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Anomalous Fluorescence Quenching of Pyrene by Methylviologen in Aqueous Solution. The Formation of Ground-State Nonfluorescent Complex between the Reactants

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The quenching of pyrene fluorescence by methylviologen in aqueous solution proceeded via both dynamic and static processes. It was shown that the formation of a ground-state "dark" complex between the reactants is responsible for the latter process.

In view of the wide interest in the property and usage of methylviologen (paraquat; 1,1'-dimethyl-4,4'-bipyridinium; MV^{2+}) cation in such areas as photochemistry and photobiology,1) it is important to understand the characteristic aspects of the photochemical behavior of this compound. For example, the photochemistry of electron donor-acceptor or charge-transfer (CT) complexes of MV^{2+} has been the subject of recent intense research.1,2) It has been pointed out recently 2,3) that the formation of ground-state CT complexes between MV^{2+} and amine-based sacrificial electron donors such as EDTA and triethanolamine has serious implications for the full understanding of typical water photoreduction systems.4)

From the above point of view, the fluorescence quenching of excited molecules by MV^{2+} is receiving increasing attention, especially in relation to photoinduced redox reactions.2,5,6) Very recently we have given a preliminary account of the fluorescence quenching of pyrene by MV^{2+} in surfactant and/or cyclodextrin solutions.7) In the present study, a special attention is paid to the anomalous quenching of pyrene fluorescence by MV^{2+} in aqueous solution. We wish to report that the crucial event in the system is the formation of a pyrene-MV^{2+} complex which results in an enhanced quenching of pyrene fluorescence.

Zone refined pyrene (Tokyo Kasei) was used as received. MV^{2+} (dichloride, Nakarai or Sigma) was twice recrystallized from methanol and dried in vacuo for 48 h. Laboratory deionized water was twice distilled. The absorption spectra of sample solutions (pyrene + MV^{2+}) were taken on a Shimadzu MPS-2000 multipurpose spectrophotometer, with a reference cell containing only an equimolar solution of MV^{2+}. The steady-state corrected fluorescence spectra were measured with an excitation wavelength of 337.1 nm on a Hitachi 850 spectrofluorometer. Fluorescence lifetime measurements were performed as described previously8) on an instrument equipped with an N_2 laser (3-4 ns pulse width) as an excitation source. The decay curves were described by a single exponential decay, even when MV^{2+} was present. In the quenching experiment, the fluorescence was measured as a function of MV^{2+}

concentration at a constant concentration of pyrene. The concentration of pyrene ([pyrene]) was fixed at 5 X 10^{-7} mol dm^{-3} unless otherwise stated. All measurements were made at 25 °C for aerated solutions. In contrast to the case of an organic solvent, the quenching by dissolved oxygen in an aqueous solution has been shown by the lifetime measurement to be unimportant.$^{9)}$

In general, fluorescence intensity (I) and fluorescence lifetime (τ) are related to quenching rate constant (k_q) and concentration of quencher ([Q]) by the Stern-Volmer equation (Eq. 1);

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] \tag{1}$$

where I_0 and τ_0 are fluorescence intensity and fluorescence lifetime in the absence of quencher, respectively. Figure 1 shows two types of the Stern-Volmer plots, I_0/I vs. [Q] and τ_0/τ vs. [Q], for the present system. The latter plot yielded a straight line (a dashed line in Fig. 1), from the slope of which the k_q value was obtained to be 5.3 X 10^9 mol^{-1} dm^3 s^{-1} in the range of [MV^{2+}] = 0 - 10 mmol dm^{-3} by using τ_0 of 166 ns in aerated water. As can be seen from Fig. 1, however, the plot of I_0/I vs. [Q] is apparently concave upwards. Such a deviation from the expected linearity can be related to the fact that the fluorescence quenching of pyrene by MV^{2+} occurs along with remarkable absorption spectral changes as is shown in Fig. 2. Upon addition of MV^{2+}, the absorption bands of pyrene showed significant bathochromic shifts. The strongest band of pyrene in pure water locates at λ_{max} = 334 nm. However, it shifts regularly to longer wavelength with increasing concen-

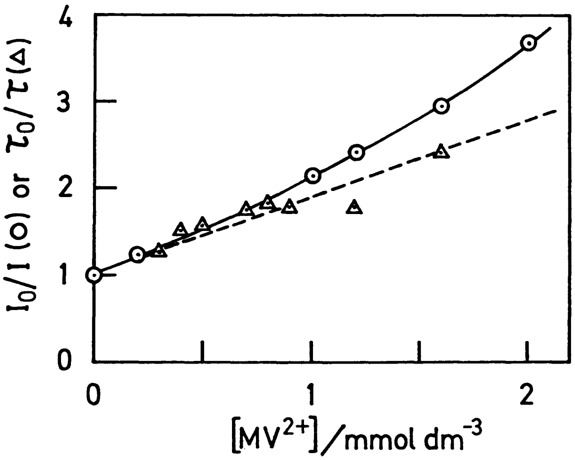

Fig. 1. Stern-Volmer plots for the fluorescence quenching of pyrene by MV^{2+}. o: I_0/I vs. [MV^{2+}]; Δ: τ_0/τ vs. [MV^{2+}]; solid line: calculated from Eq. 2 using parameters given in the text; dashed line: straight-line fit of lifetime data to Eq. 1.

