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Laser Flash Photolysis Study on the Hydrogen Atom Transfer Reaction from Triplet 2-Naphthylammonium Ion to Benzophenone. Remarkable Proton Effect[1a,b]

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The laser flash photolysis study at 355 nm in the 2-naphthylammonium ion ($\mathrm{RNH_3}^{+}$) and benzophenone (BP) system has been carried out in methanol–water (9:1 v/v) at 290 K. At first, triplet benzophenone ($^{3}\mathrm{BP}^{*}$) produced by fast intersystem crossing of $^{1}\mathrm{BP}^{*}$ excited at 355 nm is quenched by $\mathrm{RNH_3}^{+}$ with almost diffusion-controlled rates (1.1×10^{10} $\mathrm{M^{-1}\,s^{-1}}$ at $[\mathrm{H_2SO_4}] = 0.015$ M; 3.9×10^{9} $\mathrm{M^{-1}\,s^{-1}}$ at $[\mathrm{H_2SO_4}] = 0.5$ M). The triplet 2-naphthylammonium ion ($^{3}\mathrm{RNH_3}^{+*}$) is produced in the nanosecond region by triplet energy transfer from $^{3}\mathrm{BP}^{*}$ to $\mathrm{RNH_3}^{+}$ with efficiencies of 0.41 ($[\mathrm{H_2SO_4}] = 0.015$ M) and 0.33 ($[\mathrm{H_2SO_4}] = 0.5$ M) at $[\mathrm{RNH_3}^{+}] = 3.0 \times 10^{-3}$ M and at $[\mathrm{BP}] = 1.12 \times 10^{-2}$ M, competing with hydrogen abstraction of $^{3}\mathrm{BP}^{*}$ from solvent (methanol) or $\mathrm{RNH_3}^{+}$ molecules. Subsequently, in the microsecond region the hydrogen atom transfer (HT) reaction from $^{3}\mathrm{RNH_3}^{+*}$ to ground BP occurs effectively to give the naphthylamine cation radical ($\mathrm{RNH_2}^{\bullet+}$) and the ketyl radical ($>\dot{\mathrm{C}}\mathrm{OH}$). The decay rate $(\tau_{\mathrm{obsd}})^{-1}$ of $^{3}\mathrm{RNH_3}^{+*}$ increases with an increase of the BP concentration, and at higher BP concentrations a leveling off is observed. The $(\tau_{\mathrm{obsd}})^{-1}$ value decreases drastically with an increase in acid concentration. The mechanism of the HT reaction can be accounted for by the intracomplex HT reaction of the triplet exciplex $^{3}(\mathrm{RNH_3}^{+}\cdots{>}\mathrm{CO})^{*}$ with a rate constant of ca. 5×10^{6} $\mathrm{s^{-1}}$. At higher acid concentrations, the triplet complex is decomposed by protonation to give free $^{3}\mathrm{RNH_3}^{+*}$ and BP, resulting in suppression of the rate for the HT reaction.

Hydrogen atom transfer is one of the elementary processes in chemistry along with electron transfer or proton transfer. Many studies on intermolecular and intramolecular hydrogen abstraction reactions in the triplet state of carbonyl compounds have been reported.[2-15] It is known that the reaction proceeds by either hydrogen atom abstraction or electron transfer followed by proton transfer.

However, little attention has been paid to hydrogen atom transfer from triplet aromatic compounds to the ground aromatic ketones until very recently. We have demonstrated the hydrogen atom transfer (HT) reaction from naphthol (ROH) to ground benzophenone (BP) by means of laser flash photolysis.[16] In a preliminary report, the HT reaction from triplet naphthylammonium ion ($^{3}\mathrm{RNH_3}^{+*}$) to ground carbonyl compounds has been also shown.[17] It is well-known that in the excited singlet state of ROH or $\mathrm{RNH_3}^{+}$ proton transfer takes place effectively.[18] The HT reaction from $^{3}\mathrm{ROH}^{*}$ to BP was considered to proceed via the triplet exciplex $^{3}(\mathrm{ROH}\cdots{>}\mathrm{CO})^{*}$.[16] However, the direct HT reaction from $^{3}\mathrm{ROH}^{*}$ to BP without the triplet exciplex was suggested by Gorman et al.[19] Therefore, there is an ambiguity in the mechanism of the HT reaction from the triplet aromatic compounds to ground BP.

This work was carried out to answer the following questions: (1) What is the mechanism of the HT reaction from $^{3}\mathrm{RNH_3}^{+*}$ to ground BP? (2) Is there real exciplex formation in the triplet state? (3) How about the proton effect on the HT reaction? In the present paper, we report the HT reaction from $^{3}\mathrm{RNH_3}^{+*}$ (produced by triplet sensitization of BP) to BP in details by means of laser flash photolysis.

Experimental Section

Materials. 2-Naphthylamine (G. R. grade, Tokyo Kasei) was purified by repeated recrystallizations from ethanol, followed by sublimation. Benzophenone (Wako) was twice recrystallized from an ethanol–water mixture (1:1 v/v). Methanol (Spectrosol, Wako), $\mathrm{H_2SO_4}$ (97% Wako), and $\mathrm{HClO_4}$ (60% Wako) were used without further purification. Deionized water was distilled. Actual acid contents were determined by titration. In most cases, the concentration of 2-naphthylamine ($\mathrm{RNH_2}$) was 3.0×10^{-3} M in methanol containing 10% $\mathrm{H_2O}$ by volume. Benzophenone (BP) [3×10^{-3}–0.22 M] was used as a triplet sensitizer. $\mathrm{H_2SO_4}$ or $\mathrm{HClO_4}$ [0.015–1.0 M] was used as the proton source, since the counterion ($\mathrm{SO_4}^{2-}$ or $\mathrm{ClO_4}^{-}$) does not quench the triplet molecules.[20] At the acid concentration used, $\mathrm{RNH_2}$ was completely protonated in the ground state ($\mathrm{p}K_\mathrm{a} = 4.1$), and $\mathrm{RNH_3}^{+}$ had no absorption at the excitation wavelength (355 nm) in the ground state. All samples in 1- and 10-mm path-length cells were thoroughly degassed by freeze–pump–thaw cycles on a high-vacuum line. Spectral data regarding transients were obtained by a fresh sample to avoid excessive exposure to the laser pulse.

Laser Flash Photolysis Instrument. A nanosecond Nd^{3+}:YAG laser system at 355 nm (JK Lasers HY500, pulse width 8 ns, laser power 70 mJ, third harmonic) was used for sample excitation. The monitoring system consisted of a pulse UXL-150D xenon lamp (Hamamatsu), a MC-20N monochromator (Ritsu), and an HTV R928 photomultiplier (Hamamatsu, used for the detection part). The transient signal was recorded with a 100-MHz storage oscilloscope (Iwatsu TS-8123), and data analyses were carried out by use of a microcomputer (NEC, PC-9801 VM2). UV absorption spectra were recorded with Hitachi 200 and Hitachi 139 spectrophotometers. The laser experiments were carried out independently five times, and the reproducible data were carefully obtained. The laser intensity effect at 355 nm on the triplet decay

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(1) (a) This paper is dedicated to Professor Paul de Mayo (University of Western Ontario) on the occasion of his retirement. (b) The preliminary account of this paper was presented at the Symposium on Chemical Reactions, Nagaoka, Japan, July, 1988. (c) The Institute of Physical and Chemical Research, Wako Saitama 351-01, Japan.

