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Laser photolysis studies on hydrogen atom abstraction by triplet benzophenone from hydroxyanilinium ions

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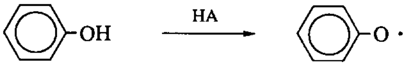
Abstract

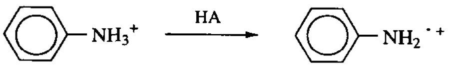
By means of 355 nm laser flash photolysis in the benzophenone–hydroxyanilinium ion system in acetonitrile–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M, it is found that the products of H-atom abstraction by triplet benzophenone from hydroxyanilinium ion are the benzophenone ketyl and hydroxyaniline cation radicals, i.e. the NH_3^+ group is more reactive to H-atom abstraction by triplet benzophenone than the OH. The more protic the hydrogen atom is, the more reactive it is found to be for H-atom abstraction by triplet benzophenone in a collision complex with charge-transfer character in the liquid phase.

1. Introduction

It is well known that triplet carbonyl compounds produce their ketyl radicals by H-atom abstraction from a variety of H-atom donors [1–8]. It has been shown by means of nano- and picosecond laser photolysis that H-atom abstraction proceeds by H-atom transfer or electron transfer followed by proton transfer [9–26]. Because the lifetimes of triplet ketones are usually in the microsecond time region, their H-atom abstractions from H-atom donors whose concentrations are less than 10^{-2} M take place upon bimolecular collision in the liquid phase at room temperature. Therefore, the collision process plays an important role in fluid media to allow triplet carbonyl compounds to perform H-atom abstraction from the H-atom donor, giving their ketyl radicals and the counter radical. When the H-donor has only one possibility to be H-abstracted, the radical formed is readily presumed. For example, in the case of H-atom abstraction from phenol, the phenoxy radical is produced [27,28], and from anilinium ion, the aniline cation radical is obtained.



(1)



(2)

Suppose that the H-atom donor contains both the substituent groups OH and NH_3^+, i.e. the H-atom donor is a hydroxyammonium ion (HAI), which upon H-atom abstraction (HA) may produce the

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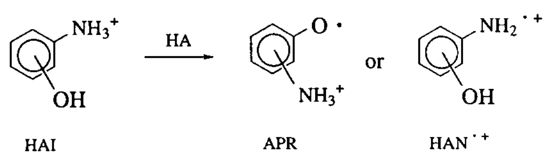
ammoniophenoxy radical (APR) or hydroxyaniline cation radical ($HAN^{\cdot +}$):



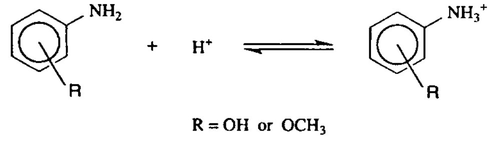
(3)

In the present Letter, we use 355 nm laser flash photolysis of the benzophenone (BP)–HAI system in aqueous acetonitrile at 295 K, and identify the products of H-atom abstraction by triplet BP ($^3BP^*$) from HAI using transient absorption spectra. The preference of H-atom transfer upon reduction of $^3BP^*$ is discussed along with the mechanism of H-atom abstraction by $^3BP^*$.

2. Experimental

Benzophenone (BP), 2-hydroxyaniline (2HAN), 3-hydroxyaniline (3HAN), 4-hydroxyaniline (4HAN) and 4-methoxyaniline (4MAN) were purified twice by vacuum sublimation. 2-Methoxyaniline (2MAN) and 3-methoxyaniline (3MAN) were purified by vacuum distillation. Acetonitrile (ACN; G.R. grade from Kanto) and deionized water were distilled for purification. A mixture of ACN and H_2O (ACN–H_2O; 1 : 1, v/v) was used as a solvent. H_2SO_4 from Wako was used as supplied.

The concentrations of BP and H_2SO_4 were 6.7×10^{-3} and 0.18 M, respectively, throughout this work. The formation of hydroxy- and methoxyanilinium ions (HAI and MAI) in ACN–H_2O (1 : 1, v/v) was completely achieved with $[H_2SO_4] = 0.18$ M judging from the absorption spectral changes according to the following acid–base equilibrium:



The concentration of HAI was less than 3×10^{-2} M. All the samples in a quartz cell with 10 mm path length were degassed by freeze–pump–thaw cycles on a high vacuum line.

The third harmonic of a nanosecond Nd^{3+}:YAG laser (355 nm) from JK Lasers HY-500 (pulse width 8 ns, laser power 40 mJ/pulse) was used for excitation at 295 K. The transient absorption spectra were taken with a USP-554 system from Unisoku, which afforded a transient spectrum with a one-shot laser pulse. The transient signals were analyzed by the least-squares best-fitting method. The detection system was reported elsewhere [29].