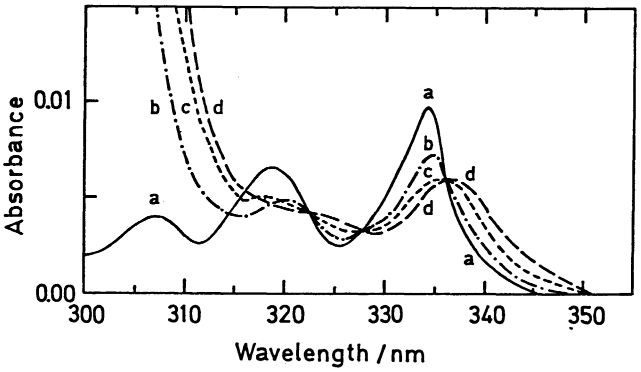

Fig. 2. Absorption spectra of pyrene-MV^{2+} system in aqueous solution. [MV^{2+}]: a) 0, b) 4, c) 9, d) 12 mmol dm^{-3}; [pyrene]: 3.25 X 10^{-7} mol dm^{-3}; path length: 1 cm.

tration of MV^{2+} and tends eventually to λ_{max} = 339 nm. Although the absorption spectra in the shorter wavelengths are disturbed by additional strong absorption due to MV^{2+} interacting with pyrene, several isosbestic points can be observed. This fact indicates the formation of a 1:1 complex between pyrene and MV^{2+} under our experimental conditions.

While the change of absorption spectrum was prominently observed (Fig. 2), the shape and position of fluorescence spectrum were scarecely altered by the addition of various amounts of MV^{2+}. The excitation spectrum of pyrene in the presence of MV^{2+} was consistent with the absorption spectrum of pyrene in pure water. Furthermore, no emission was observed upon excitation in the absorption region of the complex. These findings indicate that a ground-state nonfluorescent ("dark") complex between pyrene and MV^{2+} is formed in aqueous solution.

Taking these into account, the anomalous quenching of pyrene fluorescence by MV^{2+} can be elucidated by the following modified form of the Stern-Volmer equation:[10,11]

$$\frac{I_0}{I} = \frac{1 + k_q\tau_0[Q]}{1 - K[Q]} \tag{2}$$

where $K = \gamma(\varepsilon_c/\varepsilon_0)K_c$ and $K_c = [FQ]/[F][Q]$. Here, γ represents the efficiency of the dynamic quenching reaction, ε_c and ε_0 the molar extinction coefficients of the 1:1 dark complex, FQ, and the fluorophore (pyrene), F, respectively at the excitation wavelength, and K_c the association constant of FQ formed between F and Q in water. Equation 2 holds approximately only when $(\varepsilon_c/\varepsilon_0)K_c[Q] \ll 1$. One can rewrite Eq. 2 as:[11]

$$\frac{1 - (I/I_0)}{[Q]} = k_q\tau_0\frac{I}{I_0} + K \tag{3}$$

Application of Eq. 3 to the fluorescence-intensity data in lower concentration range of MV^{2+} gave in fact a linear relation. Thus, the values of k_q and K can be estimated to be 5.3×10^9 mol^{-1} dm^3 s^{-1} and 122 mol^{-1} dm^3, respectively. The fact that the value of k_q thus obtained is the same as that derived from the plot of τ_0/τ vs. [Q] strongly supports the validity of the dark complex model[10,12] proposed in this study. The I_0/I values calculated from Eq. 2 with the k_q and K described above are also included in Fig. 1 (a solid line). Agreement between calculated and observed I_0/I values is quite excellent.

In another experiments, we determined the association constant K_c and the value of $\varepsilon_c/\varepsilon_0$ at 337.1 nm from a Benesi-Hildebrand plot[13] in the range of $[MV^{2+}]$ = 4 - 15 mmol dm^{-3} using such absorption data as shown in Fig. 2. The values obtained were 71 mol^{-1} dm^3 and 1.8. Since $K = \gamma(\varepsilon_c/\varepsilon_0)K_c$, we can now estimate the collisional quenching efficiency γ of 0.95 which is close to an offen assumed value ($\gamma = 1$) for efficient quenchers.[11]

In view of the fact that the spectral data reveal the existence of the dark complex between pyrene and MV^{2+}, and Eqs. 2 and 3 fit the experimental data satisfactorily, it is reasonable to ascribe the observed anomalous quenching to the result of static quenching. MV^{2+} is known to form a CT complex with pyrene in methanol, with a characteristic broad absorption band (λ_{max} = 466 nm).[14] Under our experimental conditions, we have not detected any absorption in the near ultraviolet and visible regions except for that shown in Fig. 2. Furthermore, the absorption spectral change as shown in Fig. 2 was undetected in methanol solution, even when the CT absorption band appeared at 466 nm. It is of great interest that the absorption spectrum of the dark complex in water is distinctly different from that of the CT complex found in methanol. Studies on solvent and temperature effects as well as other viologens15) are now in progress in connection with the contribution of locally excited states of component molecules proposed for some electron-donor-acceptor complexes.16)

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