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# Fluorescence Quenching Process of Anthracene by Maleic Anhydride

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The time dependence of fluorescence intensity after picosecond laser excitation and the steady-state fluorescence intensity were measured in order to study the mechanism of fluorescence quenching of anthracene by maleic anhydride in 1,4-dioxane. The nonlinear relationship between the reciprocal of steady-state fluorescence intensity and quencher concentration was observed for this system and interpreted in terms of the transient effect in the quenching process. The kinetic study by picosecond laser photolysis supports this interpretation. The reaction radius ($R$) and the sum of diffusion constants of both reactants ($D$) at various temperatures were determined by applying the diffusion model of Andre *et al.* The observed values are $R=7.2$ Å, $D=1.46\times10^{-5}$ cm$^2$ s$^{-1}$ (22 °C), $1.87\times10^{-5}$ cm$^2$ s$^{-1}$ (50 °C), $2.42\times10^{-5}$ cm$^2$ s$^{-1}$ (75 °C). Studies of the main path in the quenching process by nanosecond laser photolysis suggest the existence of an extra path in the quenching process which overwhelms the fluorescent exciplex formation, the photoionization, the triplet anthracene formation, and the adduct formation.

Anthracene-maleic anhydride is one of the typical systems which undergo the photochemical Diels-Alder reaction.1) In connection with the reaction mechanism, the fluorescence quenching process is also of interest. So far, however, only a few studies have been reported on the quenching and reaction mechanisms.1–3)

Livingston *et al.* reported that the fluorescence quenching process of anthracene by maleic anhydride in 1,4-dioxane is controlled by diffusion and that the fluorescence quenching does not result appreciably in the formation of the triplet state of anthracene.2)

Concerning the reaction intermediate Kaupp proposed that the biradical intermediate should exist in the photochemical reaction between anthracence and maleic anhydride, from an analogy of the mechanism of the photochemical reaction between anthracene and dimethyl maleate.3)

Anthracene and maleic anhydride form a charge-transfer complex. In some cases an excited charge-transfer complex4) or an exciplex5) is the intermediate of photocycloaddition reaction. So it is probable that the fluorescence quenching due to charge-transfer interaction is related to the mechanism of the photoaddition reactions. Hence we studied the fluorescence quenching process of anthracene by maleic anhydride in the present paper.

## Experimental

*Measurements.* Steady-state fluorescence quenching experiments were carried out with a spectrophotofluorometer (Shimadzu; model 502) which has two double monochromators for excitation and emission. The 1,4-dioxane solution of anthracene ($7.5\times10^{-5}$ mol dm$^{-3}$) in a 1 cm square quartz cell was excited at 370 nm and the emission was measured at right angle with the excitation light. The measurements were made at room temperature (20±2 °C).

A block diagram of our picosecond emission spectroscopy apparatus was shown in Fig. 1. The excitation light pulse was the second harmonic (347.2 nm, 20 ps fwhm) of an amplified single pulse which was selected from a pulse train generated by a mode-locked ruby laser. The detection system for fluorescence from the sample was composed of a 50 cm grating monochromator, an image-converter streak camera (John Hadland; IMACON 600) coupled to a three-stage image intensifier (EMI; model 9914), and an optical multichannel analyzer (abbreviated hereafter as OMA) (PAR 1205). Fluorescence decay curves were displayed on an oscilloscope coupled to OMA. The digitized data by OMA were accumulated and processed by a desk-top computer. The fluorescence intensity of anthracene was observed at 402.5 nm. The concentration of anthracene was $7\times10^{-3}$ mol dm$^{-3}$ for the observation of the time profile of the fluorescence intensity.

