5180 J. Am. Chem. Soc. 1993, 115, 5180–5184

New Aspects on Fluorescence Quenching by Molecular Oxygen

Koichi Kikuchi,* Chika Sato, Masanori Watabe, Hiroshi Ikeda, Yasutake Takahashi, and Tsutomu Miyashi

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai 980, Japan

Received May 4, 1992

Abstract: Fluorescence quenching rate constants k_q by molecular oxygen $^3O_2(^3\Sigma_g^-)$ were measured for four anthracenecarbonitriles (AC) in acetonitrile and benzene and for five acridinium ions in acetonitrile. The k_q's for acridinium ions decrease with an increase in the free enthalpy change ΔG of full electron transfer from the first excited singlet fluorescer $^1M^*$ to $^3O_2$ in acetonitrile and become smaller than one-hundredth of the diffusion-controlled limit, k_{diff}. The k_q's for AC in acetonitrile decrease up to 5.3×10^9 M^{-1} s^{-1} with an increase in the number of cyano substituents or with an increase in ΔG in the range -0.53–$+0.25$ eV. The k_q's for AC in benzene, 3×10^9 M^{-1} s^{-1}, are only one-tenth of k_{diff}, except for 9-cyanoanthracene (CA) with 1.0×10^{10} M^{-1} s^{-1}. For both acridinium ions and AC, the energy of the second excited triplet state $^3M^*$ is much greater than that of $^1M^*$, so that $^3M^*$ cannot be produced by quenching. The energy gap ΔE between $^1M^*$ and the lowest excited triplet state ^3M is smaller than the energy 0.98 eV of singlet oxygen $^1O_2^*(^1\Delta_g)$ in the case of acridinium ions, but it is larger in the case of AC. On the basis of these results the fluorescence quenching mechanism by $^3O_2$ is discussed in detail.

Introduction

It is well-known that molecular oxygen $^3O_2(^3\Sigma_g^-)$ is an efficient fluorescence quencher. The quenching rate constants k_q have been measured for a number of aromatic molecules in fluid solutions.[1–6] The values for k_q were found to be at the diffusion-controlled limit, k_{diff} (e.g. 1.9×10^{10}–3.3×10^{10} M^{-1} s^{-1} in cyclohexane[4–6] and 2.7×10^{10}–4.3×10^{10} M^{-1} s^{-1} in acetonitrile[7]), except for a few aromatic molecules such as fluoranthenes (4.4×10^9–9.6×10^9 M^{-1} s^{-1} in cyclohexane[1,3,5,6]), *trans*-thioindigo,[7] 9,10-dicyanoanthracene (3.6×10^9 M^{-1} s^{-1} in cyclohexane,[8] 5.0×10^9 M^{-1} s^{-1} in benzene,[9] and 6.4×10^9–6.8×10^9 M^{-1} s^{-1} in acetonitrile[8,9]), and the other cyano meso-substituted anthracenes ($\sim 6 \times 10^9$ M^{-1} s^{-1} in cyclohexane[10]). The quenching by $^3O_2$ has been considered to occur through exciplex formation in the encounter complex $^3(^1M^*,^3O_2)$.[6,8,11–13] In the exciplex $^3(M,O_2)^*$, the charge-transfer (CT) state, i.e., the contact radical ion pair state $^3(^2M^{\bullet+},^2O_2^{\bullet-})$, is mixed with the locally excited (LE) state such as $^3(^1M^*,^3O_2)$, $^3(^3M^*,^3O_2)$, $^3(^3M,^3O_2)$, and $^3(^3M,^1O_2^*)$ when the energy of the LE state is close to the energy of $^3(^2M^{\bullet+},^2O_2^{\bullet-})$. Here $^1M^*$ is the first excited singlet state of the fluorescer molecule, ^3M and $^3M^*$ are the lowest and second excited triplet states, and $^1O_2^*$ is singlet oxygen, $^1O_2^*(^1\Delta_g)$. The CT from $^1M^*$ to $^3O_2$ has been supported by the fact that the k_q in the vapor phase decreases markedly with an increase in ionization potential of the fluorescer molecule when the ionization potential is higher than 9.0 eV.[14]

In a nonpolar solvent such as cyclohexane, the exciplex $^3(M,O_2)^*$ may deactivate to yield the following pairs: ^3M and $^3O_2$; ^3M and $^1O_2^*$ when the energy gap ΔE between $^1M^*$ and ^3M is greater than 0.98 eV (7882 cm^{-1}),[11] i.e., the energy of $^1O_2^*$; $^3M^*$ and $^3O_2$ when $^3M^*$ is located close to but below $^1M^*$. Indeed, the efficiency Φ_T of ^3M generation per one encounter of fluorescence quenching is close to unity in general,[13,15–20] while the efficiency of $^1O_2^*$ generation is less than unity.[6,8,20] Therefore, the quenching of $^1M^*$ by $^3O_2$ in nonpolar solvent is described by Scheme I, processes 1–3. It is noted that we cannot discriminate between processes 2 and 3 when $^3M^*$ is located below $^1M^*$, because the $^3M^*$–^3M internal conversion is too fast to detect $^3M^*$.

