respectively. The distance and bond order for benzil−*N*,*N*-diethylaniline are 1.88 Å and 0.02, respectively. Stabilization energies of both complexes are 29 kJ mol^{-1}. Charge density on the hydrogen atom is changed from 0.05 in the free molecule to only ca. 0.10 in the complex. This small charge transfer nature indicates that these complexes are not CT complexes. It should be noted that these complexes are not hydrogen-bonded complexes because complexes are formed between β-hydrogens and carbonyl O atom. The conformation is responsible for the high reaction quantum yield, $\phi_r^{com} = 1$.

The reaction yields of the triplet benzil and amines depend on the species of amines. Table 1 summarizes quenching rate constants, k_q, oxidation potential, E_{ox} vs SCE, and quantum yield of the ketyl radical from the ground state complex, ϕ_r^{com}, and free triplet benzil, ϕ_r^{free}. It is understood from Table 1 that there was no apparent relationship between k_q and E_{ox}, but ϕ_r^{free} are greatly influenced by the number of hydrogen atom of each amines. β-Hydrogen atoms which can be abstracted by carbonyl

TABLE 1: Quantum Yields of Ketyl Radical Formation for Benzil with Various Amines in Benzene and Parameters of Amines

amine	E_{ox} vs SCE (V)[a]	k_q/ 10^9 M^{-1} s^{-1}	ϕ_r^{free}	ϕ_r^{com}	No. of β-H atoms
TEA	0.97	0.6	0.31	1.0	6
N,*N*-diethylaniline	0.70	0.99	0.17	1.0	4
diethylamine	-	0.59	0.13	0[b]	4
N-ethylaniline	0.70	4.0	0.082	1.0	2
aniline	1.15	2.2	0	1.0	2[c]

[a] From ref 16. [b] Complex formation in the ground state was not detected. [c] α-Hydrogen.

O atom are counted. *N*-Ethylaniline, *N*,*N*-diethylaniline, and triethylamine have two, four, and six β-hydrogens, respectively. The greatest quantum yield was determined for the system of TEA which has the greatest number of hydrogen atoms, while the smallest was for the system of *N*-ethylaniline which has the smallest number of hydrogen atoms except for aniline. Aniline has no β-hydrogen. It is considered that the hydrogen abstraction efficiency is different from other amines with β-hydrogens. It is concluded that hydrogen abstraction takes place easily in the encounter complex with amines that have large number of β-hydrogen atoms.

Summary

Mechanisms for ketyl radical formation of benzil in the presence of various amines were investigated. Benzil ketyl radical was produced from triplet encounter complex and photoexcitation of the ground state complex. Equilibrium constant of the ground state complex was 15. Quantum yields of the ketyl radical formation from the complex were almost unity independent of the kind of amines. The conformation of the complex is responsible for the efficient hydrogen atom transfer. The quantum yields of free triplet benzil were 0−0.31 depending on the kind of the amines. The largest factor that influences the quantum yield of the ketyl radical is the number of β-hydrogen atom of amines.

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