Deactivation Mechanism of Excited Acridine and 9-Substituted Acridines in Water

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The deactivation processes of excited acridine, deuterated acridine, and 9-substituted acridines (9-methyl, 9-propyl, 9-chloro, and 9-amino) have been investigated in alkaline and acidic water. The photoreaction does not occur with the irradiation of 365-nm light. In acidic water the fluorescence lifetime τ depends only slightly on the temperature and the lowest triplet yield Φ_{ST} is negligibly low for all of the acridines. In alkaline water τ decreases and Φ_{ST} increases with increasing temperature; the intersystem crossing occurs through both temperature-dependent and temperature-independent processes. For all of the acridines except for 9-aminoacridine, the temperature-dependent process was attributed to the $S_1(\pi,\pi^*) \rightleftharpoons (+\Delta E)\ S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition and the temperature-independent process mostly to the $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ transition. The fact that the frequency factor of the temperature-dependent process increases with decreasing the energy gap between $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$ was interpreted by the vibronic interaction between these states. In the case of 9-aminoacridine, the temperature dependence of τ was tentatively attributed to the $S_1(\pi,\pi^*) \rightarrow (+\Delta E)\ T_2(n,\pi^*)$ transition, because the energy level of $T_2(n,\pi^*)$ was considered to be higher than that of $S_1(\pi,\pi^*)$ in contrast to the other acridines.

Introduction

It is well-known that the electronic relaxation of acridine (A-h_9) depends on the nature of the solvent; the lifetime τ of the lowest excited singlet state S_1 is 10.3 ns in water and 0.72 ns in ethanol at 298 K[1] and 12.5 ps in isooctane[2] and 33.3 ps in n-hexane[3] at room temperature. Such solvent dependence of τ was interpreted in terms of the hydrogen bond interaction which causes an interchange of the electronic character in S_1: π,π^* character in protic solvents and n,π^* character in aprotic solvents.[1-4] However, the fluorescence has been observed even in aprotic solvents such as ether–isopentane[5] and n-octane[6] at 77 K, and we recently observed the fluorescence in benzene at 296 K.[7] These results indicate that the nature of S_1 is of π,π^* character in all solvents.

In previous works, we investigated the deactivation mechanism of A-h_9 in poly(vinyl alcohol) film (PVA)[8] and nonreactive solvents such as water and benzene.[7] In PVA and alkaline water τ decreases and the lowest triplet yield Φ_{ST} increases with increasing temperature. In benzene Φ_{ST} is unity in the range of 278–336 K. It was concluded that (i) in PVA the energy level of $T_3(\pi,\pi^*)$ is 420–540 cm^{-1} higher than that of $S_1(\pi,\pi^*)$ and the temperature-dependent intersystem crossing occurs through the $S_1(\pi,\pi^*) \rightarrow (+\Delta E)\ T_3(\pi,\pi^*)$ transition, (ii) in water the observed activation energy is larger than the energy gap between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$ (1700–1900 cm^{-1}), so that the temperature-dependent intersystem crossing occurs through the $S_1(\pi,\pi^*) \rightleftharpoons (+\Delta E)\ S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition, and (iii) in benzene the energy levels of $S_1(\pi,\pi^*)$, $S_2(n,\pi^*)$, and $T_3(\pi,\pi^*)$ are located close to one another and the intersystem crossing occurs effectively through the latter transition without thermal activation. The deactivation mechanism of excited acridine is strongly affected by the relative positions of the energy levels of $S_1(\pi,\pi^*)$, $S_2(n,\pi^*)$, and $T_3(\pi,\pi^*)$ which depend on the nature of solvent. The energy levels are also changed with the introduction of a substituent to the parent molecule: in general a conjugative substituent causes a small-to-moderate blue shift for $n-\pi^*$ transition and a large red shift for $\pi-\pi^*$ transition, while an inductive substituent causes the reverse. In the present work we studied the substituent effect on the deactivation of excited acridine and acridinium ion in order to elucidate the deactivation mechanism.

