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Proton Transfer Reactions in the Triplet State of Benzophenone Studied by Nanosecond Laser Flash Photolysis

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Proton-transfer reactions in the triplet state of benzophenone in H_2O-acetonitrile (4:1) at 20 °C have been studied by means of nanosecond nitrogen laser flash photolysis at 337 nm. The proton association (k_1) and dissociation (k_2) rates are determined to be 5.0 (±0.5)×10^9 mol^{-1} dm^3 s^{-1} and 3.3 (±0.3)×10^9 s^{-1} respectively by a transient kinetic treatment. These rates are large enough to make an acid-base equilibrium during the lifetime of the triplet state. The acidity constants (pK_a*) in the triplet state of benzophenone obtained by the transient kinetic treatment, the Ware plot, and the $T_n \leftarrow T_1$ absorbance titration curve are the same [0.18 (±0.1)]. The pK_a* value determined by the titration method is appreciably dependent upon the delay time after the start of pulsing (the accurate value was obtained at the delay time 20 ns). There is no proton-induced quenching in the triplet state of benzophenone, since electrophilic protonation occurs at the oxygen atom in the carbonyl group. The reactive state for protonation in the triplet state is not $^3(n,\pi^*)$, but $^3(\pi,\pi^*)$, judging from the large k_1 value and the pK_a* value.

Proton-transfer reactions in the excited states of aromatic compounds are elementary processes in both chemistry and biochemistry. The acid-base properties in the excited state of aromatic compounds are closely related to electronic structure, which is considerably different from that in the ground state. A large number of studies on the acidity constants pK_a* in the excited state of aromatic compounds have been reported showing that the pK_a* values are significantly different from the acidity constants in the ground state.[1–9] It is known that the pK_a* values can be estimated by means of the Förster cycle,[1–3,10] the fluorescence titration curve,[2,3] and the triplet–triplet absorbance titration curve.[11] These methods involve the assumptions that proton transfer in the excited state is very fast and that the prototropic equilibrium may be accomplished during the lifetime in the excited state.

However, it has been shown recently that proton-induced quenching (^1k_q) is competitive with the proton-transfer reaction in the excited singlet state of naphthylamines (that is, simple acid-base equilibrium cannot be attained during the lifetime in the excited state of aromatic amines) and that a dynamic analysis containing the quenching process is, therefore, needed in order to obtain the accurate pK_a* values.[12] The dynamic analyses by means of nanosecond time-resolved spectroscopy with fluorimetry have been applied to 1-pyrenylamine,[13] 1-anthrylamine,[14] phenanthrylamines,[15] and naphthols.[16] The Stuttgart group[17] has supported our method to determine the pK_a* values of naphthylamines. Similar experimets for excited naphthols have been reported by Harris and Selinger.[18] For the proton-induced quenching mechanism, it has been demonstrated that the quenching proceeds via electrophilic protonation at one of carbon atoms of the aromatic ring in the excited singlet state, leading to proton exchange (or isotope exchange).[19] An intramolecular CT structure in the excited state is responsible for the quenching.[15,19,20] A linear relationship between the values of $\log {}^1k_q$ and the charge densities in the excited state of aromatic compounds has been shown.[20] Examples for no excited-state acid-base equilibria of aromatic compounds have been shown.[21–23] Establishment of prototropic equilibria at moderate acid concentrations have been reported for benzophenone[24,25] and phenyl ketones.[25] For the triplet state, its lifetime is relatively long enough to establish the prototropic equilibrium.[25] Very recently, it has been shown that the proton-induced quenching occurs scarcely in the triplet state of methoxynaphthalenes.[26] There has been considerable interest in photochemical and photophysical properties of aromatic compounds in the presence of protons.[27]

In the course of a study on the excited-state proton transfer reaction,[27] we became interested in the proton transfer reaction in the triplet state of benzophenone studied by nanosecond laser flash photolysis. This work was studied to answer the following questions: (1) How fast are the proton association and dissociation rates in the triplet state of benzophenone? (2) Is there really no proton-induced quenching in the triplet state? (3) How about pK_a* values in the triplet state of benzophenone determined by a transient kinetic treatment, the Ware plot, and the $T_n \leftarrow T_1$ absorbance titration curve? (4) Which is the reactive state for protonation in the triplet state, $^3(n,\pi^*)$ or $^3(\pi,\pi^*)$?