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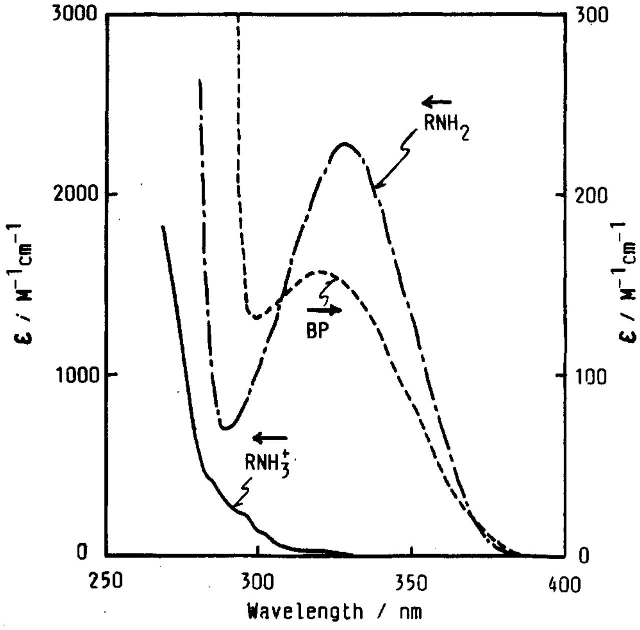

Figure 1. UV absorption spectra of BP, RNH_2, and RNH_3^+ at longer wavelengths in methanol–water (9:1 v/v). BP: λ_{max} = 332 nm, ϵ = 157 M^{-1} cm^{-1}. RNH_2: λ_{max} = 345 nm, $\epsilon = 2.3 \times 10^3$ M^{-1} cm^{-1}.

due to the triplet–triplet annihilation was checked by use of neutral density filters.

Results and Discussion

Absorption Spectra in the Ground State. Figure 1 shows the absorption spectra of benzophenone (BP), 2-naphthylamine (RNH_2), and 2-naphthylammonium ion (RNH_3^+) in the ground state, in a methanol–water mixture (9:1 v/v). RNH_2 has a π,π^* absorption around 340 nm, but not for RNH_3^+. Therefore, only BP was excited at 355 nm in the RNH_3^+–BP system. In the presence of protons ([H_2SO_4] = 0.015 M), RNH_2 was protonated completely in the ground state, since the pK_a value of RNH_2 is 4.1.[21] There was no change in absorption of RNH_3^+ in a relatively high concentration of acid, e.g., [H_2SO_4] = 0.5 M. No change in absorption of BP at 350 nm was also obtained with the addition of RNH_3^+. Therefore, it can be said that there is no interaction between BP and RNH_3^+ in the ground state. It is obvious that no protonation to BP occurs in the ground state under the concentration of H_2SO_4 used because of its large negative pK_a value (−5.7).[22]

Generation of $^3RNH_3^{+*}$ by Triplet Energy Transfer. The excited singlet state of BP ($^1BP^*$) was produced initially upon laser pulse excitation at 355 nm in the system. The triplet BP ($^3BP^*$) was formed via fast intersystem crossing with a picosecond time scale.[23,24] In the presence of RNH_3^+, $^3BP^*$ was quenched competitively by energy transfer to RNH_3^+ and by hydrogen abstraction from RNH_3^+ or solvent molecules. The triplet energy transfer from $^3BP^*$ to RNH_3^+ is possible, since the triplet energies of BP and RNH_3^+ are known to be 69.2[25] and 60.9 kcal/mol,[17] respectively.

At first, the triplet energy transfer reaction (i.e., the quenching of $^3BP^*$ by RNH_3^+) was studied. Figure 2 shows the time-resolved transient absorption spectra of BP (1.12×10^{-2} M) in the presence of RNH_3^+ (3.0×10^{-3} M) in a methanol–water mixture (9:1 v/v) at 290 K containing 0.015 M H_2SO_4, obtained by nanosecond laser flash photolysis at 355 nm. The transient spectra in the nanosecond time scale have two band maxima at 525 and 410 nm. A decrease at the 525-nm band accompanies an increase of the 410-nm peak. Moreover, one can clearly observe the existence of an isosbestic point at 460 nm. The 525-nm peak entirely corresponds to the $T_n \leftarrow T_1$ absorption band of BP.[26,27] The 410-nm peak with vibrational structures was very similar to the $T_n \leftarrow T_1$ absorption spectrum (λ_{max} = 410 nm) of naphthalene, and it was quenched markedly by dissolved oxygen. The shorter wavelength band is, therefore, ascribable to the $T_n \leftarrow T_1$ absorption spectrum of RNH_3^+.[17] The spectral change in Figure 2 shows that the triplet 2-naphthylammonium ion ($^3RNH_3^{+*}$) is produced by triplet sensitization of BP.

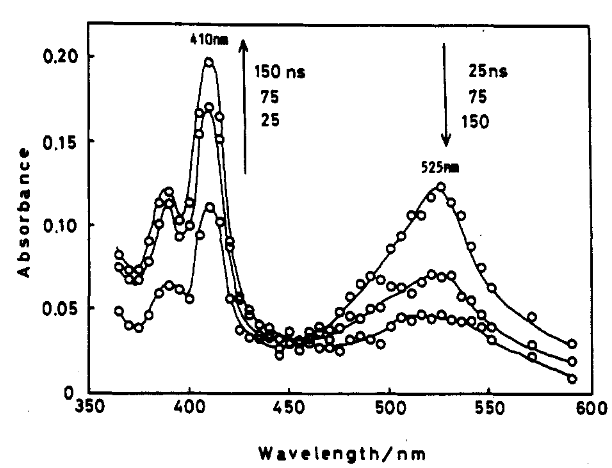

Figure 2. Nanosecond time-resolved transient absorption spectra of BP (1.12×10^{-2} M) in the presence of RNH_3^+ (3.0×10^{-3} M) in methanol–water (9:1 v/v) at 290 K containing 0.015 M H_2SO_4, obtained by laser flash photolysis at 355 nm.

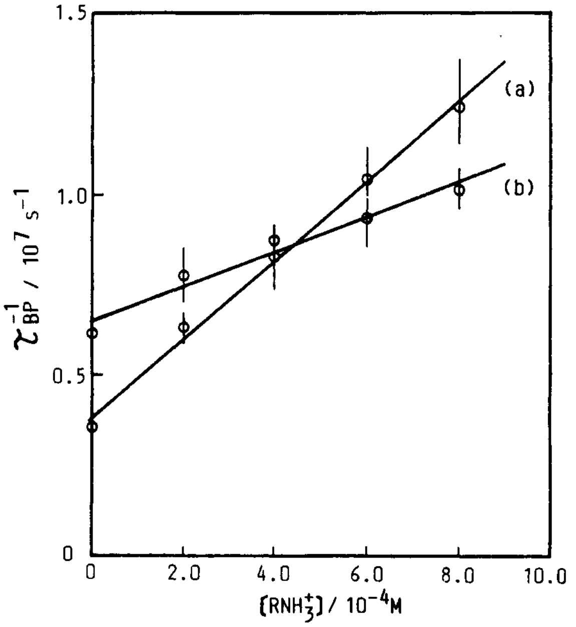

Figure 3. Stern–Volmer plots of the decay rate constants τ_{BP}^{-1} of $^3BP^*$ as a function of the concentration of RNH_3^+ in the presence of 0.015 (a) and 0.5 M (b) H_2SO_4, respectively.