3. Results and discussion

Fig. 1a shows the transient absorption spectra observed after 355 nm laser photolysis of the BP-4HAI (1.2×10^{-2} M) system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M. The absorption spectrum with a peak at 520 nm obtained 80 ns after laser pulsing is ascribable to the triplet–triplet (T–T) absorption of BP in a polar solvent [30]. As time progresses, the intensity of the T–T absorption spectrum of BP decreases according to first-order kinetics with an isosbestic point at 450 nm, accompanying an increase in intensity of new absorption bands at 435 and 545 nm. The latter is

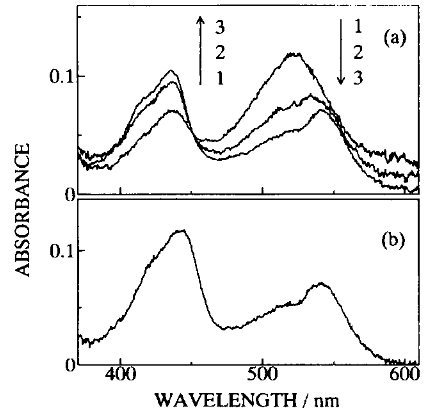
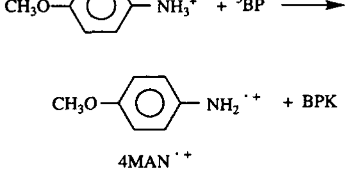


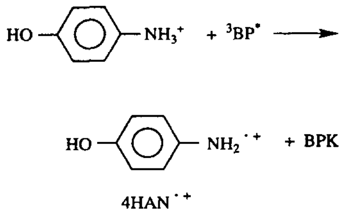
Fig. 1. (a) Transient absorption spectra observed at (1) 80 ns, (2) 300 ns and (3) 1.3 μs after 355 nm laser pulsing in the BP (6.7×10^{-3} M)–4HAI (1.2×10^{-2} M) system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M at 295 K. (b) Transient absorption spectrum at 1.2 μs obtained by 355 nm laser photolysis in the BP (6.7×10^{-3} M)–4MAI (1.2×10^{-2} M) system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M at 295 K.

due to the benzophenone ketyl radical (BPK) [31]. On the other hand, the transient absorption spectrum, shown in Fig. 1b, with absorption peaks at 445 and 545 nm at 1.2 μs observed after 355 nm laser photolysis in BP–4MAI (1.2×10^{-2} M) in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M resembles that at 1.3 μs for the BP–4HAI system. The formation of BPK indicates that H-atom abstraction by triplet BP ($^3BP^*$) from 4MAI took place to produce the 4-methoxyaniline cation radical ($4MAN^{\cdot+}$), which gave an absorption band at 445 nm in Fig. 1b since the methoxy group of $4MAN^{\cdot+}$ is inert for H-abstraction.



(4)

Therefore, the absorption band at 435 nm in the BP–4HAI system should be ascribed to the 4-hydroxyaniline cation radical ($4HAN^{\cdot+}$).



(5)

It can be concluded that the H atom of the NH_3^+ group is more reactive for H-atom abstraction by $^3BP^*$ than that of the hydroxy group. For other systems of 2- and 3-HAI, formation of the corresponding $HAN^{\cdot+}$ along with BPK could be concluded from the transient absorption spectra by comparing those of the corresponding $MAN^{\cdot+}$.

The first-order decay rate (k_{obsd}) of $^3BP^*$ was obtained at various [HAI] in order to understand the quenching mechanism involving H-atom abstraction. Fig. 2 shows plots of k_{obsd} as a function of [4HAI] measured in the BP–4HAI system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M.

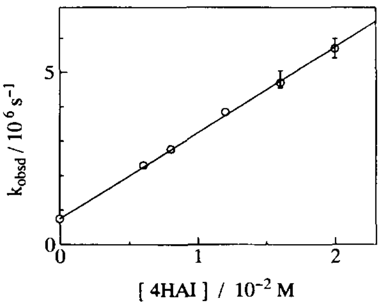


Fig. 2. Plots of the decay rate (k_{obsd}) of $^3BP^*$ as a function of [4HAI] obtained by 355 nm laser pulsing in the BP (6.7×10^{-3} M)–4HAI system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M at 295 K.

These plots show a straight line and k_{obsd} can be expressed by Eq. (6) with the decay rate constant (k_0) of $^3BP^*$ in the absence of 4HAI and quenching rate constant (k_q) of $^3BP^*$ by 4HAI:

$$k_{obsd} = k_0 + k_q[4HAI]. \qquad (6)$$

From the intercept and slope of the line, the values of k_0 and k_q were determined to be 7.5×10^5 s^{-1} and 2.5×10^8 M^{-1} s^{-1}, respectively. By the same procedure, the k_q values for 2- and 3-HAI were found to be 1.9×10^8 and 1.3×10^8 M^{-1} s^{-1}, respectively. The values are listed in Table 1.