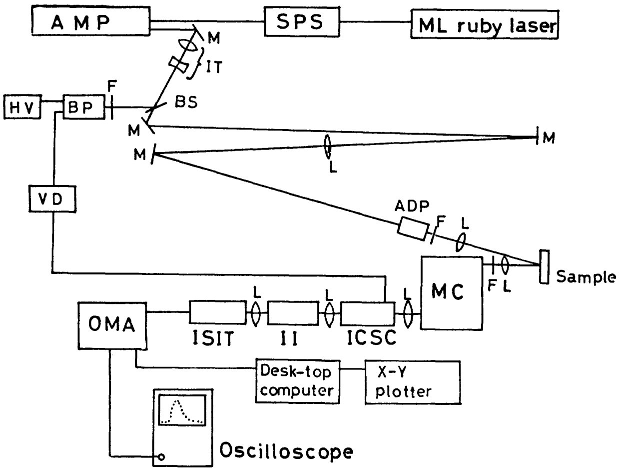

Fig. 1. Block diagram of the picosecond emission spectroscopy apparatus.
The excitation light generation system is composed of a mode-locked (ML) ruby laser, a single pulse selector (SPS), an amplifier (AMP), and an ADP crystal. The detection system is composed of a monochromator (MC), an image-converter streak camera (ICSC), an image intensifier (II), an intensified silicon intensified target tube (ISIT), an optical multichannel analyzer (OMA), an oscilloscope, a desk-top computer, and an X-Y plotter. The trigger system for ICSC is composed of a biplanar phototube (BP), a high-voltage power supply (HV), and a variable delay circuit (VD). L, M, BS, and IT represent lens, mirror, filter, beam splitter, and inverted telescop, respectively.

In the study of nanosecond laser photolysis a commercial nitrogen laser (337.1 nm, 10 ns fwhm, Molectron; model UV24) or a home-made nitrogen laser (3.7 ns fwhm) was used as an excitation light source and a Xe flash lamp with 40 μs duration was used as a monitoring light source.

The absorption spectrum measurements were carried out with a Cary 14 spectrophotometer.

Deoxygenation was done by bubbling dry nitrogen gas through the solution for 5 min.

*Materials.* The highly pure anthracene was a kind gift from Prof. Iwashima of Meisei University. Guaranteed reagent grade maleic anhydride (abbreviated to MA; Tokyo Kasei) and phthalic anhydride (Wako Pure Chemical) were sublimed *in vacuo* before use. Reagent grade pyromellitic dianhydride (Tokyo Kasei) was recrystallized twice from 1,4-dioxane and sublimed *in vacuo*. Acetonitrile (Wako Pure Chemical; spectrosol grade) was used without further purification. 1,4-Dioxane (Wako Pure Chemical) was let stand over iron (II) sulfate for several days. It was refluxed for 8 h with hydrochloric acid and water under nitrogen. Potassium hydroxide was added to the solution and the water layer was discarded. It was refluxed for 12 h with sodium under nitrogen, then distilled into flask and stoppered.

## Results and Discussion

*Steady-state Experiment.* Plot of $I_0/I$ *vs.* concentration of MA([MA]) is shown in Fig. 2 by open circles. $I_0$ and $I$ are the fluorescence intensities without and with quencher, respectively. As can be seen in the figure, the plot is nonlinear. Five possible mechanisms to explain the nonlinear relation between $I_0/I$ and [MA] are listed below: 1) (1:1) charge-transfer complex formation in the ground state between anthracene and maleic anhydride, 2) photochemical and/or thermal reactions between anthracene and maleic anhydride, 3) internal filter effect, 4) dipole-dipole energy transfer from excited anthracene to maleic anhydride, 5) the transient effect in diffusion-controlled fluorescence quenching reaction. All but the fifth mechanism are concluded to be minor by the following considerations.

Anthracene and maleic anhydride in 1,4-dioxane form a (1:1) ground state charge-transfer (CT) complex and its equilibrium constant is reported to be 0.05 mol$^{-1}$ dm$^3$.[1] At the excitation wavelength (370 nm), not only anthracene but also the CT complex can absorb light to some extent. On the assumption that light absorption by the CT complex does not contribute to fluorescence intensity at all, $I_0/I$ is represented as follows:

$$\frac{I_0}{I}=\frac{(1-10^{-C_0\varepsilon_A y})(1+K[\mathrm{MA}]\varepsilon_C/\varepsilon_A)(1+\tau k[\mathrm{MA}])}{1-10^{-C_0 y(K[\mathrm{MA}]\varepsilon_C+\varepsilon_A)/(1+K[\mathrm{MA}])}} \tag{1}$$

where $\varepsilon_C$ and $\varepsilon_A$ are the molar extinction coefficients of the complex and anthracene at the excitation wavelength, respectively. $K$ is the equilibrium constant between free anthracene and maleic anhydride and their complex. The fluorescence lifetime of anthracene without quencher is given by $\tau$ and the quenching rate constant is represented by $k$. $C_0$ is the total concentration of anthracene and $y$ is the optical path length of the cell.