In a highly polar solvent such as acetonitrile, the exciplex may dissociate to yield the radical cation $^2M^{\bullet+}$ of the fluorescer molecule and the superoxide ion $^2O_2^{\bullet-}$: Process 4 may compete with processes 1–3. Then Φ_T is expected to become smaller than unity, as confirmed by Potashnik et al.[13] They also confirmed the generation of $^2M^{\bullet+}$ when they used pyrene as the fluorescer.[13]

In the steady-state approximation, the overall quenching rate constant k_q is given by eq I,[21,22]

$$k_q = \frac{k_{diff}}{1 + \dfrac{k_{-diff}}{k_{ass}} + \dfrac{k_{-diff}}{k_{ass}}\dfrac{k_{diss}}{\sum k_i}} \qquad (I)$$

where $\sum k_i = k_1 + k_2 + k_3 + k_4$.

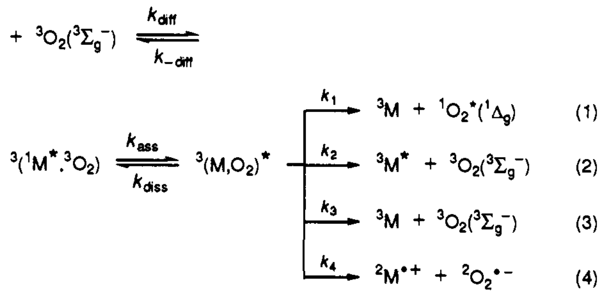
Recently we have studied the electron-transfer (ET) fluorescence quenching of anthracenecarbonitriles (AC) by aromatic

---

(1) Bowen, E. J. *Trans. Faraday Soc.* **1954**, *50*, 97–102.
(2) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455–458.
(3) Berlman, I. B.; Wirth, H. O.; Steingraber, O. J. *J. Am. Chem. Soc.* **1968**, *90*, 566–569.
(4) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612–614.
(5) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic: New York, 1971.
(6) Saltiel, J.; Atwater, A. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1988; Vol. 14, pp 1–38.
(7) Grellmann, K. H.; Hentzschel, P. *Chem. Phys. Lett.* **1978**, *53*, 545–550.
(8) Kristiansen, M.; Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 5190–5197.
(9) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 678–681.
(10) Schoof, S.; Gusten, H.; Sonntag, C. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 1068–1073.
(11) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; pp 492–517.
(12) Stevens, B.; Small, R. D., Jr. *Chem. Phys. Lett.* **1979**, *61*, 233–238.
(13) Potashnik, R.; Goldschmidt, C. R.; Ottolenghi, M. *Chem. Phys. Lett.* **1971**, *9*, 424–425.
(14) Brown, R. G.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 630–636.
(15) Richard, J. T.; West, J.; Thomas, J. K. *J. Phys. Chem.* **1970**, *74*, 4137–4141.
(16) Stevens, B.; Algar, B. E. *J. Phys. Chem.* **1969**, *73*, 1711–1715.
(17) Tibilov, S. S.; Vember, T. M.; Ermolaev, V. L.; Cherkasov, A. S. *Opt. Spectrosc.* (*Engl. Transl.*) **1975**, *39*, 362–364.
(18) Darmanyan, A. P. *Chem. Phys. Lett.* **1982**, *86*, 405–410.
(19) Kikuchi, K. *Chem. Phys. Lett.* **1991**, *183*, 103–106.
(20) Usui, Y.; Shimizu, N.; Mori, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 897–902.
(21) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834–839.
(22) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

0002-7863/93/1515-5180$04.00/0

Scheme I



molecules in acetonitrile[23-28] and found that the quenching mechanism depends on the free enthalpy change ΔG ($=E_{1/2}^{OX}-E_{1/2}^{RED}-E(^1M^*)$) of full ET in acetonitrile and the switchover of the quenching mechanism occurs at about $\Delta G = -0.4$ eV: Quenching is induced by exciplex formation when $\Delta G > -0.4$ eV, but by outer-sphere ET when $\Delta G < -0.4$ eV. Here $E_{1/2}^{OX}$ and E_2^{RED} are the oxidation potential of the electron donor and the reduction potential of the electron acceptor, respectively, $E(^1M^*)$ is the energy of $^1M^*$. In the case of fluorescence quenching by $^3O_2$, however, the switchover ΔG for the quenching mechanism has not been established. Potashnik et al. determined Φ_T for several aromatic molecules in acetonitrile.[13] The Φ_T values were greater than 0.5, although the ΔG values were more negative than -1.0 eV. Such high Φ_T values for electron donor and acceptor (EDA) systems with such highly negative ΔG values suggest that the quenching by $^3O_2$ is not induced by outer-sphere ET, but by exciplex formation. Indeed, the free radical yield of fluorescence quenching by $^3O_2$ is quite low in general.[13,15] In the case of the quenching by $^3O_2$, therefore, it is supposed that the quenching is induced by exciplex formation even when $\Delta G < -1.0$ eV.

