Communication

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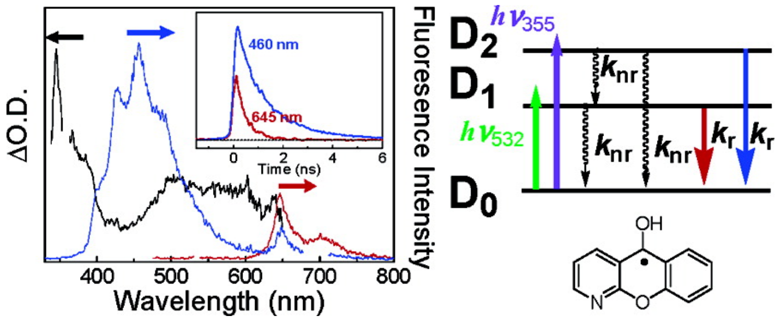

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Anomalous Fluorescence from the Azaxanthone Ketyl Radical in the Excited State

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Organic compounds mostly obey Kasha's rule, that is, emission occurs only from the lowest excited state.[1] The exception of Kasha's rule has been well-established as anomalous S_2 fluorescence from azulene and aromatic thioketones.[1−3a]

It is known that various neutral radicals show an emission from the doublet excited state.[3−6] The diphenyl ketyl radical shows an emission spectrum that is the mirror−image of the $D_1 \leftarrow D_0$ absorption.[3−6] For the benzyl and arylmethyl radicals, the difference between the absorption and emission maxima is quite large because of the quite low oscillator strength of the $D_1 \leftarrow D_0$ transition. Since these free radicals show a strong $D_m \leftarrow D_0$ absorption ($m > 1$), excitation to the D_m state generates the D_1 state followed by emission and internal conversion (IC).[3] Therefore, Kasha's rule is also valid for neutral radicals. To the best of our knowledge, there was only one report regarding the $D_2 \rightarrow D_0$ fluorescence. Obi et al. reported the dual emission ($D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$) of the thiophenoxy radical at 77 K.[4] The lifetime of the $D_2 \rightarrow D_0$ fluorescence of the thiophenoxy radical was much shorter than that of the $D_1 \rightarrow D_0$ fluorescence.[4] Furthermore, the $D_2 \rightarrow D_0$ fluorescence was not observed at room temperature.

In the present work, we studied the time-resolved absorption and fluorescence spectra of the azaxanthone (AX) ketyl radical (AXH•) in the excited state (AXH•(D_n) (n = 1 or 2)) using the nanosecond−picosecond two-color two-laser flash photolysis. An anomalous dual fluorescence of AXH• in the excited state was found. The $D_2 \rightarrow D_0$ fluorescence of AXH• had a lifetime longer than that of the $D_1 \rightarrow D_0$ fluorescence. The fluorescence quantum yield and radiative and nonradiative transition rate constants of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions were then estimated. Additionally, the absorption spectrum of AXH•(D_1) was observed for the first time. It was revealed that the anomalous emitting properties of AXH•(D_1) were caused by the pyridine ring in AX.

AXH• was generated by the photoreduction of AX.[7] Upon the first nanosecond laser (266 nm, 18 mJ pulse^{-1}, 5 ns fwhm) irradiation, the generated AX in the triplet excited state (AX(T_1)) decayed through the hydrogen abstraction from the hydrogen-donating solvent to produce AXH•(D_0) (eq 1).

$$\mathrm{AX} \xrightarrow{h\nu_{266}} \mathrm{AX(T_1)} \xrightarrow{\text{hydrogen abstraction}} \mathrm{AXH{\bullet}(D_0)} \qquad (1)$$

The absorption spectrum of AXH•(D_0) in cyclohexane (Figure 1) has peaks in the UV and visible regions similar to that in the benzophenone ketyl radical.[5] The obtained spectrum of AXH•(D_0) in Figure 1 was consistent with the reported one.[7]

The generated AXH• was excited at the visible absorption band using the second laser (532 nm, 10 mJ pulse^{-1}, 30 ps fwhm) with the delay time of 1 μs after the first laser (eq 2)

$$\mathrm{AXH{\bullet}(D_0)} \xrightarrow{h\nu_{532}} \mathrm{AXH{\bullet}(D_1)} \qquad (2)$$

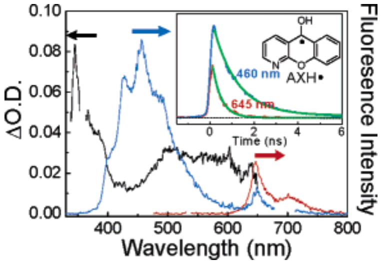

Figure 1. Absorption (black line) and fluorescence spectra of the AXH• in Ar-saturated cyclohexane at room temperature. Fluorescence spectra were obtained during the 266 and 355 nm (blue line) or 266 and 532 nm (red line) two-color two-laser flash photolysis. The absorption spectrum was obtained during the one-laser photolysis (266 nm, black line) of AX (4.0×10^{-4} M). The second laser was irradiated at 1 μs after the first laser pulse. All of the fluorescence spectra of AXH• were normalized with the corresponding absorption peaks. The inset shows kinetic traces of the fluorescence intensity of AXH• at 460 (blue line) and 645 (red line) nm.