The transient peak at 525 nm of $^3BP^*$ decays, with a single-exponential function. The decay rate of $^3BP^*$ monitored at 525 nm increases significantly with increasing the concentration of RNH_3^+. Figure 3 shows the plots of the decay rate constant (τ_{BP}^{-1}) of $^3BP^*$ as a function of the concentration of RNH_3^+ in the presence of 0.015 (a) and 0.5 M (b) H_2SO_4. The quenching of $^3BP^*$ by RNH_3^+ was found to follow a Stern–Volmer rela-

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TABLE I: Experimental Data of the Decay of $^3BP^*$ at [BP] = 1.12 × 10^{-2} M in MeOH–H_2O (9:1 v/v) at 290 K: Quenching Constant k_q, Decay Rate of $^3BP^*$ in the Absence of RNH_3^+ $(\tau_{BP}^0)^{-1}$, and Efficiencies of the Triplet Energy Transfer ϕ_{ET}, the Usual Hydrogen Abstraction from Methanol (ϕ_{HA}) and from RNH_3^+ (ϕ_{HA}'), and the RNH_3^+-Induced Quenching (ϕ_q')[a,b]

	$[H_2SO_4]$/M	
	0.015	0.5
k_q/M^{-1} s^{-1}	1.1 × 10^{10}	3.9 × 10^9
$(\tau_{BP}^0)^{-1}$/s^{-1}	3.9 × 10^6	7.1 × 10^6
ϕ_{ET}[c]	0.41	0.33
ϕ_{HA}[c]	0.24	0.14
ϕ_{HA}'[c]	0.14	0.02
ϕ_q'[c]	0.21	0.51

[a] For details, see text. [b] Errors ±10%. [c] $[RNH_3^+]$ = 3.0 × 10^{-3} M.

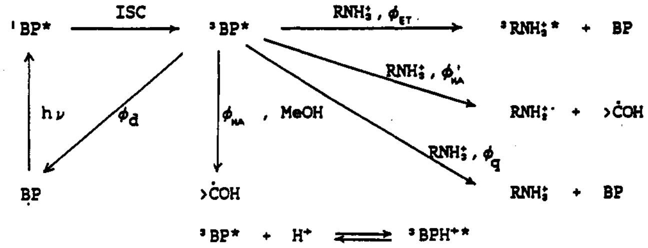
tionship. The decay rate constant (τ_{BP}^{-1}) of $^3BP^*$ can be expressed by the Stern–Volmer equation:[28]

$$\tau_{BP}^{-1} = (\tau_{BP}^0)^{-1} + k_q[RNH_3^+] \qquad (1)$$

where τ_{BP}^0 is the lifetime of $^3BP^*$ in the absence of RNH_3^+, and its value (ca. 0.26 μs at $[H_2SO_4]$ = 0.015 M or ca. 0.14 μs at $[H_2SO_4]$ = 0.5 M) entirely agrees with that obtained from the intercept of the Stern–Volmer plot in Figure 3. Here, k_q is the quenching rate constant of $^3BP^*$ by RNH_3^+. The k_q values were obtained as 1.1 × 10^{10} M^{-1} s^{-1} ($[H_2SO_4]$ = 0.015 M) and 3.9 × 10^9 M^{-1} s^{-1} ($[H_2SO_4]$ = 0.5 M), indicating that the quenching takes place with a diffusion-controlled rate. The values of k_q and $(\tau_{BP}^0)^{-1}$ in the presence of H_2SO_4 are listed in Table I. The $(\tau_{BP}^0)^{-1}$ value in the presence of $[H_2SO_4]$ = 0.5 M is greater than that of $[H_2SO_4]$ = 0.015 M. The result can be explained by the formation of the protonated triplet benzophenone ($^3BPH^{+*}$), since the pK_a value of $^3BP^*$ is 0.18 at 293 K.[29] However, the value of k_q at $[H_2SO_4]$ = 0.5 M is smaller than that at $[H_2SO_4]$ = 0.015 M. The viscosity of H_2SO_4 seems to affect the diffusion constant in a solution. Furthermore, the Coulombic interaction between the cations $^3BPH^{+*}$ and RNH_3^+ may decrease the collision rate. The absorption maximum of $^3BPH^{+*}$ is 20 nm blue-shifted compared to that of $^3BP^*$ with a large decrease in absorbance and $^3BPH^{+*}$ can be distinguished from $^3BP^*$ by its relatively short lifetime (ca. 13 ns).[29]

The quenching of $^3BP^*$ by RNH_3^+ may involve the following three processes: energy transfer (ET), hydrogen abstraction (HA) from RNH_3^+, and deactivation induced by RNH_3^+. The yields for these processes can be estimated separately by the spectral change in Figure 2. The energy-transfer efficiency ϕ_{ET} can be obtained as the concentration ratio ($[^3RNH_3^{+*}]_{max}/[^3BP^*]_{max}$). For instance, in the case of the system containing 0.015 M H_2SO_4, the concentration of $^3BP^*$ produced via fast intersystem crossing (ISC) of $^1BP^*$ by single laser pulse excitation was evaluated as ca. 1.2 × 10^{-5} M by using ε = 7800 M^{-1} cm^{-1} at 525 nm in methanol.[16] The concentration of $^3RNH_3^{+*}$ produced by triplet sensitization of BP was obtained to be 4.9 × 10^{-6} M by using ε = 16 000 M^{-1} cm^{-1} at 410 nm in a methanol–water mixture (9:1 v/v).[30] The ϕ_{ET} value was obtained as 0.41. As will be shown in the next section, the transients after completion of energy transfer are $RNH_2^{\bullet+}$ and $>\dot{C}OH$. The concentrations of $>\dot{C}OH$ and $RNH_2^{\bullet+}$ produced by the HA reaction of $^3BP^*$ from both RNH_3^+ and methanol were obtained to be 4.6 × 10^{-6} M and 1.7 × 10^{-6} M, respectively, by single laser excitation, using ε = 3220 M^{-1} cm^{-1} at 545 nm for $>\dot{C}OH$[26] and ε = 6000 (±600) M^{-1} cm^{-1} at 510 nm for $RNH_2^{\bullet+}$[30] in a methanol–water mixture (9:1 v/v). The difference (2.9 × 10^{-6} M) between the concentrations of $>\dot{C}OH$ and $RNH_2^{\bullet+}$ corresponds to the $>\dot{C}OH$ concentration produced by the HA reaction of $^3BP^*$ from solvent (methanol) molecules, since the concentration (1.7 × 10^{-6} M) of $RNH_2^{\bullet+}$ should be the same as that of $>\dot{C}OH$ produced by the HA reaction of $^3BP^*$ from RNH_3^+. The efficiency ϕ_{HA}' for the HA reaction of $^3BP^*$ from RNH_3^+ to produce $>\dot{C}OH$ plus $RNH_2^{\bullet+}$ was estimated to be 0.14, and the efficiency ϕ_{HA} for the HA reaction of $^3BP^*$ from methanol molecules was estimated as 0.24. The ϕ_d value for the decay from $^3BP^*$ to BP (see Scheme I) at $[H_2SO_4]$ = 0.015 M is negligibly small judging from the relatively small value of $(\tau_{BP}^0)^{-1}$ (3.9 × 10^6 s^{-1}). At the low concentration of H_2SO_4 (0.015 M), the ϕ_q' value for the other decay processes of $^3BP^*$ by RNH_3^+ is therefore estimated to be 0.21 from the equation $\phi_q' = 1 - (\phi_{ET} + \phi_{HA} + \phi_{HA}')$. The yields for the decay processes of $^3BP^*$ at $[H_2SO_4]$ = 0.015 and 0.5 M are also listed in Table I. At $[H_2SO_4]$ = 0.5 M, the values of ϕ_{HA} and ϕ_{HA}' for the HA processes are very small. At the higher acid concentration $[H_2SO_4]$ = 0.5 M, the HA reaction rate decreases significantly since $^3BPH^{+*}$ cannot abstract a hydrogen atom from solvent (methanol) and solute (RNH_3^+) molecules. The value of ϕ_{ET} (0.33) at $[H_2SO_4]$ = 0.5 M is small compared to that (0.41) at $[H_2SO_4]$ = 0.015 M. The triplet energy transfer between the cations ($^3BPH^{+*}$ and RNH_3^+) may be reduced by the Coulombic repulsion between them. The lifetime of $^3BPH^{+*}$ is known to be very short (ca. 13 ns).[29] That is, the large radiationless decay of $^3BPH^{+*}$ results in the relatively large ϕ_q' in contrast to that at lower acid concentration. The total quenching processes of $^3BP^*$ are described in Scheme I. It was confirmed that the process of the T–T energy transfer from $^3BP^*$ to RNH_3^+ is completed within ca. 180 ns under the experimental conditions.