For a full understanding of fluorescence quenching by $^3O_2$, it is essential to differentiate these four kinds of quenching processes and to evaluate their rate constants. For this purpose, in the present work, we studied the relation between k_q and ΔG in the range $\Delta G = -0.78$–$+0.46$ eV, using AC and acridinium ions as electron deficient fluorescers in acetonitrile.

Experimental Section

N-Methylacridinium tetrafluoroborate ($AcMe^+BF_4^-$) was synthesized by methylation of acridine with trimethyloxonium tetrafluoroborate. An analytically and spectroscopically pure sample was obtained by recrystallization from ethanol three times. 9,10-Dicyanoanthracene (DCA; Kodak) was purified with column chromatography followed by recrystallization from benzene and acetonitrile. Acridine (Ac), 9-aminoacridine (AmAc), 9-methylacridine (MeAc), 9-phenylacridine (PhAc), 9-cyanoanthracene (CA), 2,9,10-tricyanoanthracene (TrCA), and 2,6,9,10-tetracyanoanthracene (TeCA) were the same as used in previous work.[25,29,30] Trichloroacetic acid (S.P. grade, Nakarai), acetonitrile (S.P. grade, Nakarai), and benzene (S.P. grade, Dojin) were used as received. Acridinium ions except $AcMe^+$ were prepared by adding 0.1 M trichloroacetic acid into the acetonitrile solution containing one of the neutral acridines. The complete conversion of neutral acridines into acridinium ions was confirmed by the absorption and fluorescence spectra.

Fluorescence lifetimes at 298 K were measured by a time-correlated single photon counting method. Triplet-triplet (T-T) absorption spectra in the near infrared region were measured by a conventional flash apparatus with a Hamamatsu R1767 photomultiplier. Oxidation and reduction potentials versus SCE were measured in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

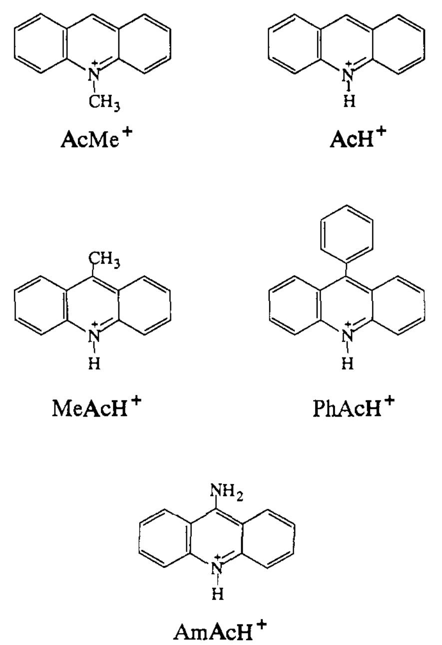


Figure 1. Acridinium ions.

Results and Discussion

Acridinium Ions. We have found that the fluorescence of acridinium ions is only slightly quenched by $^3O_2$ in acetonitrile. The structural formulas of acridinium ions employed are shown in Figure 1.

The fluorescence lifetimes τ of acridinium ions in deaerated (τ_0), aerated (τ_1), and oxygen-saturated solutions (τ_2) are listed in Table I. It is noted that the τ_0 for $PhAcH^+$ is much smaller than those for the other acridinium ions. In previous work[30] we found that the temperature-dependent internal conversion due to the sterically hindered rotation of the phenyl group participates in the deactivation of the excited singlet PhAc. The fluorescence yield for $PhAcH^+$ is the lowest among the acridinium ions (0.22 for $PhAcH^+$ and 0.66–0.96 for the other acridinium ions[29]), although the fluorescence radiative rate constant for $PhAcH^+$ is not the smallest (2.7×10^7 s^{-1} for $PhAcH^+$ and 1.9×10^7–5.3×10^7 s^{-1} for the other acridinium ions[29]). Therefore, such temperature-dependent internal conversion may be responsible for the exceptionally short lifetime ($\tau_0 = 8.1_2$ ns) of $PhAcH^+$ among acridinium ions.

Oxygen concentrations have been reported to be 1.7 and 8.1 mM in aerated and oxygen-saturated acetonitrile at 298 K, respectively.[31] The Stern–Volmer plot for τ is linear for every acridinium ion:

$$1/\tau = 1/\tau_0 + k_q[^3O_2] \qquad \text{(II)}$$

The k_q's were determined as listed in Table I. We find that the k_q's for $MeAcH^+$, AcH^+, $PhAcH^+$, and $AcMe^+$ are surprisingly small, less than one-hundredth of k_{diff}. It seems that such small values for k_q have not been reported previously. Next we consider the reason why the k_q's for these acridinium ions are so small.