Since the k_q values are smaller than the diffusion limit ($k_{dif} = 9.2 \times 10^9$ M^{-1} s^{-1}) of ACN–H_2O (1 : 1, v/v), it is obvious that the quenching of $^3BP^*$ by HAI proceeds via a collision complex, $(^3BP^* \cdots HAI)_{col}$.

The quantum yield (Φ_{rad}) for formation of BPK and $HAN^{\cdot+}$ by H-atom abstraction is expressed by

$$\Phi_{rad} = [BPK]_{max} I_{abs}^{-1} = [HAN^{\cdot+}]_{max} I_{abs}^{-1}, \qquad (7)$$

Table 1
The quenching rate constant (k_q) of $^3BP^*$ by HAI, efficiency (ψ_{rad}) of radical formation and rate constants (k_{HA}) for H-atom abstraction by $^3BP^*$ from HAI obtained in the present study [a]

Quencher	k_q [b] (10^8 M^{-1}s^{-1})	ψ_{rad} [c]	k_{HA} [b] (10^8 M^{-1}s^{-1})
2HAI	1.9	1.0	1.9
3HAI	1.3	1.0	1.3
4HAI	2.5	1.0	2.5

[a] See text for determination.
[b] Errors within 5%.
[c] Errors ±0.03.

Table 2
The molar absorption coefficient of BPK and HAN$^{+\cdot}$ ($\epsilon_\lambda^{\mathrm{BPK}}$ and $\epsilon_\lambda^{\mathrm{CR}}$) used in the present study [a]

λ (nm)	BPK [b]	2HAN$^{+\cdot}$ [c]	3HAN$^{+\cdot}$ [c]	4HAN$^{+\cdot}$ [c]
395	300	850(± 100)	–	–
435	450	–	2200(± 200)	5450(± 300)
455	650	–	2700(± 200)	–
545	3220	≈ 0	≈ 0	200

[a] In $M^{-1}cm^{-1}$.
[b] Data from Ref. [32].
[c] Calculated on the basis of the value of $\epsilon_\lambda^{\mathrm{BPK}}$ at 545 nm (3220 $M^{-1}cm^{-1}$ [31]). See Ref. [32] for the procedure.

where $[\mathrm{BPK}]_{\max}$ and $[\mathrm{HAN}^{\cdot+}]_{\max}$ are the net concentrations of BPK and HAN$^{\cdot+}$ produced by H-atom abstraction, respectively, and I_{abs} represents the photon flux of the incident laser pulse absorbed by BP at 355 nm. I_{abs} was determined by using the T–T absorption of BP in ACN at 520 nm as an actinometer [32]. $[\mathrm{BPK}]_{\max}$ and $[\mathrm{HAN}^{\cdot+}]_{\max}$ can be estimated by Eq. (8):

$$[\mathrm{BFK}]_{\max} = [\mathrm{HAN}^{\cdot+}]_{\max} = \Delta \mathrm{OD}_\lambda \left(\varepsilon_\lambda^{\mathrm{BPK}} + \varepsilon_\lambda^{\mathrm{CR}} \right)^{-1} \tag{8}$$

where $\Delta\mathrm{OD}_\lambda$ is the maximum absorbance at a wavelength (λ) due to the radical formation, $\varepsilon_\lambda^{\mathrm{BPK}}$ and $\varepsilon_\lambda^{\mathrm{CR}}$ are the molar absorption coefficients of BPK and HAI$^{\cdot+}$ at λ nm, respectively, as enumerated in Table 2. With the use of Eqs. (7) and (8), the experimental values of Φ_{rad} were determined and plotted in Fig. 3 for the BP–4HAI system.

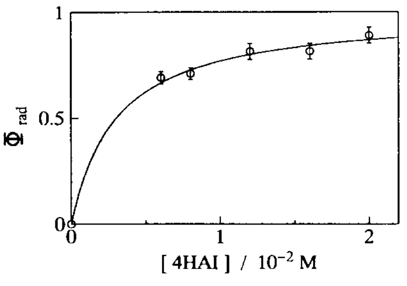


Fig. 3. Plots of the quantum yield (Φ_{rad}) determined at 435 nm for radical formation versus [4HAI] obtained in the BP (6.7×10^{-3} M)–4HAI system in ACN–H_2O (1 : 1, v/v) with $[H_2SO_4] = 0.18$ M at 295 K. The solid curve was calculated by Eq. (9). See text for details.