SCHEME I



Time-Resolved Transient Absorption Spectra of the Hydrogen Atom Transfer Reaction from $^3RNH_3^{+*}$ to BP. Figure 4 shows the typical time-resolved transient absorption spectra of the hydrogen atom transfer (HT) reaction at the microsecond region in the presence of $[H_2SO_4]$ = 0.015 (a) and 0.5 M (b) for the BP (1.12 × 10^{-2} M) and RNH^{3+} (3.0 × 10^{-3} M) system in methanol–water (9:1 v/v) at 290 K, obtained by nanosecond laser flash photolysis at 355 nm. After the triplet ET reaction from $^3BP^*$ to RNH_3^+, the HT reaction takes place from $^3RNH_3^{+*}$ to BP, resulting in the formation of both $>\dot{C}OH$ and $RNH_2^{\bullet+}$. The time-resolved spectra in Figure 4a have three peaks at 410, 510, and 545 nm. The shorter wavelength band at 410 nm decreases accompanying an increase of the intensity of the longer wavelength bands at 510 and 545 nm with lapse of time. Moreover, an isosbestic point at 455 nm can be clearly observed in the time-resolved spectra. As mentioned above, the 410-nm band corresponds to the $T_n \leftarrow T_1$ absorption spectrum of RNH_3^+,[17] and the 510- and 545-nm bands correspond to the absorption spectra of $RNH_2^{\bullet+}$[17] and $>\dot{C}OH$,[26,27] respectively, as can be seen in Figure 5. These results show that the HT reaction originates from the triplet state of RNH_3^+ regardless of the concentration of acid used. However, the HT reaction is strongly affected by the acid concentration, as can be seen in Figure 4. First, the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ in the presence of $[H_2SO_4]$ = 0.015 and 0.5 M are 2.4 × 10^6 and 2.0 × 10^5 s^{-1}, respectively. The formation of both radicals ($RNH_2^{\bullet+}$ and $>\dot{C}OH$) is reduced markedly at $[H_2SO_4]$ = 0.5 M. By use of the reference spectra of $^3RNH_3^{+*}$, $RNH_2^{\bullet+}$, and $>\dot{C}OH$ with suitable multiplication factors, the transient spectra in Figure 4 could be reproduced well, indicating that the transients in Figure 4 consist of three species. Therefore, it can be said that there is no triplet naphthylamine ($^3RNH_2^*$) under the experimental condition. This result is reasonable, since the pK_a value of $^3RNH_3^{+*}$ (3.3)[31] is large enough to keep the pro-

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(30) $RNH_2^{\bullet+}$ and $>\dot{C}OH$ are produced by hydrogen atom transfer from $^3RNH_3^{+*}$ to BP with a 1:1 ratio. By use of the known ε value[26] of $>\dot{C}OH$ at 545 nm, the ε value at 510 nm for $RNH_2^{\bullet+}$ can be readily determined.

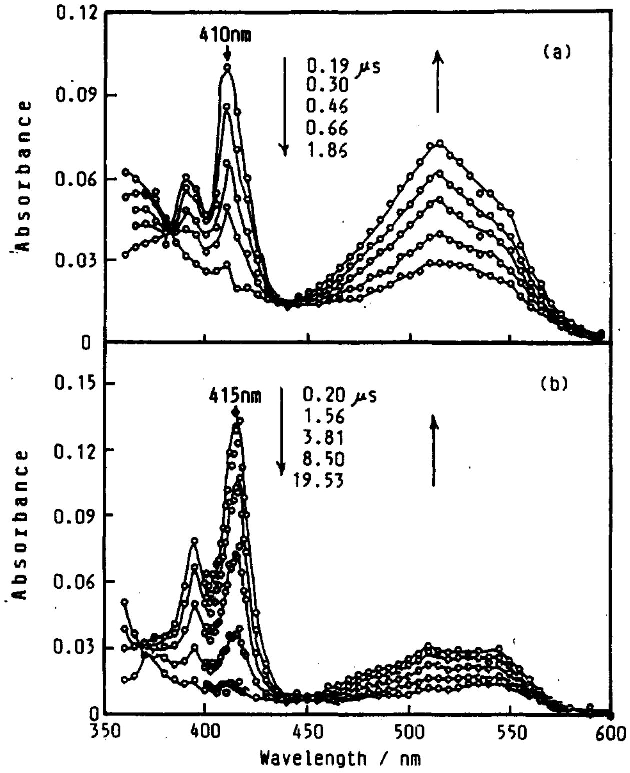

Figure 4. Time-resolved transient absorption spectra of the $[RNH_3^+] = 3.0 \times 10^{-3}$ M and $[BP] = 1.12 \times 10^{-2}$ M system on the microsecond time scale in the presence of 0.015 (a) and 0.5 M (b) H_2SO_4, obtained by laser flash photolysis at 355 nm.

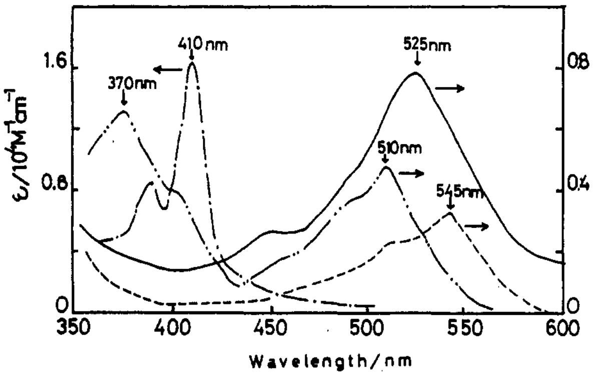

Figure 5. Reference absorption spectra of $^3RNH_3^{+*}$ (410 nm), $^3BP^*$ (525 nm), $RNH_2^{\cdot+}$ (510 nm), and $>\dot{C}OH$ (545 nm). See text.

tonated structure in the triplet state at $[H_2SO_4] \geq 0.015$ M.

The efficiency of the HT reaction from $^3RNH_3^{+*}$ to BP can be evaluated easily as the product formation ratio $([RNH_2^{\cdot+}]_{HT}/[^3RNH_3^{+*}]_{ET}$ or $[>\dot{C}OH]_{HT}/[^3RNH_3^{+*}]_{ET})$, since the concentration of $RNH_2^{\cdot+}$ produced by the HT reaction from $^3RNH_3^{+*}$ to BP should be the same as that of $>\dot{C}OH$. The efficiency of the HT reaction in the presence of H_2SO_4 (0.015 or 0.5 M) was obtained at 0.95 or 0.31, respectively. It is obvious that the efficiency of the HT reaction is affected considerably by addition of protons. These results are opposite to the HT reaction from triplet 1-naphthol ($^3ROH^*$) to BP, since the HT reaction is enhanced by addition of protons in the ROH–BP system.[32] Accordingly, the HT reaction in the present RNH_3^+ BP system was named as the proton-controlled hydrogen atom transfer reaction in contrast to the proton-enhanced hydrogen atom transfer reaction in the ROH–BP system.[32]

Secondly, the $T_n \leftarrow T_1$ absorption spectrum of RNH_3^+ (λ_{max} = 410 nm) at $[H_2SO_4] = 0.5$ M resembles that at $[H_2SO_4]$ = 0.015 M. However, the transient peak (λ_{max} = 415 nm) of $^3RNH_3^{+*}$ at the higher acid concentration 0.5 M H_2SO_4 is slightly shifted to the red by 5 nm, and its vibrational structures become rather sharp.