Since the energy of $^1O_2^*$ is 0.98 eV,[11] the simultaneous generation of ^3M and $^1O_2^*$ by quenching is possible only when the energy gap ΔE between $^1M^*$ and ^3M is greater than 0.98 eV. $E(^1M^*)$'s for acridinium ions were determined in acetonitrile (containing 0.1 M trichloroacetic acid except for the solution of $AcMe^+$) as listed in Table I. The energies $E(^3M)$ of ^3M for

---

(23) Kikuchi, K.; Niwa, T.; Takahasi, Y.; Ikeda, H.; Miyashi, T.; Hoshi, M. *Chem. Phys. Lett.* **1990**, *173*, 421–424.

(24) Kikuchi, K.; Hoshi, M.; Niwa, T.; Takahashi, Y.; Miyashi, T. *J. Phys. Chem.* **1991**, *95*, 38–42.

(25) Kikuchi, K.; Takahashi, Y.; Hoshi, M.; Niwa, T.; Katagiri, T.; Miyashi, T. *J. Phys. Chem.* **1991**, *95*, 2378–2381.

(26) Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403–408.

(27) Kikuchi, K. *J. Photochem. Photobiol., A* **1992**, *65*, 149–156.

(28) Kikuchi, K.; Katagiri, T.; Niwa, T.; Takahashi, Y.; Suzuki, T.; Ikeda, H.; Miyashi, T. *Chem. Phys. Lett.* **1992**, *193*, 155–160.

(29) Kasama, K.; Kikuchi, K.; Nishida, Y.; Kokubun, H. *J. Phys. Chem.* **1981**, *85*, 4148–4153.

(30) Kikuchi, K.; Hattori, Y.; Sato, C.; Kokubun, H. *J. Phys. Chem.* **1990**, *94*, 4039–4042.

(31) Achord, J. M.; Hussey, C. L. *Anal. Chem.* **1980**, *52*, 601–602.

Table I. Fluorescence Lifetimes in Deaerated (τ_0), Aerated (τ_1), and Oxygen-Saturated (τ_2) Acetonitrile, Quenching Rate Constants k_q, Energies of the First Excited Singlet ($E(^1M^*)$), Lowest Excited Triplet ($E(^3M)$), and Second Excited Triplet ($E(^3M^*)$), and the Free Enthalpy Change ΔG of Full Electron Transfer from Fluorescer to $^3O_2$

fluorescer	τ_0 (ns)	τ_1 (ns)	τ_2 (ns)	k_q (M^{-1} s^{-1})	$E(^1M^*)$ (eV)	$E(^3M)$ (eV)	$E(^3M^*)$ (eV)	ΔG (eV)
$AmAcH^+$	15.8 ± 0.2	15.2 ± 0.2	12.3 ± 0.2	$(2.2 \pm 0.2) \times 10^9$	2.91	2.32	3.45	−0.78
$MeAcH^+$	28.0 ± 0.4	27.7 ± 0.3	26.8 ± 0.2	$(1.9 \pm 0.2) \times 10^8$	2.82	1.97	3.19	+0.27
AcH^+	29.7 ± 0.3	29.5 ± 0.1	28.8 ± 0.1	$(1.3 \pm 0.2) \times 10^8$	2.82	2.01	3.24	+0.37
$PhAcH^+$	$8.1_2 \pm 0.03$	$8.0_7 \pm 0.03$	$7.9_5 \pm 0.03$	$(3.5 \pm 1.2) \times 10^8$	2.73	1.91	3.13	+0.41
$AcMe^+$	33.1 ± 0.1	32.9 ± 0.1	32.3 ± 0.3	$(1.0 \pm 0.2) \times 10^8$	2.75	>1.79	>3.03	+0.46

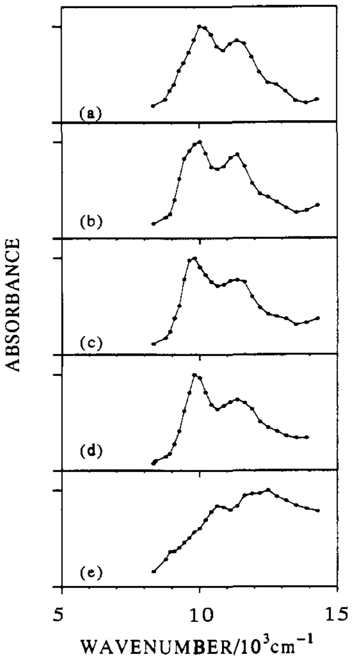


Figure 2. Triplet–triplet absorption spectra of acridinium ions in acetonitrile: (a) $AcMe^+$, (b) AcH^+, (c) $MeAcH^+$, (d) $PhAcH^+$, and (e) $AmAcH^+$.