Experimental

Materials. Benzophenone (a G. R. grade product from Tokyo Kasei) was purified by repeated recrystallizations from H_2O-EtOH mixtures. Sulfuric acid (97%, Wako) was used without further purification. Distilled water and acetonitrile (G. R. grade, Wako) were used as a H_2O-CH_3CN mixture (4:1 by volume). The concentration of benzophenone was 3.2×10^{-3} mol dm^{-3}. The pH values of samples were recorded with a pH meter (Corning M-125). The samples were thoroughly degassed by freeze-pump-

Table 1. Transient Absorbance (Ab^0) at 525 nm at 20 ns after the Start of Pulsing, Observed Decay Constant ($\tau_{\rm obsd}^{-1}$) and Lifetime ($\tau_{\rm obsd}$) of the 525 nm Transient at Different Acidities

pH or H_0	wt. % H_2SO_4[a)]	Ab^0	$\tau_{\rm obsd}^{-1}/10^6\ {\rm s}^{-1}$ [b)]	$\tau_{\rm obsd}$/ns[b)]
7.00		0.0506	0.74	1.35×10^3
2.33		0.0506	0.84	1.19×10^3
1.07		0.0466	9.62	104
0.64		0.0406	17.9	56
0.28		0.0281	30	33
−0.43[a]	11.4	0.0108	67	15
−1.67[a]	29.3	0.0021	77	13
−2.34[a]	38.9	0.0032	77	13

a) Data taken from M. J. Jorgenson, D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963). b) Errors within 5%.

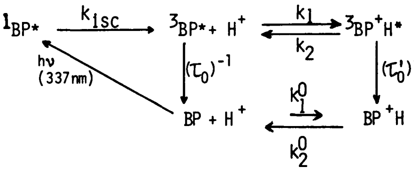
thaw cycles on a high vacuum line. All experiments were carried out at 20 °C.

Nanosecond Laser Flash Experiments. Laser flash photolysis studies were carried out using a nanosecond N_2 laser system at 337 nm (Japan Dynamic JS-1000L; pulse width 5 ns, laser power 5 mJ). The monitoring system consisted of a pulsed UXL-150D xenon lamp. A MC-20N monochromator (Ritsu) and a HTV R928 photomultiplier tube were used for the detection part. The transient signal was recorded with a transient memory (Kawasaki Electronica, MR-50E) and a 100 MHz storage oscilloscope (Iwatsu TS-8123).

Results and Discussion

Nanosecond Laser Flash Photolysis of Benzophenone. It is well known that triplet formation through intersystem crossing is very rapid (<10 ps),[28] according to the El-Sayed's rule.[29] For benzophenone (BP), a strong absorption band with a maximum at 525 nm (ε=7800 mol^{-1} dm^3 cm^{-1})[30] was observed just after pulsing, which decayed by first-order kinetics with a decay rate of $(\tau_0)^{-1}=7.4\times10^5$ s^{-1}. This band is ascribed to the $T_n \leftarrow T_1$ absorption.[31,32] The protonated benzophenone triplet, ^{3}BP$^+$H*, has a very weak absorption band at 505 nm.[25] The ^{3}BP$^+$H* species produced in a 4 mol dm^{-3} H_2SO_4 solution decayed with a lifetime of 13 ns. The observed decay rate of triplet benzophenone (^{3}BP*) monitored at 525 nm increased significantly with an increase of proton concentration. The experimental data of the 525 nm transient absorbance (Ab) at 20 ns after the start of pulsing and the observed decay rate constants ($\tau_{\rm obsd}^{-1}$) or the apparent lifetimes ($\tau_{\rm obsd}$) in various acid concentrations are summarized in Table I. Judging from the relatively low value of absorbance at 525 nm, there is no triplet–triplet annihilation of BP under the experimental conditions. There is little or no quenching of ^{3}BP* by the counter anion SO_4^{2-}.[33]

Dynamic Analyses by Means of a Transient Kinetic Treatment. The experimental results can be accounted for by Scheme 1.