Upon excitation, AXH• showed a fluorescence peak at 645 nm (Figure 1). The fluorescence spectrum of AXH•(D_1) was similar to that of the xanthone ketyl radical in the D_1 state.[6] It is suggested that the fluorescence peak at 645 nm corresponded to the $D_1 \rightarrow D_0$ transition. The fluorescence from AXH• in the lowest excited state (AXH•(D_1)) was observed for the first time.

Next, AXH• was excited at the UV absorption band using the second laser (355 nm, 1 mJ pulse^{-1}, 30 ps fwhm) with the delay time of 1 μs after the first laser (eq 3)

$$\mathrm{AXH{\bullet}(D_0)} \xrightarrow{h\nu_{355}} \mathrm{AXH{\bullet}(D_2)} \qquad (3)$$

A new strong fluorescence with peaks at 428 and 456 nm appeared upon excitation with the 355 nm laser (Figure 1) as well as the 645 nm fluorescence band. Since the fluorescence of AX at 420 nm after the 355 nm single laser excitation is negligible under the same experimental conditions, the fluorescence should be derived from AXH• in the higher excited state. From an energetic consideration, the fluorescence can be attributed to the $D_2 \rightarrow D_0$ transition.

To the best of our knowledge, there has been no report of the fluorescence of neutral radicals in the higher excited doublet state at room temperature. Although the same experiment was carried out with xanthone and benzophenone ketyl radicals, only the $D_1 \rightarrow D_0$ fluorescence was observed during the 266 and 355 nm two-color two-laser flash photolysis. Therefore, it is suggested that the pyridine ring in AX plays an important role in the anomalous emitting property of AXH•. The frontier orbitals of azulene have a quite different spatial distribution from that of naphthalene.[2e] In the case of AXH•, the symmetry of the frontier orbitals should also be broken compared with those of xanthone. It is possible that the lower symmetry of the frontier orbitals may cause the poor Franck−Condon factor for the $D_2 \rightarrow D_1$ relaxation.

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Table 1. Fluorescence Lifetimes (τ_f), Quantum Yields (Φ_f), Radiative Rate Constants (k_r), Nonradiative Rate Constants (k_{nr}) of D_1-D_0 and D_2-D_0 Transition of AXH•

transition	τ_f (ns)	k_r (10^6 s^{-1})	k_{nr} (10^8 s^{-1})	Φ_f
D_1-D_0	0.40	2.0 ± 0.5	25	0.0008 ± 0.0002
D_2-D_0	1.0	50 ± 15	9.5 ± 0.2[a]	0.05 ± 0.02

[a] Equal to $k_{nr}(D_2 \rightarrow D_0) + k_{nr}(D_2 \rightarrow D_1)$.

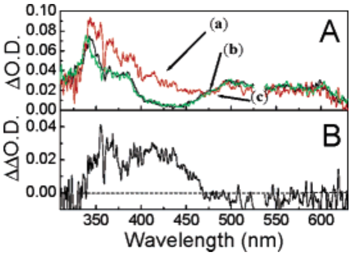

Figure 2. Transient absorption spectra observed at 0.2 (red line (a)) and 5 ns (green line (b)) after the second laser irradiation during the two-color two-laser photolysis (266 and 532 nm), and the spectrum during the one-laser photolysis (266 nm, black line (c)) of AX (1.0×10^{-4} M) (A) in Ar-saturated cyclohexane. The second laser was irradiated at 1 μs after the first laser pulse. The transient absorption spectrum of AXH•(D_1) (B) was obtained by subtracting spectrum (c) from spectrum (a). The blank space around 532 nm in the spectra was due to the residual SHG of the Nd^{3+}:YAG laser.

The energy gaps between the D_1 and D_0, D_2 and D_1, and D_2 and D_0 states of AXH• ($\Delta E(D_1-D_0)$, $\Delta E(D_2-D_1)$, and $\Delta E(D_2-D_0)$, respectively) were determined to be 1.9, 0.8, and 2.7 eV, respectively, from the fluorescence maxima. The reasonably large $\Delta E(D_2-D_1)$ causes the D_2 fluorescence of AXH•. The absence of the $D_2 \rightarrow D_0$ fluorescence of the benzophenone ketyl radical despite the large $\Delta E(D_2-D_1)$ (1.3 eV) suggested that the poor Franck−Condon factor for the $D_2 \rightarrow D_1$ relaxation was also important for the $D_2 \rightarrow D_0$ fluorescence.