The absorbance, $A$, of anthracene solution containing maleic anhydride of the concentration [MA] at the excitation wavelength (370 nm) and the absorbance, $A_0$, of anthracene solution without quencher at the same wavelength have the following relationship.

$$A/A_0=\left(1+K\frac{\varepsilon_C}{\varepsilon_A}[\mathrm{MA}]\right)\bigg/(1+K[\mathrm{MA}]) \tag{2}$$

Here $K$=0.05 mol$^{-1}$ dm$^3$. Then we can estimate $\varepsilon_C/\varepsilon_A$ from the observed $A/A_0$, which is 3.4. Furthermore, from the data in the low quencher concentration region (below 0.074 mol dm$^{-3}$) in Fig. 2, $\tau k$ is estimated to be 61.4 mol$^{-1}$ dm$^3$. Combining the respective values of $\varepsilon_A$(2.7×10$^6$ mol$^{-1}$ cm$^2$), $C_0$(7.5×10$^{-5}$ mol dm$^{-3}$) and $y$ (1 cm) with $K$, $\varepsilon_C/\varepsilon_A$ and $\tau k$, the $I_0/I$ values represented by Eq. 1 can be calculated as the function of [MA]. The results are shown by a dashed curve in Fig. 2. We can see from this figure that the values calculated by Eq. 1 are much smaller than the observed ones. Therefore we conclude that the ground state complex formation (mechanism 1) is a minor contributing factor in the nonlinear relationship between $I_0/I$ and [MA].

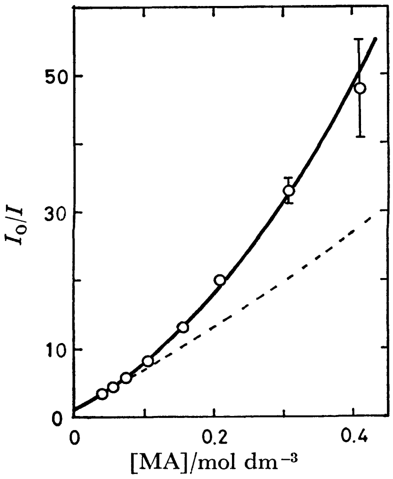

Fig. 2. Results of the steady-state intensity measurement of fluorescence from anthracene quenched by maleic anhydride in 1,4-dioxane at 20°C.
Open circles, experimental values; solid curve, calculated values for $I_0/I$ from Eq. 3 with parameters from Table 1; dashed curve, calculated values for $I_0/I$ from Eq. 1.

The decrease in the anthracene concentration by photochemical and/or thermal reactions with maleic anhydride during the measurement may decrease the fluorescence intensity of anthracene. The decrease was determined to be 1.6% at [MA]=0.42 mol dm$^{-3}$ by the absorption spectrum measurement. Mechanism 2, thus, contributes little to the nonlinearity of $I_0/I$-[MA] plot.

The internal filter effect (mechanism 3) is estimated from the increase in absorbance brought about by the addition of maleic anhydride in the wavelength region of fluorescence. The maximum quencher concentration in the steady-state experiment is 0.42 mol dm$^{-3}$, and the maximum increase in absorbance in the fluorescence spectral region was 0.01 (388 nm). This means that the fluorescence intensity is reduced by this effect by 2.3%. The decrease of 2.3% in the intensity is much less than the observed decrease of 44%. Consequently mechanism 3 can be ruled out.

According to Förster's theory the rate constant for the dipole-dipole energy transfer depends on the overlap of the fluorescence spectrum of an energy donor and the absorption spectrum of an energy acceptor. In the present case there is no overlap between the fluorescence spectrum of anthracene and the absorption spectrum of maleic anhydride. So we can rule out mechanism 4.

According to the modified theory by Andre *et al.* on the diffusion-controlled fluorescence quenching process, $I_0/I$ is expressed by the following equation.⁶⁾

$$I_0/I = \exp(NV[\text{MA}])\,(1+4\pi RDN\tau[\text{MA}])\,Y^{-1} \qquad (3)$$

where $R$ is a reaction distance. $D$ represents the sum of diffusion constants of a fluorophor and a quencher, and $N$ is Avogadro's number devided by 1000. $Y$ and $V$ are represented as follows:

$$Y = 1-(b/a^{1/2})\pi^{1/2}\exp(b^2/a)\,\text{erfc}\,(b/a^{1/2}),$$

$$\text{erfc}\,(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty}\exp(-u^2)\text{d}u, \quad V = \frac{4\pi}{3}(R^3-R'^3),$$

$$a = \frac{1}{\tau} + 4\pi RDN[\text{MA}], \quad b = 4R^2(\pi D)^{1/2}N[\text{MA}]$$

where $R'$ is a collisional distance which is taken as the sum of molecular radius of anthracene (3.51 Å) and that of maleic anhydride (2.63 Å). The molecular radii were determined from Lebas volume.⁷⁾

$R$ and $D$ were determined by fitting the above theoretical expression to the observed dependence of $I_0/I$ on [MA] shown in Fig. 2. In actuality the least-squares method was used for the determination. The values best fitted to the observed $I_0/I$-[MA] curve are listed in Table 1.