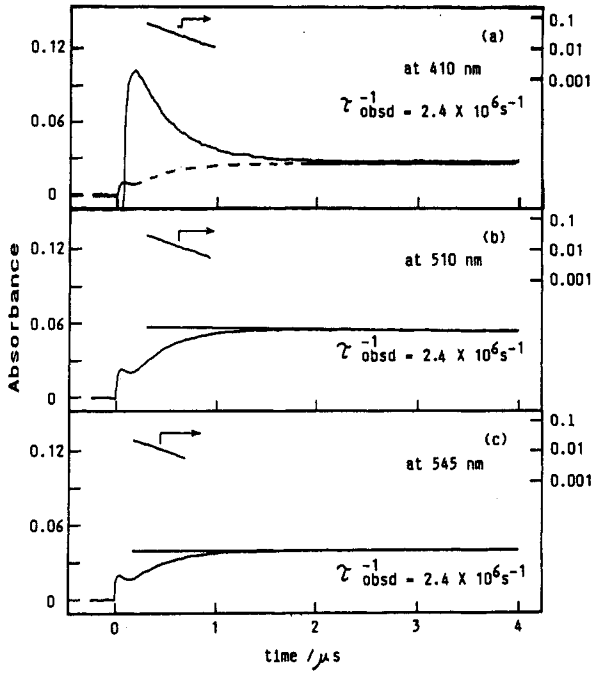

Figure 6. Time traces of the transient absorption species monitored at the corresponding peaks ($^3RNH_3^{+*}$ (a), $RNH_2^{\cdot+}$ (b), and $>\dot{C}OH$ (c)) in the presence of $[H_2SO_4] = 0.015$ M, obtained by laser flash photolysis at 355 nm in the RNH_3^+ (3.0×10^{-3} M) – BP (1.12×10^{-2} M) system in MeOH–H_2O (9:1) at 290 K.

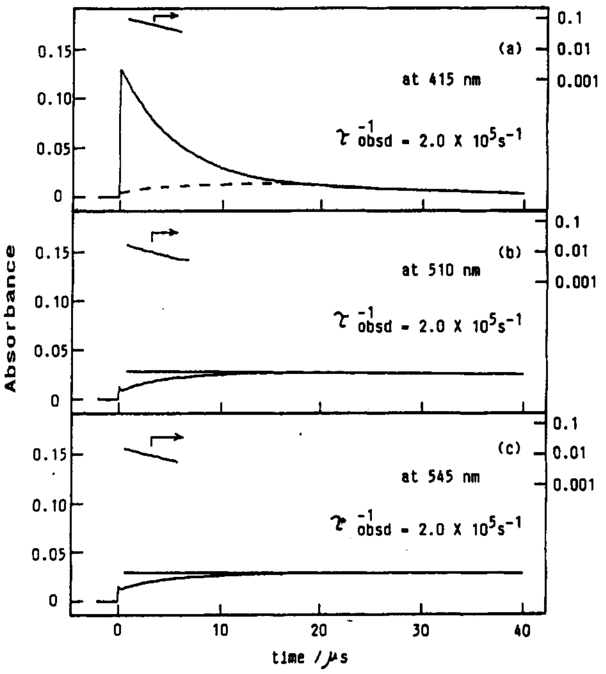

Figure 7. Time traces of the transient absorption species ($^3RNH_3^{+*}$ (a), $RNH_2^{\cdot+}$ (b), and $>\dot{C}OH$ (c)) in the presence of $[H_2SO_4] = 0.5$ M, obtained by laser flash photolysis at 355 nm in the RNH_3^+ (3.0×10^{-3} M) – BP (1.12×10^{-2} M) system in MeOH–H_2O (9:1) at 290 K.

Lifetimes of the Transient Species. Figures 6 and 7 show the typical time traces of the transient absorption species obtained by laser flash photolysis at 355 nm in the RNH_3^+–BP system ($[BP] = 1.12 \times 10^{-2}$ M and $[RNH_3^+] = 3.0 \times 10^{-3}$ M) in the presence of $[H_2SO_4] = 0.015$ M (Figure 6) and $[H_2SO_4] = 0.5$ M (Figure 7) in methanol-water (9:1 v/v) at 290 K, monitored at their peaks ($^3RNH_3^{+*}$, $RNH_2^{\cdot+}$, and $>\dot{C}OH$) as shown in Figure 4.

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For determination of the lifetime of the transient species, especially for $^3RNH_3^{+*}$, there is a problem, since the rise part of both radical components ($RNH_2^{\bullet+}$ and $>\dot{C}OH$) generated by the HT reaction is involved considerably in the decay absorption of $^3RNH_3^{+*}$ (see Figure 5). So far, the decay rate constant of the transient has been calculated simply by subtraction of the rise part corresponding to the radical absorption (the extrapolation method). However, this method does not accurately reflect the rise part of radicals. Accordingly, the following method was used to correct the rise part of radicals to the decay rate of $^3RNH_3^{+*}$. The observed absorbance (OD_{obsd}) at 410 nm (the absorption maximum of $^3RNH_3^{+*}$) can be written as

$$OD_{obsd}(t) = OD_{^3RNH_3^+}(t) + OD_{RNH_2^{\bullet+}}(t) + OD_{>\dot{C}OH}(t) \qquad (2)$$

where $OD_{^3RNH_3^+}(t)$, $OD_{RNH_2^{\bullet+}}(t)$, and $OD_{>\dot{C}OH}(t)$ denote the optical densities (OD) of actual concentrations of the corresponding species as a function of the delay time (t). The net absorbance $OD_{^3RNH_3^+}(t)$ of $^3RNH_3^{+*}$ at 410 nm can be expressed as

$$OD_{^3RNH_3^+}(t) = OD_{obsd}(t) - \frac{\epsilon_{RNH_2^{\bullet+}}(410) + \epsilon_{>\dot{C}OH}(410)}{\epsilon_{RNH_2^{\bullet+}}(510) + \epsilon_{>\dot{C}OH}(510)} OD_{obsd,510}(t) \qquad (3)$$

where $\epsilon_{RNH_2^{\bullet+}}(410)$, $\epsilon_{>\dot{C}OH}(410)$, $\epsilon_{RNH_2^{\bullet+}}(510)$, and $\epsilon_{>\dot{C}OH}(510)$ denote the molar extinction coefficients of radicals ($RNH_2^{\bullet+}$ and $>\dot{C}OH$) at the corresponding wavelengths written in parentheses. The value of $\{\epsilon_{RNH_2^{\bullet+}}(410) + \epsilon_{>\dot{C}OH}(410)\}/\{\epsilon_{RNH_2^{\bullet+}}(510) + \epsilon_{>\dot{C}OH}(510)\}$ was equal to 0.50 in the system. Here, $OD_{obsd,510}(t)$ is the observed absorbance of $RNH_2^{\bullet+}$ as a function of the delay time t. Therefore, the decay rate constant $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ can be expressed as

$$(\tau_{obsd})^{-1}t = -\ln OD_{^3RNH_3^{+*}}(t) + \text{constant} \qquad (4)$$

The kinetic analysis for the decay of $^3RNH_3^{+*}$ was carried out by using the above method. On the other hand, the rise rate for the radical formation can be obtained by the extrapolation method, as shown in Figures 6 and 7.