$AmAcH^+$, AcH^+, and $MeAcH^+$ were already determined as listed in Table I.[29] The triplet state of 9-cyanoanthracene ($E(^3M)$ = 1.79 eV[23,26]) is not quenched by $AcMe^+$, and hence, $E(^3M)$ for $AcMe^+$ is greater than 1.79 eV. $E(^3M)$ for $PhAcH^+$ was determined to be 1.91 eV by applying the Förster cycle:[32] $E(^3M)$ for PhAc was already determined to be 1.88 eV.[30] The pK_a values for the triplet and the ground state for PhAc were determined to be 5.0 and 5.4, respectively. We find that ΔE is less than 0.98 eV for every acridinium ion. Therefore, process 1 cannot take place.

The T–T absorption of any acridinium ion is not observed by direct flash excitation, but by triplet–triplet energy transfer,[33,34] indicating null intersystem crossing (ISC). High fluroescence yield[29] and null triplet yield for acridinium ions indicate that both ISC transitions, $^1M^*$–^3M and $^1M^*$–$^3M^*$–^3M, are much slower than the radiative deactivation. The former ISC with large ΔE is slow according to the energy gap law.[29,35] The latter ISC is slow because of the higher location of $^3M^*$ than $^1M^*$. Figure 2 shows the T–T absorption spectra of acridinium ions in the near infrared region. The sharp bands at around 10 000 cm^{-1} are attributable to the 0–0 bands of the ^3M–$^3M^*$ transition except for $AmAcH^+$: 10 000 cm^{-1} for $AcMe^+$ and AcH^+; 9800 cm^{-1} for $MeAcH^+$ and $PhAcH^+$. The broad band at 10 600 cm^{-1} for $AmAcH^+$ is not considered to be the 0–0 band. The 0–0 band for $AmAcH^+$ is supposed to be located at the edge of T–T absorption, ca. 1500 cm^{-1} (energy of structural vibration) below the broad band. The energies $E(^3M^*)$ for $^3M^*$ are determined as listed in Table I. For every acridinium ion $E(^3M^*)$ is much greater than $E(^1M^*)$, and hence, process 2 cannot take place.

In the exciplex the fluorescer molecule may act as the electron donor and $^3O_2$ as the electron acceptor and vice versa. To form the exciplex the LE state and the contact radical ion pair (RP) state have to mix with each other. This requires a small energy gap $|\Delta G|$ between the LE state and the RP state. The energy of the LE state is equal to $E(^1M^*)$. First we consider the RP state consisting of an acridinium dication radical (e.g. $^2AcH^{\bullet++}$) and a superoxide ion ($^2O_2^{\bullet-}$). $E_{1/2}{}^{OX}$'s for acridinium ions were determined in acetonitrile: 2.27, 2.25, 2.15, 2.20, and 1.19 V versus SCE for $AcMe^+$, AcH^+, $MeAcH^+$, $PhAcH^+$, and $AmAcH^+$, respectively. $E_{1/2}{}^{RED}$ for $^3O_2$ was reported to be −0.94 V versus SCE in acetonitrile.[36] Using these values and $E(^1M^*)$'s ΔG can be calculated as listed in Table I. Since ΔG ranges from −0.78 to +0.46 eV, the exciplex may be formed without or with thermal activation.

Second we consider the alternative RP state consisting of an acridine semiquinone radical (e.g. $^2AcMe^{\bullet}$) and an oxygen radical cation ($^2O_2^{\bullet+}$). $E_{1/2}{}^{OX}$ for $^3O_2$ has been evaluated to be ca. 5.3 V versus SCE in acetonitrile.[37] $E_{1/2}{}^{RED}$ for $AcMe^+$ was determined to be −0.48 V versus SCE in acetonitrile. If $E_{1/2}{}^{RED}$ is not so different among acridinium ions, the energy for the RP state consisting of an acridinium semiquinone radical and $^2O_2^{\bullet+}$ is considered to be much greater than 5 eV. Then ΔG will be greater than 2 eV for every acridinium ion. Therefore, such an RP state cannot participate in exciplex formation.

Consequently, the quenching of acridinium ions can be induced by exciplex formation followed by processes 3 and 4. The rate k_{ass} of exciplex formation within the encounter complex may decrease with an increase in ΔG, particularly when exciplex formation is endothermic ($\Delta G > 0$ eV). Then, k_q is expected to decrease with an increase in ΔG. This is confirmed by the present results, if $PhAcH^+$ is not taken into account. The k_q for $PhAcH^+$ seems to be greater than those for $MeAcH^+$, AcH^+, and $AcMe^+$, although the experimental error involved in k_q is largest for $PhAcH^+$. Darmanyan[38] studied the fluorescence quenching of 9,10-diphenylanthracene by $^3O_2$ and found that the internal conversion due to sterically hindered rotation of the phenyl group is enhanced upon the quenching by $^3O_2$. Therefore, the exceptionally large value of k_q for $PhAcH^+$ may be attributed to such internal conversion. Since process 3 is exothermic while process 4 is endothermic in the case of $MeAcH^+$, AcH^+, and $AcMe^+$, the dominant quenching pathway of these acridinium ions is considered to be exciplex formation followed by process 3 alone. It is noteworthy that the rate of quenching due to exciplex formation followed by process 3 is less than one-hundredth of k_{diff} when $\Delta G \geq +0.27$ eV.