TABLE 1. THE REACTION DISTANCES ($R$'s) AND THE SUMS OF DIFFUSION CONSTANTS ($D$'s)

| | $R$/Å | $D/10^{-5}$ cm² s⁻¹ | Temp/°C |
|---|---|---|---|
| From steady-state experiment | 7.4 | 1.3 | 20±2 |
| From decay curves | | | |
| [MA]/mol dm⁻³ | | | |
| 0.214 | 7.2±1.4 | 1.56±0.4 | 22±1 |
| 0.428 | 7.2±0.7 | 1.36±0.2 | 22±1 |
| 0.208 | 7.2±0.7 | 1.87±0.2 | 50±1 |
| 0.202 | 7.2±0.7 | 2.42±0.2 | 75±1 |

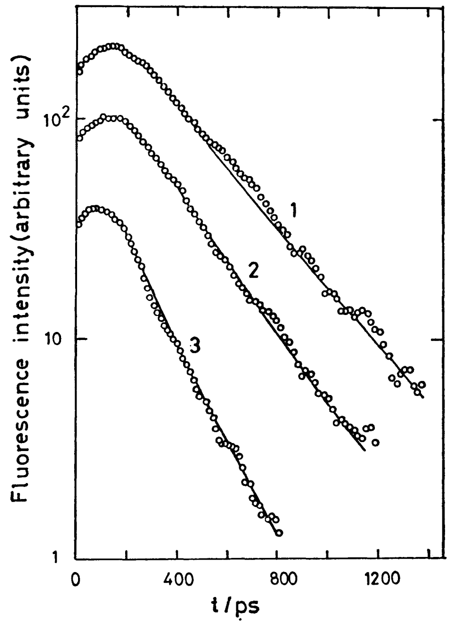

Fig. 3. Time dependence of anthracene fluorescence intensity quenched by MA in 1,4-dioxane.
Curve 1, [MA]=0.208 mol dm⁻³ at 50°C; curve 2, [MA]=0.202 mol dm⁻³ at 75°C; curve 3, [MA]=0.428 mol dm⁻³ at 22°C. Open circles are the observed values and solid lines the best fitted curves calculated by using the parameters in Table 1 and the corresponding MA concentration.

*Picosecond Emission Spectroscopy.* The transient effect in the diffusion-controlled fluorescence quenching process can be observed directly by the picosecond laser photolysis technique. We can ascertain the applicability of the diffusion model to this system by comparing $R$ and $D$ values obtained by the picosecond photolysis technique with those obtained from the steady-state experiment.

The observed decay curves at various conditions are shown in Fig. 3 by open circles. In order to analyze these curves one must take into account the time profile of excitation pulse, $P(t)$, and the response function of the detection system, $G(t)$. The output from the detection system, $H(t)$, is given by the convolution integral as follows:

$$H(t) = \int_{-\infty}^{\infty}\int_{-\infty}^{t'} G(t-t')P(s)F(t'-s)\text{d}s\text{d}t', \qquad (4)$$

where $F(t)$ is the undistorted response function of the fluorescent system. $P(t)$ is assumed to be a Gaussian function with a parameter determined by the laser pulse width which was measured by two-photon fluorescence technique. $G(t)$ is also assumed to be a Gaussian function whose parameter is determined by the observed width of the excitation light pulse. If the fluorescent systems (anthracene molecules in the case of the present experiment) are quenched by the other molecules (maleic anhydride molecules) by the diffusion-controlled process, $F(t)$ is expressed in terms of $\exp(-at-2bt^{1/2})$. $H(t)$ was obtained numerically by computer calculation with various sets of $R$ and $D$ values. $R$ and $D$ were then estimated from the curve best fitted to the observed time profile of the fluorescence intensity.

The solid curves in Fig. 3 are the calculated curves of $H(t)$ that best fitted for the observed values. $R$ and $D$ values determined from these decay curves are listed in Table 1. The errors were estimated by comparing the caculated $H(t)$'s with the observed decay curves. $R$ and $D$ obtained from the decay curves at 22 °C agree well with those obtained from the steady-state experiment. This agreement justifies the application of the diffusion model to the fluorescence quenching process of anthracene by maleic anhydride in 1,4-dioxane.