The fluorescence lifetimes (τ_f) of AXH•(D_1) and AXH•(D_2) were measured at the peak positions of the fluorescence spectrum. All of the fluorescence decay curves were well fitted with the single exponential decay functions (Figure 1). The τ_f values of AXH•(D_1) and AXH•(D_2) were determined to be 0.40 and 1.0 ns, respectively. The τ_f of AXH•(D_1) was independent of the excitation wavelength (355 or 532 nm). It is remarkable that AXH•(D_2) showed a τ_f value longer than that of AXH•(D_1). The longer τ_f of AXH•(D_2) indicates that the $D_2 \rightarrow D_1$ IC is slow.

The fluorescence quantum yields (Φ_f) of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ fluorescence ($\Phi_f(D_1-D_0)$ and $\Phi_f(D_2-D_0)$, respectively) were estimated to be 0.0008 ± 0.0002 and 0.05 ± 0.02, respectively, using tetraphenylporphyrin and benz[*a*]anthracene as the respective references (Table 1).[1b] It is noteworthy that the $\Phi_f(D_2-D_0)$ value was much higher than $\Phi_f(D_1-D_0)$.

The emitting properties of AXH• resemble those of azulene in the S_2 state in the following points. First, the $\Phi_f(D_2-D_0)$ was much higher than $\Phi_f(D_1-D_0)$. Second, τ_f of the $D_2 \rightarrow D_0$ fluorescence was longer than that of the $D_1 \rightarrow D_0$ fluorescence.[2]

Immediately after the second 532 nm laser irradiation of AXH•(D_0), the growth of new transient absorption peaks at 360 and 420 nm was observed (Figure 2). The decay lifetimes (τ_0) estimated from the absorption decay were essentially the same as τ_f estimated from the fluorescence decay at 645 nm (i.e., the D_1 state). Thus, these transient absorption bands were attributed to the $D_l \leftarrow D_1$ and $D_m \leftarrow D_1$ transitions ($l > m > 1$). The transient absorption spectrum of AXH•(D_1) exhibited two absorption peaks, from which the transition energies from the D_1 state to the two higher excited doublet states (D_l and D_m) were estimated to be around 3.4 and 3.0 eV, respectively.

Upon excitation with the second 532 nm laser, the bleaching and recovery of AXH•(D_0) were observed (see Supporting Information). It is noteworthy that the recovery of AXH•(D_0) after the second 532 nm laser was complete. The complete recovery of AXH•(D_0) indicates that AXH•(D_1) was inert to solvent under the present experimental conditions. The decay of AXH•(D_1) can also be attributed to radiative and nonradiative relaxation processes. Therefore, the τ_f value can be expressed as eq 3

$$\tau_f = 1/(k_r + k_{nr}) \tag{3}$$

where k_r and k_{nr} are the rate constants of the radiative and nonradiative relaxation processes from the AXH•(D_1), respectively. From eq 3, the $k_r + k_{nr}$ value for the $D_1 \rightarrow D_0$ transition was estimated to be 2.5×10^9 s^{-1}. The Φ_f and $k_r + k_{nr}$ values have a relation expressed by eq 4

$$\Phi_f = k_r/(k_r + k_{nr}) \tag{4}$$

From eq 4, the k_r and k_{nr} values for the $D_1 \rightarrow D_0$ transition ($k_r(D_1 \rightarrow D_0)$ and $k_{nr}(D_1 \rightarrow D_0)$, respectively) were estimated to be $(2.0 \pm 0.5) \times 10^6$ and $(2.5) \times 10^9$ s^{-1}, respectively (Table 1). Since no bleaching was observed following the 266 and 355 nm two-step excitation by the nanosecond laser flash photolysis, the contribution of the chemical reaction to the deactivation process of AXH•(D_2) was also negligible. Thus, the $k_r(D_2 \rightarrow D_0)$ and $k_{nr}(D_2 \rightarrow D_0) + k_{nr}(D_2 \rightarrow D_1)$ values were estimated to be $(5.0 \pm 1.5) \times 10^7$ and $(9.5 \pm 2.0) \times 10^8$ s^{-1}, respectively. $k_r(D_2 \rightarrow D_0)$ was 2.5 times greater than $k_r(D_1 \rightarrow D_0)$, although $k_{nr}(D_2 \rightarrow D_0) + k_{nr}(D_2 \rightarrow D_1)$ was smaller than $k_{nr}(D_1 \rightarrow D_0)$ by a factor of 2.5, despite the smaller ($D_2 \rightarrow D_1$) energy gap. The slower k_{nr} of the higher excited state is similar to that of azulene.

In summary, we found the anomalous dual fluorescence of AXH• at room temperature, indicating that AXH• is a new example of a neutral radical which violates Kasha's rule.

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Supporting Information Available: Kinetic traces of AXH•(D_0) and AXH•(D_1). This material is available free of charge via the Internet at http://pubs.acs.org.

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