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Mechanism of Dye-Sensitized Reaction of Excited Singlet of Anthracene Derivatives through Triplet Energy Transfer and the Annihilation Processes

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(Received May 16, 1994)

Absorption of visible light by acridine orange (AOH^+) brought about the photoaddition of CCl_4 to the excited singlet of anthracene derivatives, ($^1A^*$), which occurred by the direct excitation with UV light. From the dependence of the quantum yields on the concentrations of CCl_4 and A and on the light intensity in ethanol solution, a mechanism involving the triplet energy transfer from $^3AOH^+$ to A and the annihilation of ^3A to form $^1A^*$ is proposed.

Electronic energy transfer from the triplet state of some organic dyes such as xanthene and acridine dyes to anthracene derivatives can occur where the dye is excited in a mixed solution. Two molecules of produced triplet anthracenes react successively to form the singlet excited and the ground state molecules through the triplet–triplet annihilation process.[1,2] Provided that the annihilation proceeds predominantly, ultraviolet (UV) emission from singlet excited anthracenes can be observed by the excitation of dye with visible light through the mechanism of sensitized delayed fluorescence (SDF).[3—5] The main process of the reaction can be given by Eqs. 1, 2, 3, 4, 5, 6, and 7 and a scheme shown in Fig. 1.

Choosing the photoaddition reaction of carbon tetrachloride to anthracene derivatives (A) as a case for the selective reaction to a singlet excited state ($^1A^*$) in this investigation, we attempted to discover whether the UV-induced photochemical reactions of A occurred by irradiation with visible light to a dye sensitizer such as acridine orange (AOH^+), i.e., a large up-hill reaction of the electronic energy. Referring to the mechanism of SDF from anthracene reported by Kikuchi et al., the main processes of the reaction (Eqs. 1, 2, 3, 4, 5, 6, and 7) and the scheme in Fig. 1 can be expressed as follows, where ($^3A^3A$) means an encounter complex between two triplet molecules (^3A).[3—6] It has been reported that the photoaddition reaction of CCl_4 occurs essentially as Eq. 7 in the case of direct excitation to A by UV irradiation.[7—11]

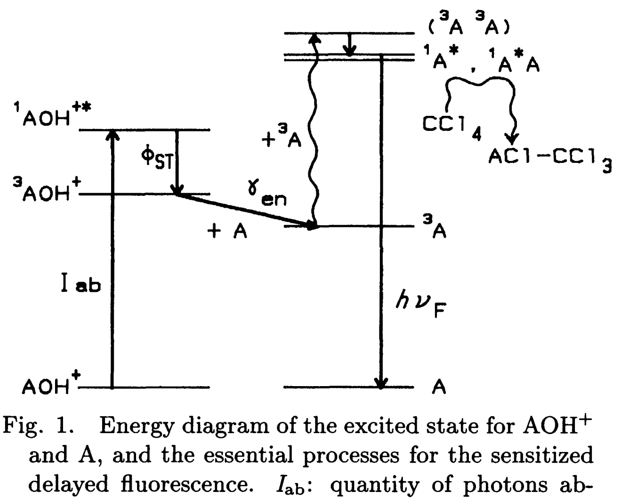

Fig. 1. Energy diagram of the excited state for AOH^+ and A, and the essential processes for the sensitized delayed fluorescence. I_{ab}: quantity of photons absorbed by AOH^+, ϕ_{ST}: intersystem crossing probability from $^1AOH^{+*}$ to $^3AOH^+$, γ_{en}: efficiency of the energy transfer, $h\nu_F$: UV or blue fluorescence from $^1A^*$ state.