The ΔG for $AmAcH^+$ is negative enough to produce the exciplex with the diffusion-controlled limit:[23] $k_{ass} \gg k_{-diff}$. Nevertheless, k_q for $AmAcH^+$ is only one-tenth of k_{diff}. Therefore, processes 3 and 4 are not so rapid as to give the diffusion-controlled

---

(32) Förster, Th. *Z. Elektrochem. Ber. Bunsen-Ges. Phys. Chem.* **1950**, *54*, 531–535.

(33) Nishida, Y.; Kikuchi, K.; Kokubun, H. *J. Photochem.* **1980**, *13*, 75–81.

(34) Kikuchi, K. *Triplet–Triplet Absorption Spectra*; Bunshin: Tokyo, 1989; pp 21, 32.

(35) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; pp 153–237.

(36) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083–6088.

(37) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1986**, *108*, 6063–6065.

(38) Darmanyan, A. P. *Chem. Phys. Lett.* **1982**, *91*, 396–400.

Table II. Fluorescence Lifetimes in Deaerated (τ_0), Aerated (τ_1), and Oxygen-Saturated (τ_2) Acetonitrile, Quenching Rate Constants k_q, Energies of the First Excited Singlet ($E(^1M^*)$), Lowest Excited Triplet ($E(^3M)$), and Second Excited Triplet ($E(^3M^*)$), and the Free Enthalpy Change ΔG of Full Electron Transfer from Fluorescer to $^3O_2$

fluorescer	τ_0 (ns)	τ_1 (ns)	τ_2 (ns)	k_q (M^{-1} s^{-1})	$E(^1M^*)$ (eV)	$E(^3M)$ (eV)	$E(^3M^*)$ (eV)	ΔG (eV)
CA	17.1 ± 0.2	11.5 ± 0.3	5.7 ± 0.02	$(1.6 \pm 0.2) \times 10^{10}$	3.04	1.79	3.24	−0.53
DCA	16.5 ± 0.1	12.7 ± 0.1	8.3 ± 0.2	$(1.0 \pm 0.1) \times 10^{10}$	2.89	1.65	3.19	−0.06
TrCA	17.7 ± 0.2	14.8 ± 0.4	8.4 ± 0.1	$(7.0 \pm 0.4) \times 10^{9}$	2.89	1.64	3.10	+0.09
TeCA	17.7 ± 0.2	15.1 ± 0.4	10.4 ± 0.2	$(5.3 \pm 0.4) \times 10^{9}$	2.89	1.64	3.10	+0.25

quenching: $k_3 + k_4 \ll k_{diss}$. The participation of processs 1 and/or 2 in the quenching is the prerequisite for the diffusion-controlled quenching even when the exciplex is formed at the diffusion-controlled limit.

Anthracenecarbonitriles. The values of τ for AC in acetonitrile are listed in Table II. The Stern–Volmer plot for τ is linear in the case of CA, TrCA, and TeCA. The k_q's for CA, TrCA, and TeCA are listed in Table II. In the case of DCA the Stern–Volmer plot is linear up to the oxygen concentration of ca. 2 mM. At oxygen concentrations above 2 mM, however, the plot deviates downward from the straight line. The deviation increases with increasing oxygen concentration. Such deviation is evidence for exciplex formation. Then k_q is determined from the Stern–Volmer plot at oxygen concentrations below 2 mM, where the steady-state approximation may be still valid. The k_q thus obtained, 1.0×10^{-1} s^{-1}, is somewhat larger than that reported previously.[8,9] We find that the k_q's decrease with an increase in the number of cyano substituents.

Both $E(^1M^*)$ and $E(^3M)$ for AC have already been determined as listed in Table II.[25,28] Since ΔE is greater than 0.98 eV for every AC, the simultaneous generation of ^3M and $^1O_2^*$ is energetically possible in the quenching, and hence, process 1 can take place.

The 0–0 bands of ^3M–$^3M^*$ transitions for AC are located in the near infrared region:[34] 805 nm for DCA; 850 nm for CA, TrCA, and TeCA. $E(^3M^*)$'s for AC were determined as listed in Table II. Since $E(^3M^*)$ is much greater than $E(^1M^*)$ for every AC, process 2 cannot take place.

$E_{1/2}^{OX}$'s for AC were determined in acetonitrile as follows: 1.57 V for CA; 1.89 V for DCA; 2.04 V for TrCA; 2.20 V for TeCA. The ΔG's for producing an AC radical cation and the superoxide ion $^2O_2^{\bullet -}$ were calculated as listed in Table II. We find that k_q decreases with an increase in ΔG, indicating the participation of the CT from AC to $^3O_2$ in the quenching.