Scheme 1.

where BP and ^{3}BP* represent the ground and triplet states of benzophenone respectively, τ_0 and τ_0' the lifetimes of ^{3}BP* (in the absence of protons) and ^{3}BP$^+$H* respectively, k_1 and k_2 the protonation and dissociation rate constants in the triplet state, respectively, and ^{3}BP$^+$H* protonated benzophenone triplet. At the highest acidities used, the ground state of benzophenone is unprotonated,since the pK_a value in the ground state of BP is very low (−5.7).[34] when BP is excited by a laser pulse at 337 nm, ^{3}BP* is produced very quickly within 10 ps[28] via fast intersystem crossing[29] of the singlet state of benzophenone (^{1}BP*).

At first, a transient kinetic treatment for the acid-base reaction of benzophenone has been made. The decay function of $Ab(t)$ of the transient absorbance at 525 nm for ^{3}BP* can be expressed as[35]

$$Ab(t) = c(e^{-\lambda_1 t}+Ae^{-\lambda_2 t}) \tag{1}$$

where c denotes the constant and $A=(X-\lambda_1)(\lambda_2-X)^{-1}$. The decay parameters λ_1 and λ_2 are

$$\lambda_{1,2} = \frac{1}{2}[X+Y\mp\{(Y-X)^2+4k_1k_2[\mathrm{H}^+]\}^{1/2}] \tag{2}$$

where $X=\tau_0^{-1}+k_1[\mathrm{H}^+]$ and $Y=(\tau_0')^{-1}+k_2$. The observed decay function at 525 nm is approximately the same as the undistorted decay function of Eq. 1, since the pulse width is relatively small (5 ns). The experimental value of τ_0^{-1} (7.4×10^5 s^{-1}) was used. The values of k_1, k_2, and $(\tau_0')^{-1}$ were varied. With use of the values of λ_1 and λ_2 obtained from Eq. 2, fitting of the decay function of $Ab(t)$ was carried out. Figure 1a shows the observed and calculated results of the function $Ab(t)$ at 20 °C at the concentrations of protons (1) $8.5_2\times10^{-2}$, (2) 0.22_8, and (3) 0.52_1 mol dm^{-3}. The best fitted values of λ_1 and λ_2 as a function of [H$^+$] are shown in Fig. 1b. The values of k_1, k_2, and $(\tau_0')^{-1}$ were determined to be 5.0 ($\pm$0.5)$\times10^9$ mol^{-1} dm^3 s^{-1}, 3.3 ($\pm$0.3)$\times10^9$ s^{-1}, and 7.9 ($\pm$0.7)$\times10^7$ s^{-1}, respectively. The value of the protonation rate constant (k_1) is close to that of the diffusion rate. It is noteworthy that the value of $(\tau_0')^{-1}$ obtained is approximately the same as the decay rate constant (7.7×10^7 s^{-1}) of ^{3}BP$^+$H* at higher acid concentrations (see Table 1). The values of k_1 and k_2 are very much greater than those of the competitive processes: i.e., $k_1 \gg \tau_0^{-1}$; $k_2 \gg (\tau_0')^{-1}$. That is, an acid-base equilibrium in Scheme 1 is established in the excited