$$AOH^+ \xrightarrow{I_{ab}} {}^1AOH^{+*} \xrightarrow{\phi_{ST}} {}^3AOH^+ \tag{1}$$

$$^3AOH^+ \xrightarrow{k_{Td}} AOH^+ \tag{2}$$

$$^3AOH^+ + A \xrightarrow{k_{en}} AOH^+ + {}^3A \tag{3}$$

$$^3A \xrightarrow{k_{TD}} A \tag{4}$$

$$^3A + {}^3A \xrightarrow{k_{TT}} ({}^3A{}^3A) \longrightarrow {}^1A^* + A, \quad A + A \tag{5}$$

$$^1A^* \longrightarrow A + h\nu_F \tag{6}$$

$$^1A^* + CCl_4 \longrightarrow ClACCl_3, \quad A + CCl_4 \tag{7}$$

Experimental

Materials. Acridine orange (hydrochloride) $C_{15}H_{20}N_3Cl$ was recrystallized three times from ethanol. Zone-refined anthracene (An) was used. The derivatives of 9-methylanthracene (MA), 9-phenylanthracene (PA), 9,10-dimethylanthracene (DMA), and 9,10-diphenylanthracene (DPA) were recrystallized from ethanol. Carbon tetrachloride (Tokyo Kasei, UGR) was used as received. Each sample was deaerated by bubbling with argon gas (99.9%) for at least 30 min.

Procedures. A sample in a cell (1 cm×1 cm×4 cm) was irradiated at 25 °C in a steady-light illumination apparatus with 500 W and 1 kW tungsten lamps of which the light intensities, I_0 were 9.3×10^{-9} and 1.8×10^{-7} $mol\,cm^{-2}\,s^{-1}$ respectively, using Eosine Y aqueous solution for conventional actinometry.[12] The quantum yield of the sensitized photoaddition of CCl_4 to anthracene was calculated from the change in absorption spectra and the light quantities. Quantum yield of the photoaddition to anthracene by direct UV-irradiation was similarly obtained from the disappearance rate and UV-light intensity (Hg 365 nm) using the actinometer of potassium trioxalate ferrate(III). Laser flash photolysis was done by using a pulsed dye laser (Phase R. 2100B; dye G4; excitation 500 nm; FWHM of pulse: 500 ns) and a usual monitoring system composed of a light source, a monochromator, and a transient recorder.[13]

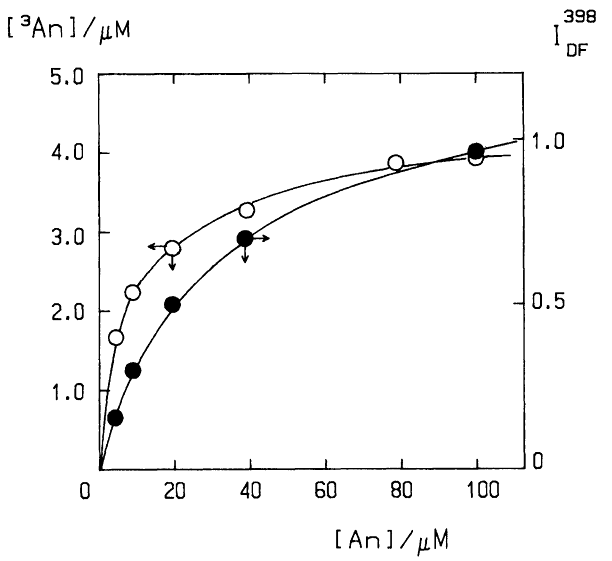

Fig. 2. Effect of anthracene (An) concentration on maximum yield of ^{3}An and the relative intensity of sensitized delayed fluorescence, $I_{\mathrm{DF}}{}^{398}$ through the energy transfer. (pulsed laser-excitation, $[\mathrm{AOH}^+]=5$ μM).

Results and Discussion

Kinetic investigation of the triplet energy transfer in Eq. 3 in two component system of AOH$^+$/A was done in ethanol. Increasing the concentration of the added anthracene derivative ($\approx$ 70 μM, 1 M=1 mol dm^{-3}), ^{3}AOH$^+$ was completely quenched through the energy transfer and ^{3}A was produced in amounts approximately equimolar with ^{3}AOH$^+$ by a laser-flash excitation, as shown in Fig. 2 for anthracene as an energy acceptor. From the result, it was suggested that the energy transfer from ^{3}AOH$^+$ to A occurred without any deactivation, i.e., almost 100% efficiency in the transfer reaction. The concentration effect in quenching by A on the observed rate constant (k_{A}) or ^{3}AOH$^+$ decay was expressed as $k_{\mathrm{A}}=k_{\mathrm{Td}}+k_{\mathrm{en}}[\mathrm{An}]=5.5\times10^3+5.4\times10^9\ [\mathrm{An}]\ \mathrm{s}^{-1}$. Rate constants of the energy transfer (k_{en}) can be obtained from the analysis on concentration effect of A for the decay of ^{3}AOH$^+$ and are listed in Table 1.