It is informative to compare the k_q for TeCA with those for AcH$^+$ and MeAcH$^+$, because the ΔG's for these compounds are close to one another. The k_q for TeCA is 1 order of magnitude greater than those for these acridinium ions. The quenching of these acridinium ions is considered to occur only through endothermic exciplex formation followed by process 3 alone. In the case of TeCA, in contrast, processes 1 and 3 can take place. Therefore, the participation of process 1 in exciplex deactivation is responsible for the greater value of k_q for TeCA than for these acridinium ions.

The quenching of CA in acetonitrile may be induced by highly exothermic exciplex formation: $k_{ass} \gg k_{-diff}$. Although exciplex formation is followed by process 1 in addition to processes 3 and 4, the k_q is slightly smaller than k_{diff}: $k_q \approx (1/2)k_{diff}$. This means that $k_{diss}/(k_1 + k_3 + k_4) \approx k_{ass}/k_{-diff} \gg 1$. It is suggested, therefore, that the participation of process 2 in exciplex deactivation is necessary for the diffusion-controlled quenching even when exciplex is formed at the diffusion-controlled limit.

Table III. Fluorescence Lifetimes in Deaerated (τ_0), Aerated (τ_1), and Oxygen-Saturated (τ_2) Benzene, Quenching Rate Constants k_q, and the Free Enthalpy Change ΔG of Full Electron Transfer from Fluorescer to $^3O_2$ in Benzene

fluorescer	τ_0 (ns)	τ_1 (ns)	τ_2 (ns)	k_q (M^{-1} s^{-1})	ΔG (eV)
CA	12.6 ± 0.1	10.0 ± 0.2	5.7 ± 0.1	$(1.1 \pm 0.1) \times 10^{10}$	+0.32
DCA	12.5 ± 0.3	11.6 ± 0.3	9.3 ± 0.3	$(3.0 \pm 0.2) \times 10^{9}$	+0.64
TrCA	14.5 ± 0.2	13.4 ± 0.3	10.0 ± 0.1	$(3.2 \pm 0.3) \times 10^{9}$	+0.79
TeCA	13.4 ± 0.1	12.5 ± 0.2	9.4 ± 0.3	$(3.2 \pm 0.3) \times 10^{9}$	+0.95

The RP state is greatly destabilized in nonpolar solvent. To study the quenching mechanism of AC in a highly positive region of ΔG, we measured τ in benzene. The Stern–Volmer plot for τ is linear for every AC. The values for τ and k_q are listed in Table III. In the calculation of k_q the oxygen concentrations of 1.91 and 9.18 mM at 298 K were used for the aerated and the oxygen-saturated benzene solutions.[39] The ΔG's for CA, DCA, TrCA, and TeCA in benzene are evaluated by the Born equation[40,41] as listed in Table III. The k_q for CA is greater than those for the other AC, but it is only slightly smaller than that in acetonitrile. The quenching of CA in benzene may be induced by exciplex formation followed by processes 1 and 3, because the ΔG is more negative than +0.4 eV. It is quite interesting that the k_q's for DCA, TrCA, and TeCA are nearly constant, only one-tenth of k_{diff}. One may suppose that the k_q of 3×10^9 M^{-1} s^{-1} is the rate constant of exciplex formation followed by processes 1 and 3. However, the quenching of these AC is not considered to be induced by exciplex formation. If the quenching is induced by exciplex formation, k_{ass} is expected to decrease extremely with increasing ΔG in such a highly positive region of ΔG as ΔG = +0.64–+0.95 eV. Therefore, the exchange energy transfer in the encounter complex $^3(^1M^*,^3O_2)$ is considered to be more plausible as the quenching mechanism for AC in benzene, excluding CA:

Scheme II

$$^1M^* + {}^3O_2(^3\Sigma_g^-) \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftharpoons}} {}^3(^1M^*,{}^3O_2) \xrightarrow{k_1'} {}^3M + {}^1O_2^*(^1\Delta_g) \qquad (1')$$

(when $\Delta G > 0.4$ eV and $\Delta E \geq 0.98$ eV)

The rate constant k_1' of exchange energy transfer does not depend on ΔG, but on the difference in the excitation energy between energy donor and acceptor.[42] As the variation in both $E(^1M^*)$ and $E(^3M)$ is quite small among DCA, TrCA, and TeCA, k_1' is considered to be nearly the same among these AC. The rate constant k_{-diff} for diffusional separation of the encounter complex into the precursor molecules is not so different among AC. Therefore, $k_q = k_{diff}k_1'/(k_{-diff} + k_1')$ is expected to be nearly constant in agreement with the experimental results. The quenching rate constant, 3×10^9 M^{-1} s^{-1}, is regarded as the rate constant of direct exchange energy transfer: $k_1' \approx (1/10)k_{-diff}$. This is consistent with the previous results reported for DCA that the k_q in cyclohexane is the same as that in benzene and the overall quantum yield $\Phi(^1O_2^*)$ for $^1O_2^*$ generation is 2.0 in cyclohexane[8,20] (the quenching of ^3M by $^3O_2$ generates $^1O_2^*$), although the $\Phi(^1O_2^*)$ in benzene, 1.66 ± 0.35[43]–1.86 ± 0.12,[9]

---

(39) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973; p 89.