With these methods, the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ was obtained to be 2.6×10^6 s^{-1} from the slope in Figure 6a, and the rise rates $(\tau_{obsd})^{-1}$ of both the radicals $RNH_2^{\bullet+}$ and $>\dot{C}OH$) were 2.6×10^6 s^{-1} from the slopes in Figure 6b,c in the presence of $[H_2SO_4] = 0.015$ M. In the presence of $[H_2SO_4] = 0.5$ M, the decay rate $(\tau_{obsd})^{-1}$ was obtained as 2.0×10^5 s^{-1} from the slope in Figure 7a, and the rise rate constant $(\tau_{obsd})^{-1}$ of the radicals was 2.0×10^5 s^{-1} from the slopes in Figure 7b,c. The results show that both $RNH_2^{\bullet+}$ ($\lambda_{max} = 510$ nm) and $>\dot{C}OH$ ($\lambda_{max} = 545$ nm) radicals are produced from $^3RNH_3^{+*}$.

Mechanism of the Hydrogen Atom Transfer Reaction in the RNH_3^+–BP System. A bimolecular reaction can be treated as a pseudo-first-order reaction when the concentration of one of the reacting species is much greater than that of the other. In the HT reaction from $^3RNH_3^{+*}$ to BP, the concentration of BP [3×10^{-3}–0.22 M] is much greater than that of $^3RNH_3^{+*}$ ($\sim 10^{-5}$ M). Hence, this reaction is to be the case:

$$^3RNH_3^{+*} + BP \xrightarrow{k_{HT}} RNH_2^{\bullet+} + >\dot{C}OH \qquad (5)$$

If the HT reaction between $^3RNH_3^{+*}$ and BP to produce the radicals ($RNH_2^{\bullet+}$ and $>\dot{C}OH$) occurred by collision in nature, the Stern–Volmer plot of the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ vs [BP] would be a straight line according to

$$(\tau_{obsd})^{-1} = \tau_0^{-1} + k_q[BP] \qquad k_q = k_{HT} + k_q' \qquad (6)$$

where τ_0^{-1} denotes the decay rate constant of $^3RNH_3^{+*}$ in the absence of BP, and k_q' is the quenching rate constant of $^3RNH_3^{+*}$ induced by BP.

Figure 8 shows the plots of the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ as a function of the concentration of BP in the presence of H_2SO_4. The experiments were carried out independently more than three times. The value of $(\tau_{obsd})^{-1}$ increases with an increase in the BP concentration, and it decreases with an increase in the H_2SO_4 concentration. However, there is a leveling off at higher BP concentrations, especially at lower H_2SO_4 concentrations ($\lesssim$0.05 M). This result cannot be interpreted in terms of a simple quenching mechanism of the triplet RNH_3^+ by BP as shown in eq 6.

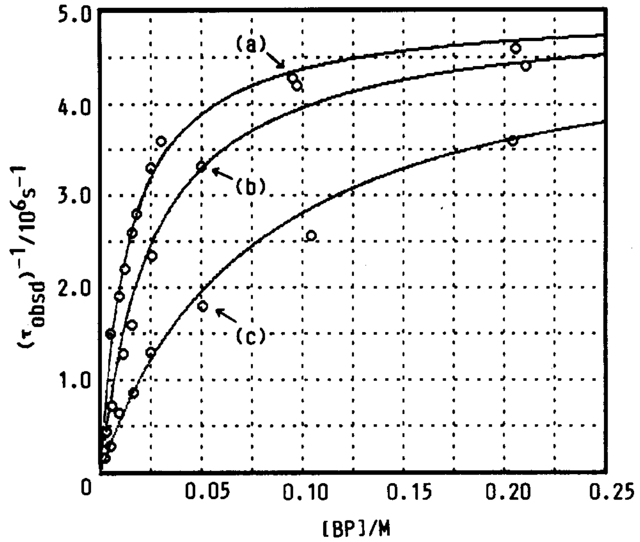
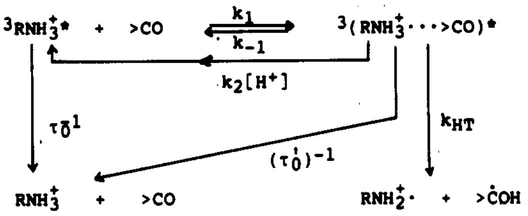


Figure 8. Plots of the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ as a function of [BP] monitored at 410 nm in the presence of 0.015 (a), 0.05 (b), and 0.2 M H_2SO_4 (c). The solid curve denotes the calculated one from eq 7, which agrees with the experimental data. For details, see text.

SCHEME II



where $(\tau')^{-1} = k_{HT} + (\tau_0')^{-1}$ and $K_1 = k_1/k_{-1}$

No formation of the ground-state complex between RNH_3^+ and BP is concluded judging from the triplet energy transfer profile from $^3BP^*$ to RNH_3^+ under the experimental condition. The leveling off, therefore, is suggested to be due to an equilibrium of the complex between $^3RNH_3^{+*}$ and BP. The decay of the T–T absorption of RNH_3^+ in the presence of BP (3×10^{-3}–0.22 M) follows the first-order kinetics beyond 0.15 μs after a laser pulse. It is, therefore, likely that the equilibrium in the excited state is completed within 0.18 μs after the pulse. The HT reaction may take place via the triplet exciplex $^3(RNH_3^+\cdots>CO)^*$ but not via a purely collisional reaction.

The experimental results can be accounted for by Scheme II, where >CO denotes BP, $^3(RNH_3^+\cdots>CO)^*$ is the 1:1 triplet complex between $^3RNH_3^{+*}$ and BP, k_1 and k_{-1} are the rate constants for the formation and decomposition of the triplet exciplex respectively, $(\tau_0)^{-1}$ is the decay rate of free $^3RNH_3^{+*}$, $(\tau_0')^{-1}$ is the decay rate of $^3(RNH_3^+\cdots>CO)^*$ without k_{HT}, and k_{HT} is the rate constant for the HT reaction. Here, k_2 denotes the decomposition rate constant of the triplet complex by protonation, resulting in the reproduction of free $^3RNH_3^{+*}$ plus >CO. The $T_n \leftarrow T_1$ transient absorption spectrum of $^3(RNH_3^+\cdots>CO)^*$ seems to be similar to that of free $^3RNH_3^{+*}$, suggesting that the triplet complex is a locally excited triplet state. In other words, $^3(RNH_3^+\cdots>CO)^*$ presumably has a sandwich structure with a very weak charge-transfer interaction. The complex may be protonated at higher acid concentrations to give the protonated triplet complex $^3(RNH_3^+\cdots>C^+OH)^*$. Subsequently, the protonated complex may decompose rapidly into free $^3RNH_3^{+*}$ + >CO + H$^+$, since the dication complex should be very unstable due to the Coulombic repulsion. The rate for the HT reaction is reduced considerably with an increase in the acid concentration.

TABLE II: Kinetic Data of $^3RNH_3^{+*}$ in MeOH–H_2O (9:1 v/v) at 290 K: Equilibrium Constant K_1, Rate Parameter k_2'/k_{-1}, and Rate Constants τ_0^{-1} and $(\tau')^{-1}$

K_1/M^{-1}	$(k_2'/k_{-1})/M^{-1}$	$\tau_0^{-1}/10^4\ s^{-1}$	$(\tau')^{-1b}/10^6\ s^{-1}$
110 (±10)	40 (±5)	~1	5 (±0.5)

[a] For details, see Scheme II and eq 7. [b] $(\tau')^{-1} = k_{HT} + (\tau_0')^{-1} \simeq k_{HT}$ at lower acid concentration (e.g., $[H_2SO_4] = 0.015$ M).

As a result, the value of $(\tau_{obsd})^{-1}$ becomes significantly small at higher acid concentrations. It is noteworthy that the protonation of the ground BP is impossible under the experimental condition, because the ground-state pK_a value of BP is negatively large (−5.7).[22] Therefore, the ground-state protonation of BP is excluded.