The sensitized delayed fluorescence, SDF from ^{1}A* was observed during the period of ^{3}A decay, monitoring it at $\lambda_{\max}=398$ nm for An. The time-integrated intensity of SDF increased with the added concentration of An as shown in Fig. 2 (A=An). The SDF intensity, $I_{\mathrm{DF}}{}^{398}$ is proportional to the square of ^{3}A concentration assuming the main processes of Eqs. 5 and 6.[3—5] These results for anthracene derivatives were confirmed from the fact that the slope of 2 in the linear relationship between $\log I_{\mathrm{DF}}{}^{398}\ (t)$ vs. $\log\,[^3\mathrm{A}](t)$ for the time dependent quantities was obtained in a laser flash experiment.

In the case of the addition of CCl$_4$ in ethanol solution (AOH$^+$/A/CCl$_4$ system), the value of $I_{\mathrm{DF}}{}^{398}$ decreased efficiently but the yields of ^{3}A were little affected as shown in Fig. 3 (A=An). Also, the kinetic behavior of ^{3}AOH$^+$ and ^{3}A was not affected by the addition of CCl$_4$ (< 1 M). Although the formation of a charge transfer complex between A and CCl$_4$ has been reported at higher concentrations of CCl$_4$, the contribution of the complex to the SDF quenching by CCl$_4$ in the processes from Eq. 1 to Eq. 7 can be neglected because the dynamic quenching of ^{1}A* by CCl$_4$ proceeds at the concentration range of $[\mathrm{CCl_4}]\leqq1$ M, predominantly.[7,14—17] Therefore, the observed SDF quenching by CCl$_4$ was due to the reaction of Eq. 7.

It was reported that the photoreaction of CCl$_4$ to ^{1}A* was observed and the 9,10-adduct of Cl and CCl$_3$ to A, ClACCl$_3$, was a major product in Eq. 7, involving the quenching of fluorescence from ^{1}A* according to the CCl$_4$ photoaddition.[7—10] The maximum value of the quantum yield, $Q_{-\mathrm{A}}$, for the disappearance by direct excitation to An was measured as $Q_{-\mathrm{An}}{}^{\max}=0.6$ (i.e., A=An). In the mixture of AOH$^+$/A/CCl$_4$ in ethanol, AOH$^+$ sensitized photoaddition of CCl$_4$ to A was confirmed to occur from the fact that the same change in the absorption spectrum was observed as that for direct excitation to A. Figure 4 shows the effects of CCl$_4$ concentration on the quantum yield for the sensitized photoaddition ($\Phi_{-\mathrm{A}}$). A large increment of $\Phi_{-\mathrm{A}}$ was observed around 0.3 M of CCl$_4$, which was comparable to the concentration quenching for SDF in Fig. 3. The maximum yields of $\Phi_{-\mathrm{A}}$ for anthracene derivatives were listed in Table 1 under the irradiation with light intensity (I_0) of 1.8×10^{-7} mol cm^{-2} s^{-1}. From the processes of Eqs. 1, 2, 3, 4, 5, 6, and 7, $\Phi_{-\mathrm{A}}$ for the disappearance of A by the AOH$^+$ sensitized reaction is expressed as follows:

$$\Phi_{-\mathrm{A}}=Q_{-\mathrm{A}}P_{\mathrm{s}}k_{\mathrm{TT}}[^3\mathrm{A}]_{\mathrm{s}}{}^2/I_{\mathrm{ab}} \tag{8}$$

where $Q_{-\mathrm{A}}$ is the quantum yield for the disappearance of A on CCl$_4$ photoaddition by direct excitation to A, P_{s} is the efficiency of ^{1}A* production in the following Eq. 5b, I_{ab} is the absorbed light quantities by AOH$^+$ and $[^3\mathrm{A}]_{\mathrm{s}}$ is the concentration of ^{3}A in a stationary state. The $Q_{-\mathrm{A}}$ value depended on the concentration of CCl$_4$ and the maximum values were obtained as 0.60 for An, 0.40 for MA, 0.31 for PA, 0.65 for DMA, and 0.44 for DPA.