The temperature dependence of $D$ can be estimated by using the Stokes-Einstein equation:

$$D = \frac{k_\text{B}T}{6\pi\eta}(r_\text{An}{}^{-1}+r_\text{MA}{}^{-1}) \qquad (5)$$

where $k_\text{B}$ and $T$ have ordinary meanings. $\eta$ is the viscosity of the solvent. $r_\text{An}$ and $r_\text{MA}$ are the radii of anthracene and maleic anhydride, respectively. Anthracene and maleic anhydride molecules are, in fact, not spherical. However, for the sake of simplicity we applied the above equation, and the radii of anthracene and maleic anhydride were determined by using Lebas volume.7) The calculated $D$'s are $1.18\times10^{-5}$ cm$^2$ s$^{-1}$ (22 °C), $2.03\times10^{-5}$ cm$^2$ s$^{-1}$ (50 °C), and $2.97\times10^{-5}$ cm$^2$ s$^{-1}$ (75 °C). A fairly good agreement is obtained with the $D$'s obtained from the picosecond photolysis experiment.

*The Main Path in Fluorescence Quenching Process.* Following four possibilities for the main path in fluorescence quenching by the quencher were examined; 1) the formation of fluorescent exciplex, 2) photochemical Diels-Alder reaction, 3) the enhancement of intersystem crossing by charge-transfer interaction,8) 4) photoionization. The possibility of formation of fluorescent exciplex was denied, because no detectable fluorescence appeared in the range from 375 nm to 750 nm by the addition of maleic anhydride to the 1,4-dioxane solution of anthracene. The adduct formation is not the main path in fluorescence quenching process because the quantum yield of the adduct formation was reported to be 0.026 at 26 °C with [MA]=0.5 mol dm$^{-3}$.1)

Table 2. The dependence of absorbance of the $T_n \leftarrow T_1$ transition of anthracene immediately after excitation on maleic anhydride concentration

| [MA]/mol dm$^{-3}$ | Absorbance of $T_n \leftarrow T_1$ transition |
|---|---|
| 0 | 0.309 |
| 0.116 | 0.058 |
| 0.290 | 0.024 |
| 0.580 | too weak to be observed |

The absorbance was monitored at 425 nm. The concentration of anthracene is $3.9\times10^{-3}$ mol dm$^{-}$.$^{3}$

The dependence of absorbance of the $T_n \leftarrow T_1$ transition immediately after excitation on quencher concentration was studied by nanosecond laser photolysis. The results are shown in Table 2. The absorbance decreases remarkably as the quencher concentration increases. Maleic anhydride absorbs excitation light at 337.1 nm. However, the effect of this absorption upon the absorbance of the $T_n \leftarrow T_1$ transition is negligibly small, because the molar extinction coefficient at 337.1 nm is 1260 times smaller for maleic anhydride than for anthracene. Furthermore, the first excited triplet state ($T_1$) of anthracene was not drastically quenched by maleic anhydride, since at [MA]=0.32 mol dm$^{-3}$ the lifetime of $T_1$ of anthracene was longer than 2 μs. Therefore we conclude that the intersystem crossing of anthracene cannot be enhanced by maleic anhydride.

The possibility of photoionization was examined by the nanosecond laser photolysis techniques. The anthracene cation radical, whose absorption maximum was near 720 nm,9,10) was not observed at [anthracene]= $10^{-2}$ mol dm$^{-3}$ and [MA]=1 mol dm$^{-3}$ in either 1,4-dioxane or acetonitrile. In the cases of anthracene ($2.7\times10^{-3}$ mol dm$^{-3}$) and pyromellitic dianhydride ($2.2\times10^{-2}$ mol dm$^{-3}$), and anthracene ($2.4\times10^{-3}$ mol dm$^{-3}$) and phthalic anhydride ($1.9\times10^{-2}$ mol dm$^{-3}$) in acetonitrile, the anthracene cation radical was observed by using the same experimental equipment. The quantum yield of photoionization is expected to increase with the increase in electron affinity of the acceptor. The electron affinities of pyromellitic dianhydride, maleic anhydride, and phthalic anhydride are 0.85 eV, 0.57 eV, and 0.15 eV, respectively.11) The quantum yield of photoionization is very small for the system containing anthracene and maleic anhydride in acetonitrile compared with the others. This means that an extra channel which overwhelms the photoionization process should exist in the quenching process of excited singlet state anthracene by maleic anhydride. The process may be, for example, a formation of the biradical intermediate proposed by Kaupp,3) or a formation of a very short-lived ion-pair whose main decay path is neither fluorescent exciplex formation, free ion formation, triplet anthracene formation, nor adduct formation.

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