On the assumption that the equilibrium holds in the excited state as shown in Scheme II, the decay rate $(\tau_{obsd})^{-1}$ as a function of [BP] at different H_2SO_4 concentrations can be expressed as follows:

$$(\tau_{obsd})^{-1} = \frac{\tau_0^{-1} + K_1[BP](\tau')^{-1}(1 + k_2'(k_{-1})^{-1}[H_2SO_4])^{-1}}{1 + K_1[BP](1 + k_2'(k_{-1})^{-1}[H_2SO_4])^{-1}} \quad (7)$$

where $(\tau')^{-1} = k_{HT} + (\tau_0')^{-1}$ and $K_1 = k_1/k_{-1}$. Actually, we should use the proton concentration in eq 7 instead of $[H_2SO_4]$. However, we used the concentration of H_2SO_4 in the equation because the proton activity in the mixed solvent (MeOH:H_2O 9:1 v/v) is unknown. Therefore, we used $k_2'[H_2SO_4]$ instead of $k_2[H^+]$. The value of τ_0^{-1} was obtained as $\sim 1.0 \times 10^4\ s^{-1}$ (i.e., τ_0 = ca. 100 μs) in the absence of BP upon direct excitation of RNH_3^+ at 266 nm at 290 K, though the quantum yield for the $^3RNH_3^{+*}$ formation was very low. The τ_0^{-1} value is, therefore, negligibly small in the present system. The parameters K_1, k_2'/k_{-1}, and $(\tau')^{-1}$ in eq 7 can be evaluated by best fitting both the plots of $(\tau_{obsd})^{-1}$ vs [BP] (Figure 8) at 0.015, 0.05, and 0.2 M H_2SO_4. The calculated values for $(\tau_{obsd})^{-1}$ are shown by solid lines in Figure 8, which fairly fit the experimental results. The values of K_1, k_2'/k_{-1}, and $(\tau')^{-1}$ were determined as 110 (±10) M^{-1}, 40 (±5) M^{-1}, and 5.0 (±0.5) × $10^6\ s^{-1}$, respectively. These data are listed in Table II. The intracomplex HT reaction in the triplet exciplex to give $RNH_2^{\bullet+}$ plus $>\dot{C}OH$ at low acid concentrations (e.g., 0.015 M H_2SO_4) takes place very effectively (the efficiency is 0.95). This result suggests that the deactivation rate of the triplet exciplex due to intersystem crossing to the ground state is considerably slow compared to k_{HT}. That is, the k_{HT} value is evaluated to be ca. 5 × $10^6\ s^{-1}$.

We can estimate the fraction α of $^3(RNH_3^+\cdots>CO)^*$ in the excited-state equilibrium using the following equation:

$$\alpha = \frac{K_1[BP](1 + k_2'(k_{-1})^{-1}[H_2SO_4])^{-1}}{1 + K_1[BP](1 + k_2'(k_{-1})^{-1}[H_2SO_4])^{-1}} \quad (8)$$

For example, the α values of the triplet complex at 0.015 and 0.5 M H_2SO_4 at [BP] = 1.12 × 10^{-2} M are obtained as 0.44 and 0.055, respectively. This result indicates that the triplet complex is decomposed into free $^3RNH_3^{+*}$ plus BP at higher acid concentrations, resulting in a drastic decrease of $(\tau_{obsd})^{-1}$ (i.e., a significant decrease of the apparent HT rate).

Remarkable Proton Effect on the Hydrogen Atom Transfer Reaction in the $^3RNH_3^{+*}$–BP System. The proton effect on the HT reaction in the $^3RNH_3^{+*}$–BP system has been studied in various H_2SO_4 concentrations (0.015–1 M). Figure 9 shows the plot of the decay rate $(\tau_{obsd})^{-1}$ monitored at 415 nm as a function of H_2SO_4 in the presence of BP ([BP] = 1.12 × 10^{-2} M) at 290 K.

The value of $(\tau_{obsd})^{-1}$ decreases drastically with increasing the concentrations of H_2SO_4, and it becomes almost constant at the H_2SO_4 concentration higher than 0.5 M. The dependence of $(\tau_{obsd})^{-1}$ on the acid concentration can be explained by Scheme II. This observation is in striking contrast to the proton effect on the HT reaction of the ROH–BP system in which the value of $(\tau_{obsd})^{-1}$ of $^3ROH^*$ increases with an increase of the concentration of H_2SO_4.[32] The values of $(\tau_{obsd})^{-1}$ vs $[H_2SO_4]$ calculated by eq 7 (K_1 = 110 M^{-1}, k_2'/k_{-1} = 40 M^{-1}, τ_0^{-1} = 1 × $10^4\ s^{-1}$, and $(\tau')^{-1}$ = 5 × $10^6\ s^{-1}$) are depicted by the solid line in Figure 9, which are in good agreement with the experimental data. The fractions α of the triplet complex at [BP] = 1.12 × 10^{-2} M as a function of $[H_2SO_4]$ are calculated by eq 8, which are shown in Figure 10. The α value decreases significantly with increasing the H_2SO_4 concentration. The equilibrium $^3RNH_3^{+*}$ + >CO ⇄ $^3(RNH_3^+\cdots>CO)^*$ is apparently shifted to the free $^3RNH_3^{+*}$ + >CO side by the proton effect as described above. In fact, the transient spectrum at 0.2 μs after a pulse is altered slightly by the concentration of H_2SO_4: the vibrational structures of the absorption band around 410–415 nm become narrow on going from low to high concentration of H_2SO_4. This result suggests that the absorption band of $^3(RNH_3^+\cdots>CO)^*$ is broad compared to that of free $^3RNH_3^{+*}$.

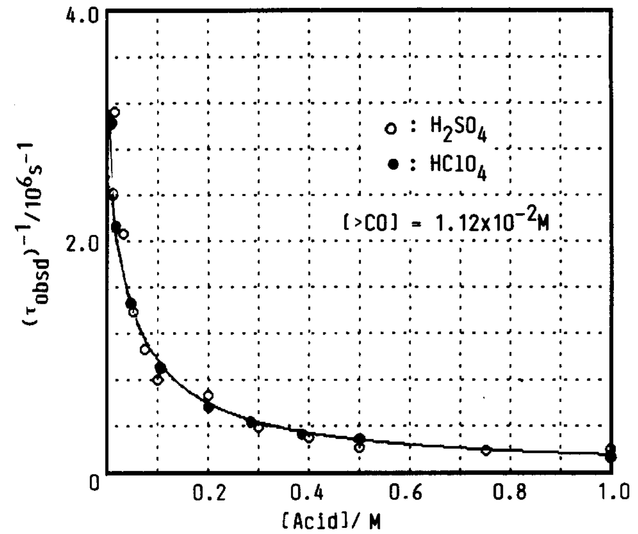


Figure 9. Plots of the decay rate $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ monitored at 410 nm as a function of various concentration of acid [H_2SO_4 (○), $HClO_4$ (●)] in the presence of [BP] = 1.12 × 10^{-2} M. The solid curve denotes that calculated by using eq 7, which agrees with the experimental data. For details, see text.

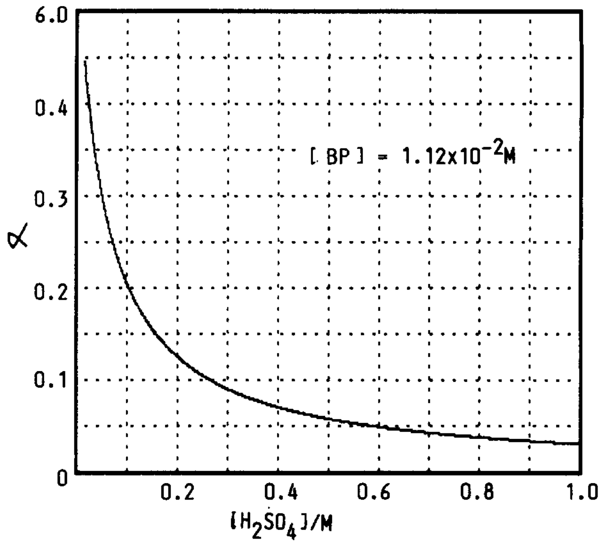


Figure 10. Dependence of the fraction α of $^3(RNH_3^+\cdots>CO)^*$ on the H_2SO_4 concentration.