Referring to the kinetic treatment of the TT annihilation for anthracene dimerization by Saltiel et al. and introducing the detailed processes Eqs. 5a, 5b, 5c, and 5d against Eq. 5, the expression for $[^3\mathrm{A}]_{\mathrm{s}}$ is given as in Eq. 9 from the following equations.[6]

$$^3\mathrm{A}+{}^3\mathrm{A}\longrightarrow({}^3\mathrm{A}{}^3\mathrm{A}) \tag{5a}$$

$$({}^3\mathrm{A}{}^3\mathrm{A})\longrightarrow{}^1\mathrm{A}^*+\mathrm{A},\quad({}^1\mathrm{A}^*\mathrm{A}),\quad P_{\mathrm{s}} \tag{5b}$$

$$({}^3\mathrm{A}{}^3\mathrm{A})\longrightarrow{}^3\mathrm{A}+{}^3\mathrm{A},\quad{}^3\mathrm{A}+\mathrm{A},\quad P_{\mathrm{t}} \tag{5c}$$

$$({}^3\mathrm{A}{}^3\mathrm{A})\longrightarrow\mathrm{A}+\mathrm{A} \tag{5d}$$

Table 1. Rate Constants of Energy Transfer (k_{en}), and Maximum Quantum Yields of the AOH$^+$ Sensitized Photoaddition to Anthracene Derivatives ($\Phi_{-A}{}^{max}$) and of the Sensitized Delayed Fluorescence ($\Phi_{SF}{}^{max}$)

A (Φ_F)	k_{en}/M^{-1}s^{-1}	$\Phi_{-A}{}^{max}$ a)	$\Phi_{SF}{}^{max}$ b)
Anthracene (0.30)	5.4×10^9	0.03	0.011
9-Methylanthracene (0.33)	5.3×10^9	0.018	0.015
9-Phenylanthracene (0.49)	3.9×10^9	0.0073	0.014
9,10-Dimethylanthracene (0.89)	2.4×10^9	0.019	0.040
9,10-Diphenylanthracene (0.89)	3.4×10^9	0.0092	0.026

a) $I_0 = 1.8\times10^{-7}$ mol cm^{-2} s^{-1}. $\gamma_{en} = 0.7$ was estimated under [A]=50 μM.
b) $\gamma_{en} = k_{en}[A]/(k_{TD}+k_{en}[A])$. $\gamma_{en}=1$ was assumed at the higher concentration of A in Eq. 12 (see text).

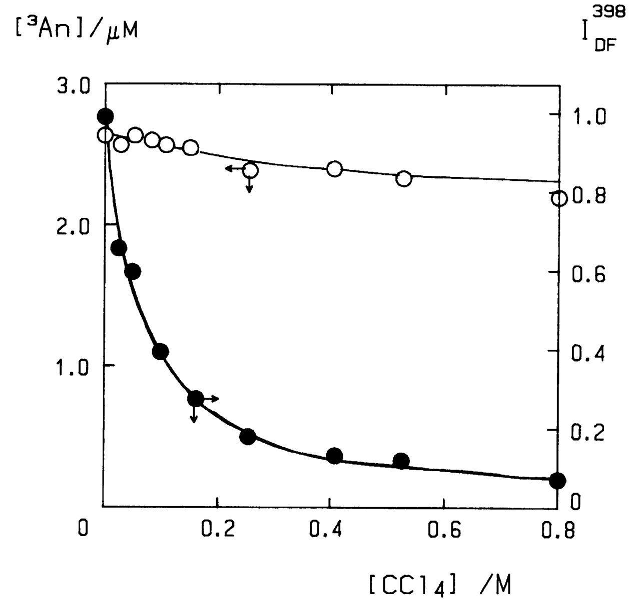

Fig. 3. Effect of CCl$_4$ concentration on the intensity, $I_{DF}{}^{398}$ and the yield of ^{3}An through the energy transfer. (pulsed laser-excitation, [AOH$^+$]=5 μM, [An]=20 μM).