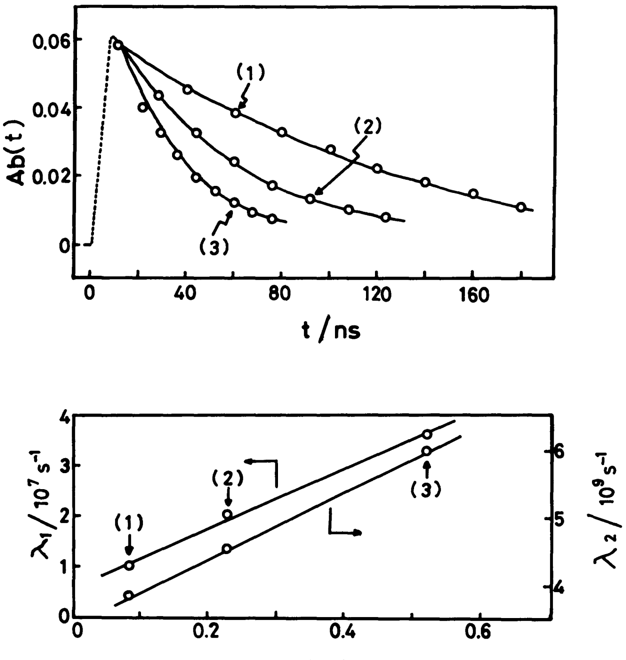


Fig. 1. (a) The decay function $Ab(t)$ of the 525 nm transient at the concentration of protons: (1) $8.5_2\times10^{-2}$, (2) 0.22_8, (3) 0.52_1 mol dm^{-3}. Circle: observed; solid curve; calculated. (b) The decay parameters λ_1 and λ_2 fitted to $Ab(t)$ as a function of [H$^+$]; e.g., (1)$\lambda_1=1.0\times10^7$s^{-1}, $\lambda_2=3.8\times10^9$s^{-1}; (2) $\lambda_1=2.0\times10^7$s^{-1} and $\lambda_2=4.5\times10^9$s^{-1}; and (3) $\lambda_1=3.5\times10^7$s^{-1} and $\lambda_2=5.9_5\times10^9$s^{-1}. For details see text.

state. The value of K_a^* ($=k_2/k_1$) was evaluated to be 0.66 mol dm^{-3}. The acidity constant of triplet benzophenone (pK_a^*) was determined to be 0.18 by means of the transient kinetic treatment. Very recently, a similar treatment has been employed in the hydrogen-atom transfer reaction from triplet naphthol to ground benzophenone.[30)]

The Ware Plot. In the above section, it is shown that the prototropic equilibrium in the triplet state of BP is established within the triplet lifetime. Therefore, the Ware equation[36)] can be applied to the present system. The Ware equation reads

$$\{\tau_{\mathrm{obsd}}^{-1}-\tau_0^{-1}\}^{-1}=\{(\tau_0')^{-1}-\tau_0^{-1}\}^{-1}\left\{1+\frac{K_a^*}{[\mathrm{H}^+]}\right\}. \qquad (3)$$

The Ware plot of $(\tau_{\mathrm{obsd}}^{-1}-\tau_0^{-1})^{-1}$ as a function of $[\mathrm{H}^+]^{-1}$ is shown in Fig. 2. From the slope and intercept, the values of K_a^* and $(\tau_0')^{-1}$ are determined as 0.64 mol dm^{-3} and 7.5×10^7 s^{-1} respectively. The pK_a^* value is evaluated to be 0.19 from the Ware plot. As for $(\tau_0')^{-1}$ the values obtained by the decay rate constant of ^{3}BP$^+$H*, the transient kinetic treatment, and the Ware plot are approximately the same each other within experimental errors. The pK_a^* value (0.19) obtained is approximately the same as that (0.18) determined by the transient kinetic treatment.