Hydrogen Atom Transfer Reaction in the $^3RNH_3^{+*}$–BP System under Various Conditions. The HT reaction has been studied with $HClO_4$ as a proton source. The experiments were carried out under the same condition as those in the case of H_2SO_4 ($[^3RNH_3^+]$ = 3.0 × 10^{-3} M, [BP] = 1.12 × 10^{-2} M in MeOH–H_2O 9:1 at 290 K). Figure 9 shows the plots of the decay rates $(\tau_{obsd})^{-1}$ of $^3RNH_3^{+*}$ as a function of the concentration of $HClO_4$ at [BP] = 1.12 × 10^{-2} M at 290 K, indicating that the effect of $HClO_4$

on $(\tau_{obsd})^{-1}$ is very similar to that of H_2SO_4. The decay rate $(\tau_{obsd})^{-1}$ obtained experimentally in the $HClO_4$ system agrees with the fitting curve using the parameters obtained in the case of H_2SO_4 ($K_1 = 110\ M^{-1}$, $k_2'/k_{-1} = 40\ M^{-1}$, $\tau_0^{-1} = 1 \times 10^4\ s^{-1}$, and $(\tau')^{-1} = 5 \times 10^6\ s^{-1}$). Thus, the parameters obtained in the presence of H_2SO_4 can be used for the system in the presence of $HClO_4$. H_2SO_4 is known to behave almost as a monoprotonic acid even in dilute aqueous solution.[33] Therefore, H_2SO_4 acts as a monovalence acid in the mixed solvent (9:1) (MeOH–H_2O).

In the above section, it is concluded that the HT reaction depends significantly on the acid concentration as well as [BP]. It is also important to study the effect of the counterion SO_4^{2-} on the HT reaction. Na_2SO_4 was used as a counteranion source, since neither Na^+ nor SO_4^{2-} quenches the triplet molecules.[20] To examine salt effects on the HT reaction, Na_2SO_4 (0.5 M) was added to the typical system ($[RNH_3^+] = 3.0 \times 10^{-3}$ M, $[BP] = 1.12 \times 10^{-2}$ M, and $[H_2SO_4] = 0.015$ M in 9:1 MeOH–H_2O at 290 K). For the above system, both the transient spectra and their lifetimes were the same as those in the absence of the salt, showing that there was no salt effect on the HT reaction under the experimental condition.

Intracomplex Hydrogen Atom Transfer. In a previous paper,[16] we reported that the triplet naphthol, $^3ROH^*$, reacts with BP to yield $RO^\bullet$ and $>\dot{C}OH$. The rate constant, k_T, for the decay of $^3ROH^*$ increases with an increase in the concentration of BP. At high concentrations of BP, the Stern–Volmer plot, k_T vs [BP], exhibits slight convex curvature, suggesting that $^3ROH^*$ and BP form a weak charge-transfer complex: the equilibrium constant is obtained as 16.7 M^{-1}. Later, Gorman and co-workers[19] claimed that the plot makes a strictly straight line in the range $[BP] < 3 \times 10^{-2}$ M.

The present work has shown that, in contrast to the case of the ROH–BP system, the rate constant for the decay of $^3RNH_3^{+*}$ levels off at high concentrations of BP, clearly indicating that $^3RNH_3^{+*}$ and BP form the triplet exciplex with the equilibrium constant 110 M^{-1}. The absorption spectrum of the exciplex is found to be (1) similar to that of free $^3RNH_3^{+*}$ and (2) rather broad compared to that of free $^3RNH_3^{+*}$. Presumably, the charge-transfer interaction between $^3RNH_3^{+*}$ and BP is weak. When $[H_2SO_4] = 0$, eq 7 is transformed to

$$(\tau_{obsd})^{-1} = (\tau_0^{-1} + K_1[BP](\tau')^{-1})(1 + K_1[BP])^{-1} \qquad (9)$$

This is the same equation that the decay rate constant in the ROH–BP system is interpreted.[16] On the basis of eq 9, it is concluded that the plot of $(\tau_{obsd})^{-1}$ vs [BP] gives a straight line only when $K_1[BP] \ll 1$, while the plot tends to show convex curvature with an increase in the value of $K_1[BP]$. As mentioned above, the equilibrium constant K_1 in the RNH_3^+–BP system is 1 order of magnitude greater than that in the ROH–BP system. Thus, the Stern–Volmer plot in the RNH_3^+–BP system becomes significantly convex compared to that in the ROH–BP system.

In an earlier study on proton-assisted electron transfer,[32,34] it has been revealed that the triplet methoxynaphthalene, $^3ROMe^*$, reacts with BP in the presence of protons to yield methoxynaphthalene cation radical, $ROMe^{\bullet+}$, plus $>\dot{C}OH$. This result, in agreement with the present study, is interpreted by assuming that $^3ROMe^*$ and BP form a triplet exciplex.[32] The lifetime of the triplet exciplex is found to be a little shorter than that of free $^3ROMe^*$, probably owing to the weak charge-transfer interaction. On the other hand, the triplet exciplexes $^3(ROH\cdots{>}CO)^*$ and $^3(RNH_3^+\cdots{>}CO)^*$ have their lifetimes markedly shorter than those of free $^3ROH^*$ and $^3RNH_3^{+*}$ because of the fast intracomplex hydrogen atom transfer reaction that principally dominates their lifetimes.

Summary

The triplet 2-naphthylammonium ion ($^3RNH_3^{+*}$) is produced in the nanosecond time scale by the triplet energy transfer from triplet benzophenone ($^3BP^*$) to RNH_3^+ with efficiencies of 0.41 ($[H_2SO_4] = 0.015$ M) and 0.33 ($[H_2SO_4] = 0.5$ M) at $[^3RNH_3^+] = 3.0 \times 10^{-3}$ M and at $[BP] = 1.12 \times 10^{-2}$ M, competing with the hydrogen abstraction of $^3BP^*$ from solvent (methanol) or RNH_3^+ molecules as shown in Scheme I.

In the microsecond time scale, the hydrogen atom transfer (HT) reaction from $^3RNH_3^{+*}$ to BP occurs effectively to yield the 2-naphthylamine cation radical ($RNH_2^{\bullet+}$) plus the benzophenone ketyl radical ($>\dot{C}OH$). At a lower acid concentration (0.015 M), the efficiency for HT from $^3RNH_3^{+*}$ to BP is evaluated as 0.95.

The mechanism of the HT reaction can be accounted for by the intracomplex HT reaction of the triplet exciplex $^3(RNH_3^+\cdots{>}CO)^*$ as shown in Scheme II. The kinetic parameters in Scheme II are determined to be $K_1 = 110\ M^{-1}$, $k_2'/k_{-1} = 40\ M^{-1}$, $\tau_0^{-1} = 1 \times 10^4\ s^{-1}$, and $(\tau')^{-1} = 5 \times 10^6\ s^{-1}$. The reaction rate for the intracomplex HT process in $^3(RNH_3^+\cdots{>}CO)^*$ is obtained as ca. $5 \times 10^6\ s^{-1}$.

The HT reaction decreases drastically with an increase of the acid (H_2SO_4 or $HClO_4$) concentration. At higher acid concentrations the triplet complex is decomposed by protonation to give free $^3RNH_3^{+*}$ plus BP.

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