$$[{}^3\mathrm{A}]_s = \frac{-k_{TS} + \sqrt{k_{TS}{}^2 + 4\phi_{ST}\gamma_{en}I_{ab}k_{TT}(2-P_t)}}{2k_{TT}(2-P_t)} \qquad (9)$$

where ϕ_{ST} is an intersystem crossing probability of AOH$^+$ (=0.30), γ_{en} is an efficiency of the energy transfer for Eqs. 2 and 3, k_{TS} is the observed rate constant of ^{3}A decay ($=k_{TD}+k$[A]), P_s and P_t are the efficiencies of ^{1}A* and ^{3}A formation from (^{3}A^{3}A) through Eqs. 5b and 5c respectively. For example, $P_t=1.44$ for anthracene.[6] Substituting Eq. 9 into Eq. 8, the effect of I_{ab} on Φ_{-A} values is expressed as Eq. 10.

$$\Phi_{-A} = \frac{Q_{-A}P_s}{2k_{TT}(2-P_t)^2 I_{ab}} Y$$

$$Y = k_{TS}{}^2 + 2\phi_{ST}\gamma_{en}I_{ab}k_{TT}(2 - P_t) - k_{TS}\sqrt{k_{TS}{}^2 + 4\phi_{ST}\gamma_{en}I_{ab}k_{TT}(2-P_t)} \qquad (10)$$

The experimental results are shown in Fig. 5 for AOH$^+$/A/CCl$_4$ system in ethanol. Since the approximation of $k_{TS} \ll k_{TT}[^3\mathrm{A}]_s$ can be hold for the higher intensity of irradiation and the first and third terms in Y in Eq. 10 are negligible, the maximum value, $\Phi_{-A}{}^{max}$ is given as follows;[18]

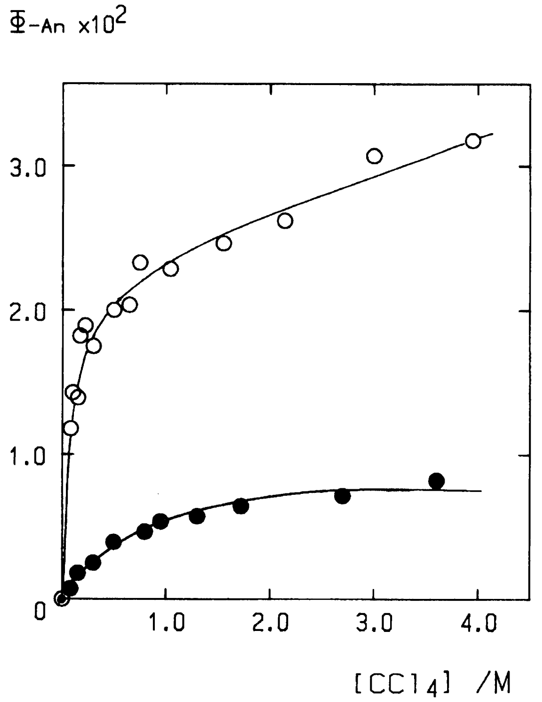

Fig. 4. Effect of CCl$_4$ concentration on the Φ_{An} values. ([AOH$^+$]=10 μM, [An]=20 μM, ●: $I_0=9.3\times10^{-9}$ mol cm^{-2} s^{-1}, ○: $I_0=1.8\times10^{-7}$ mol cm^{-2} s^{-1})

$$\Phi_{-A}{}^{max} = \phi_{ST}\gamma_{en}P_s(2-P_t)^{-1}Q_A \qquad (11)$$

Putting $\phi_{ST}=0.3$, $\gamma_{en}=0.7$ at [An]=50 μM, $Q_{-An}=0.6$, $P_t=1.44$, and the $\Phi_{-A}{}^{max}$ value of 0.03 for anthracene (A=An) in Table 1, we obtain a P_s value of 0.13. Introducing these values and the rate constants of k_{TT} and k_{TS} into Eq. 9, a simulation curve is drawn in Fig. 5 as dotted line for An. Comparing with Saltiel's value of $P_s=0.16$ obtained for the photodimerization mechanism of An by direct excitation, it is suggested from the coincidence of the P_s value that the sensitized photoaddition proceeds as shown in Fig. 1.