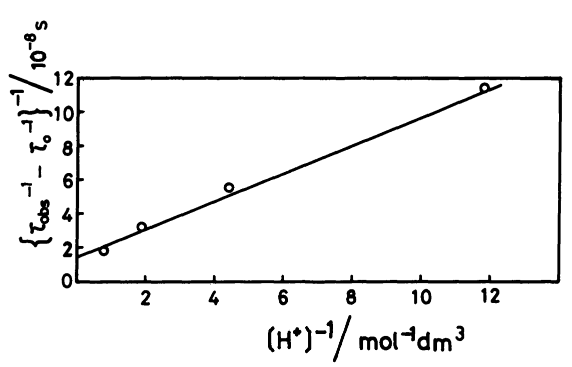


Fig. 2. The Ware plot of $[\tau_{\mathrm{obsd}}^{-1}-\tau_0^{-1}]^{-1}$ vs. $[\mathrm{H}^+]^{-1}$. See text.

Triplet-Triplet Absorbance Titration Curve. This method is the most popular one to estimate the pK_a^* value in the triplet state, when a prototropic equilibrium is established within the lifetime in the excited state.[11)] Usually, the pK_a^* value can be estimated from the midpoint of the $T_n\leftarrow T_1$ absorbance titration curve obtained by nanosecond laser flash photolysis or microsecond flash photolysis just after pulsing. However, little attention has been paid to a relation between the pK_a^* value and the delay time to measure the titration curve. Here, it is demonstrated that there is a large dependence of the pK_a^* value upon the decay time. Figure 3 shows the dependence of the $T_n\leftarrow T_1$ absorbance titration curve on the delay time after the start of pulsing. The midpoint of the titration curve is shifted to higher pH values with an increase of the delay time. The pK_a^* value (0.18) obtained by the titration method at 20 ns after the start of pulsing is the best fit to that obtained by the transient kinetic analysis or the Ware plot. This value is positively deviated as the delay time increases, since the decay rate $[(\tau_0')^{-1}=7.7\ (\pm0.3)\times10^7\ \mathrm{s}^{-1}]$ of ^{3}BP$^+$H* is extremely large compared to that $[\tau_0^{-1}=7.4\times10^5\ \mathrm{s}^{-1}]$ of free ^{3}BP*. The short lifetime (13 ns) of ^{3}BP$^+$H*, the triplet benzophenone protonated at the oxygen atom of the carbonyl group, is not due to the proton-induced quenching, but the decay nature of ^{3}BP$^+$H* itself. In the triplet state of BP, electrophilic attack occurs on the oxygen atom of the carbonyl group of ^{3}BP* to produce ^{3}BP$^+$H*, since intramolecular charge migration from phenyl groups to the carbonyl group takes place appreciably in ^{3}BP* as discussed later. There is no electrophilic protonation (i.e., proton-induced quenching)[19)] at one of carbon atoms of aromatic rings under the experimental conditions. The proton association and dissociation rates (k_1 and k_2) in the triplet state of BP are very fast enough to make an acid-base equilibrium within the lifetime in the excited state as stated above. Therefore, the delay time at 20 ns after the start of pulsing is a reasonable time to measure the titration curve in the present system.