(40) Born, M. *Z. Phys.* **1920**, *1*, 45–48.

(41) Weller, A. *Z. Phys. Chem., Neue Folge* **1982**, *133*, 93–98.

(42) Sandros, K. *Acta Chem. Scand. (1947–1973)* **1964**, *18*, 2355–2374.

(43) Dobrowolski, D. C.; Ogilby, P. R.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 2261–2263.

might be slightly less than 2.0. It is interesting that the direct exchange energy transfer does not occur at the diffusion-controlled limit, although it is exothermic and multiplicity-allowed, and that its rate constant is very close to the rate constant of triplet quenching by $^3O_2$.[6]

On the basis of the ΔG dependence of k_q for acridinium ions we have neglected the following quenching pathway in Scheme II.

$$^1M^* + {}^3O_2(^3\Sigma_g^-) \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftharpoons}} {}^3(^1M^*,{}^3O_2) \xrightarrow{k_{3'}} {}^3M + {}^3O_2(^3\Sigma_g^-) \quad (3')$$

$$(\text{when } \Delta G > 0.4 \text{ eV})$$

In the encounter complex, processes 1′ and 3′ may compete with exciplex formation. The rate of exciplex formation decreases extremely with increasing ΔG in the highly positive region of ΔG, while processes 1′ and 3′ do not depend on ΔG. As a result, the contribution of processes 1′ and 3′ to the quenching becomes significant in the highly positive region of ΔG. In the case of $AcMe^+$ with $\Delta G = +0.46$ eV the k_q is 1.0×10^8 M^{-1} s^{-1} and process 1′ cannot take place. Therefore, the rate of quenching induced by process 3′ is 1.0×10^8 M^{-1} s^{-1} at most: $k_q = 1.0 \times 10^8$ M^{-1} s^{-1} $> k_{diff}k_{3'}/(k_{-diff} + k_{3'})$. Assuming $k_{diff} = 3 \times 10^{10}$ M^{-1} s^{-1} in acetonitrile, we obtain $k_{3'} < (1/300)k_{-diff}$. Since $k_{1'} \approx (1/10)k_{-diff}$ in benzene, $k_{3'}$ is smaller than $(1/10)k_{1'}$, although k_{-diff} is 2 or 3 times greater in acetonitrile than in benzene.

Summary

Based on the present work three prerequisites for the diffusion-controlled fluorescence quenching by $^3O_2$ can be deduced: (i) exothermic exciplex formation, $\Delta G < 0$ eV; (ii) the $^1M^*$–^3M energy gap greater than 0.98 eV, $\Delta E > 0.98$ eV; and (iii) the location of $^3M^*$ close to but below $^1M^*$, $E(^1M^*) \geq E(^3M^*)$.

(I) When none of these prerequisites is satisfied, k_q is much smaller than k_{diff}. This is the case with acridinium ions except $AmAcH^+$: $k_q < (1/100)k_{diff}$. (II) When only the first prerequisite is satisfied, k_q is smaller than k_{diff}. This is the case with $AmAcH^+$: $k_q \approx (1/10)k_{diff}$. (III) When only the second is satisfied, k_q is smaller than k_{diff}. This is the case with TrCA and TeCA in acetonitrile and AC in benzene: $k_q = (1/3)k_{diff}$–$(1/8)k_{diff}$. (IV) When the first and the second are satisfied, k_q is slightly smaller than k_{diff}. This is the case with CA and DCA in acetonitrile: $k_q < k_{diff}$. (V) When all the prerequisites are satisfied, k_q is close to k_{diff}. This is the case with many aromatic hydrocarbons.

A number of aromatic hydrocarbons satisfy the first prerequisite even in a nonpolar solvent such as cyclohexane, because the ΔG's in cyclohexane are evaluated to be more negative than −0.1 eV. The second and/or third are also satisfied by many aromatic hydrocarbons, because the location of $^3M^*$ close to but below $^1M^*$ and the large energy gap between $^1M^*$ and ^3M are the general features of aromatic hydrocarbons. Therefore, the k_q's for many aromatic hydrocarbons are expected to be close to k_{diff} in accordance with experimental observations.[1,3,5,6] In the case of fluoranthene the ΔG is calculated to be +0.38 eV in cyclohexane: $E(^1M^*) = 3.05$ eV, $E_{1/2}^{OX} = 1.64$ V versus SCE in acetonitrile. The ΔE is calculated to be 0.76 eV using $E(^3M) = 2.29$ eV.[19] Since the first and the second prerequisites are not satisfied, the k_q is expected to be smaller than k_{diff} in agreement with the observation, $k_q = 4.4 \times 10^9$ M^{-1} s^{-1} in cyclohexane.[3,5,6]

Acknowledgment. We are greatly indebted to Professor H. Kokubun for valuable comments and to Dr. A. Umehara of Fuji Photofilm Co. for supplying 9-phenylacridine.