Maximum yield of AOH$^+$ sensitized delayed fluorescence from ^{1}A* ($\Phi_{SF}{}^{max}$) can be estimated in a similar

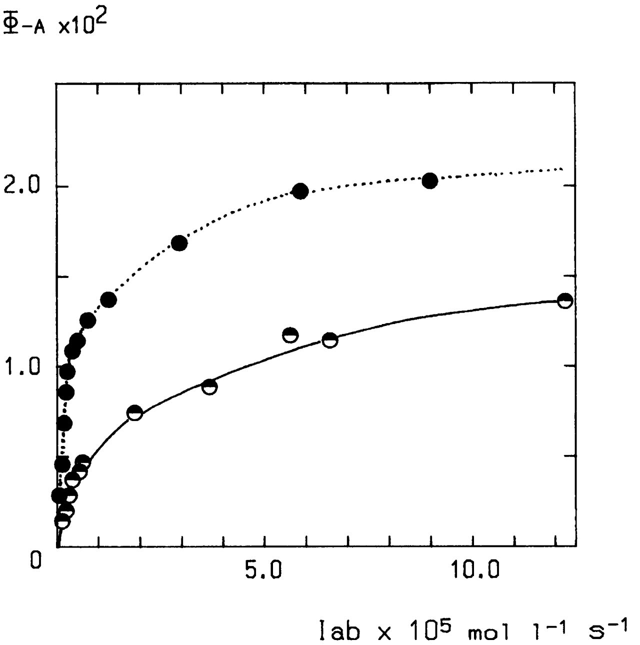

Fig. 5. Effect of light intensity on the $\Phi_{-\mathrm{A}}$ values. (●: [AOH$^+$]=10 μM, [An]=20 μM, [CCl$_4$]=0.3 M, ⊖: [AOH$^+$]=10 μM, [MA]=50 μM,[CCl$_4$]=0.5 M.)

manner as Eq. 12;

$$\Phi_{\mathrm{SF}}{}^{\mathrm{max}} = \phi_{\mathrm{ST}}\gamma_{\mathrm{en}}P_{\mathrm{s}}(2 - P_{\mathrm{t}})^{-1}\Phi_{\mathrm{F}} \qquad (12)$$

Using P_{s} $(2 - P_{\mathrm{t}})^{-1}$ values as the SDF parameter which was obtained from Eq. 11 and the reported fluorescence yields of A (Φ_{F}), the approximate values of $\Phi_{\mathrm{SF}}{}^{\mathrm{max}}$ are calculated from Eq. 12.[19] The data are listed in Table 1.

When DMA (or MA) was used as the energy acceptor, the decrease in the absorption by the irradiation to AOH$^+$ was observed without CCl$_4$ and a new absorption band with λ_{max}=213 nm appeared. Warming the solution after the irradiation in the dark, the absorption at 213 nm disappeared and the original absorption of DMA (or MA) recovered, quantitatively. The photoproduct was identified as the dimer DMA with head-to-tail structure of (DMA)$_2$ by ^{1}H NMR (CDCl$_3$) δ=3.10 (6H), 1.70 (12 H). It was suggested that AOH$^+$ sensitized photodimerization of DMA (or MA) occurred from these results. The quantum yields, Φ_{A2} of DMA and MA disappearance for photodimerization were 0.0033 (MA) and 0.0022 (DMA), respectively. The effect of light intensity on Φ_{A2} was observed similarly with that in Fig. 5. Since Φ_{A2} values are very small, the contribution to the sensitized photoaddition processes will be negligible at the higher concentration of CCl$_4$.

This work was supported by a Grant-in-Aid for Scientific Research No. 03303001 from the Ministry of Education, Science and Culture.

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