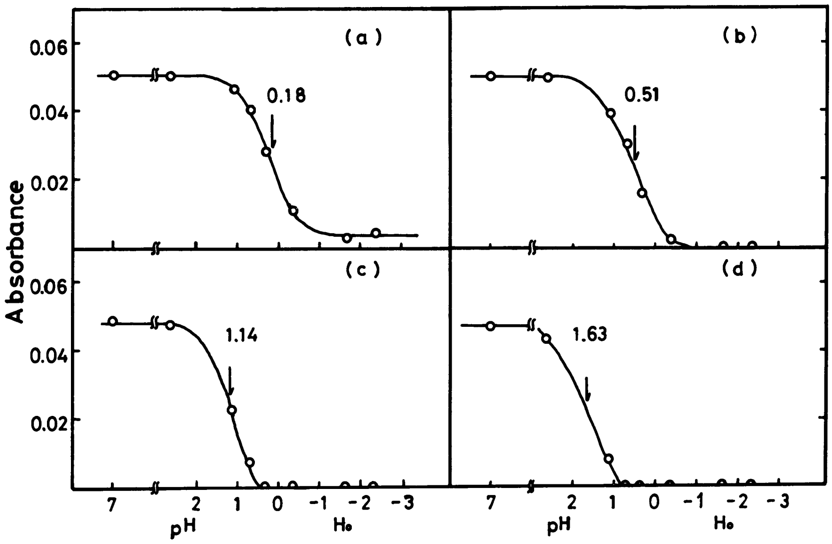


Fig. 3. The 525 nm transient absorbance curves observed at various delay times: (a) 20 ns, (b) 40 ns, (c) 100 ns, and (d) 200 ns after the start of pulsing.

Electronic Structure of Triplet Benzophenone. It is known that the lowest triplet state of BP is $^3(n,\pi^*)$ even in polar media.[37] There is a problem whether the reactive state of $^3BP^*$ for protonation is $^3(n,\pi^*)$ or $^3(\pi,\pi^*)$. In a previous paper,[25] the pK_a^* value for aromatic ketones is expressed as

$$pK_a^* = \rho^*\sigma^* + (pK_a^*)_0 \tag{4}$$

where ρ^* is equal to -1.33 and $(pK_a^*)_0$ denotes the pK_a^* value of acetophenone (0.60). The +I effect of a substituent of the carbonyl group increases the charge density (i.e., basicity) at the oxygen atom of the carbonyl group, resulting in an increase of the pK_a^* value. For BP, a positive deviation from the line according to Eq. 4 is observed.[25] The pK_a^* value of BP (0.18) has a greater value than that (-0.2) expected from its σ^* value ($+0.600$).[38] This fact cannot be explained by the difference in the lowest triplet character between $^3(n,\pi^*)$ (BP) and $^3(\pi,\pi^*)$ (phenyl alkyl ketones) in polar media. The charge density at the carbonyl group in the $^3(n,\pi^*)$ state should be smaller than that in the $^3(\pi,\pi^*)$ state, since the former state involves back charge transfer (from the carbonyl group to the phenyl ring). Both $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are perturbed by one another because the energy separation between them is very small in polar media, as has been discussed previously.[25,33b] The rapid rate of k_1 for protonation to $^3BP^*$ strongly supports that the reactive state of $^3BP^*$ is not $^3(n,\pi^*)$ but $^3(\pi,\pi^*)$. The $^3(\pi,\pi^*)$ state may have an intramolecular CT structure; charge migration from phenyl groups to the carbonyl group occurs in polar media, leading to a relatively high basicity in the triplet state. Thus, it can be understood that the pK_a^* value (0.18) in the triplet state of benzophenone increases drastically compared to that (-5.7)[34] in the ground state.

Concluding Remarks

The following remarks can be drawn from the results reported: (1) The protonation (k_1) and proton dissociation (k_2) rate constants in the triplet state of benzophenone in H_2O-CH_3CN (4:1) at 20 °C are determined to be 5.0 ($\pm$0.5)$\times 10^9$ mol^{-1} dm^3 s^{-1} and 3.3 ($\pm$0.3)$\times 10^9$ s^{-1} respectively by means of a transient kinetic treatment. These rates are very much greater than those of their competitive decay processes, leading to produce an acid-base equilibrium in the excited state. (2) There is no proton-induced quenching in $^3BP^*$, because protons attack the oxygen atom of the carbonyl group. (3) The pK_a^* values for $^3BP^*$ obtained by means of the transient kinetic treatment, the Ware plot, and the $T_n \leftarrow T_1$ absorbance titration method are the same (0.18±0.1) each other. The pK_a^* value determined by the titration curve depends upon the delay time to measure its curve; the accurate pK_a^* value is obtained at the delay time 20 ns after the start of pulsing. (4) The reactive state for protonation in the triplet state of benzophenone is not $^3(n,\pi^*)$ but $^3(\pi,\pi^*)$, considering the relatively large protonation rate k_1 and the pK_a^* value.

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