The Φ_{rad} value obtained increases non-linearly with increasing [4HAI]. On the other hand, Φ_{rad} can be formulated by Eq. (9) with the use of the kinetic parameters (k_0 and k_q) and efficiency (ψ_{HA}) of H-atom abstraction by ^{3}BP* from HAI:

$$\Phi_{\mathrm{rad}} = k_q[\mathrm{HAI}]\psi_{\mathrm{HA}}\Phi_{\mathrm{isc}}\left(k_0 + k_q[\mathrm{HAI}]\right)^{-1}, \tag{9}$$

where Φ_{isc} stands for the quantum yield for intersystem crossing of BP (1.0 [33]). With the use of Eq. (9) and experimental values of k_0 and k_q, the ψ_{HA} values were given by 'best-fitting' to be 1.0 ± 0.03 for all BP–HAI systems employed in the present study. The solid curve in Fig. 3 was calculated for the Φ_{rad} value by Eq. (9) and $\psi_{\mathrm{HA}} = 1.0$. The unity of ψ_{HA} indicates that the decay process of ^{3}BP* is all due to H-atom abstraction from HAI. Such a high efficiency can be rationalized as follows. As stated above, the H-atom abstraction by ^{3}BP* from HAI proceeds in a collision complex. Immediately after completion of H-atom abstraction in $(^3\mathrm{BP}^* \cdots \mathrm{HAI})_{\mathrm{col}}$, a triplet radical pair, $^3(\mathrm{BPK} + \mathrm{HAN}^{\cdot+})$, would be formed according to the spin-conservation rule. Since back H-atom transfer is difficult in the triplet multiplicity, the triplet radical pair completely dissociates into BPK and HAN$^{\cdot+}$ by solvation, resulting in a high radical yield. It is shown that the quenching process of ^{3}BP* by HAI is totally due to H-atom abstraction.

On the other hand, the rate constant (k_{HA}) of H-atom abstraction by ^{3}BP* from HAI can be represented by Eq. (10):

$$k_{\mathrm{HA}} = k_q \psi_{\mathrm{HA}}. \tag{10}$$

With the use of the k_{HA} and ψ_{HA} obtained, the values of k_{HA} were found to be equal to those of k_q and are listed in Table 1. The mechanism of H-atom abstraction for the present system is explained by Eqs. (11)–(13):

$$^3\mathrm{BP}^* + \mathrm{HAI} \xrightarrow{k_{\mathrm{dif}}} (^3\mathrm{BP}^* \cdots \mathrm{HAI})_{\mathrm{col}} \tag{11}$$

$$(^3\mathrm{BP}* \cdots \mathrm{HAI})_{\mathrm{col}} \xrightarrow{k_{\mathrm{HA}}} {}^3(\mathrm{BPK} + \mathrm{HAN}^{\cdot+}) \tag{12}$$

$$^3(\mathrm{BPK} + \mathrm{HAN}^{+\cdot}) \rightarrow \mathrm{BPK} + \mathrm{HAN}^{\cdot+} \tag{13}$$

In the present study, from the transient absorption spectrum after H-atom abstraction, the counter radical of BPK was found to be not the ammoniophenoxy radical (APR) but HAN$^{\cdot+}$. The k_{HA} value obtained was 10^8 M^{-1} s^{-1}. The $HAN^{\cdot +}$ was not produced via intramolecular H-atom transfer (intra-HT) from APR since intra-HT in the ground state usually proceeds in the time region of a millisecond [34].

When ${}^3BP^*$ causes H-atom abstraction or electron transfer with quenchers (Q) in solution, the collision complex has a weak charge-transfer interaction such as $({}^3BP^{*\delta} \cdots Q^{\delta+})_{col}$.

The preference of H-atom abstraction in $({}^3BP^* \cdots HAI)_{col}$ can be explained by supposing that the BP site is comparatively electron-rich due to a slight electron migration from HAI. On the other hand, by comparing the pK_a values of aniline (4.63 at 25°C [35]) and phenol (9.89 at 20°C [35]), it can be considered that the H atom of the NH_3^+ group is relatively more protic than that of the hydroxy one. Since the protic H atom is ready to transfer due to Coulombic attraction, $HAN^{\cdot +}$ is predominantly produced.

4. Conclusion

By 355 nm laser flash photolysis in the BP–HAI system, it was found that $HAN^{+\cdot}$ was predominantly produced by H-atom abstraction by ${}^3BP^*$. The preference of H-atom abstraction by ${}^3BP^*$ was rationalized by considering the charge-transfer character of the collision complex. It was found that the more protic the H atom is, the more reactive it is for H-atom abstraction by ${}^3BP^*$ in collision complexes in the liquid phase.

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