Experimental Section

Materials. Acridine (C.P. grade, Tokyo Kasei) was recrystallized from an ethanol–water mixture after pretreatment with activated charocal in ethanol. Deuterated acridine (A-d_9) (Merck Sharp and Dohme) was purified by vacuum sublimation. 9-Chloroacridine (9-CA) was synthesized and purified according to the method of Albert and Ritchie[9] and further purified by vacuum sublimation immediately before the experiment. 9-Aminoacridine (9-AA) was precipitated by neutralizing 9-aminoacridine hydrochloride (G.R. grade, Nakarai Kagaku) solution and purified by the method of thin-layer chromatography.

9-Methylacridine (9-MA) was prepared from a mixture of diphenylamine and glacial acetic acid in the presence of anhydrous zinc chloride according to the procedure of Bernthsen.[10] 9-Propylacridine (9-PA) was prepared from a mixture of diphenylamine and n-butyric acid in a manner similar to that for 9-MA.[11] G.R. grade ethanol and methanol (Wako Junyaku) were used without further purification. Water was distilled twice.

Apparatus and Procedure. The absorption spectrum was recorded on a Hitachi EPS-3T spectrophotometer. The fluorescence spectrum was measured with a modified Hitachi EPU spectrophotometer the spectral response of which was calibrated in units of relative quanta per wavenumber using quinine sulfate in 1.0 N sulfuric acid, 4-(dimethylamino)-4′-nitrostilbene in o-dichlorobenzene,[12]

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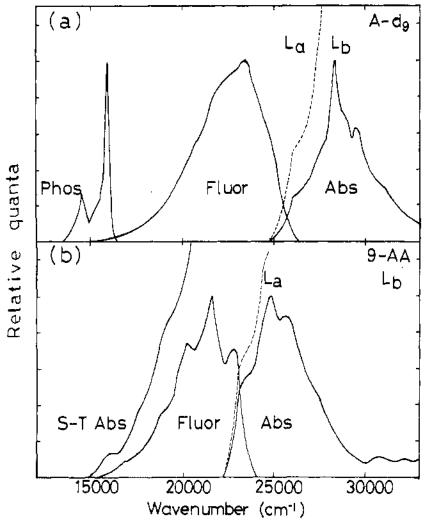

Figure 1. (a) Absorption, fluorescence, and phosphorescence spectra of A-d_9. (b) Absorption, fluorescence, and $S_0 \rightarrow T_1$ absorption spectra of 9-AA.

and 2-aminopyridine in 1.0 N sulfuric acid.[13] The phosphorescence spectrum was measured with a photon counter NF RC-545A, an HTV-R649 photomultiplier, and an Ushio USH-102D high-pressure mercury lamp as an exciting light source. The T–T absorption spectrum in the visible region was measured with an ordinary flash apparatus. The T–T absorption spectrum in the near-infrared region was measured with a HTV R-406 photomultiplier and an Ushio J6B-24-300W halogen lamp as a monitoring light source. Either a Hoya U-2 filter or a Toshiba UVP filter was used for the excitation. When τ was longer than 8 ns, it was measured with an RCA 1P 28 photomultiplier and a Tektronix 7904-7S14 sampling oscilloscope and an N_2 laser (fwhm, 7 ns) as an exciting light source. When τ was shorter than 10 ns, it was measured with a phase fluorometer modulated at 10.7 MHz. The fluorescence yield Φ_F was determined by using quinine sulfate in 1.0 N sulfuric acid ($\Phi_F = 0.546$ at 298 K[14]) as a standard solution. The pH of the sample solution at 296 K was adjusted to be 12.7 for the alkaline solution or 1.2 for the acidic solution by the addition of NaOH or H_2SO_4. Sample solutions were degassed by freeze–pump–thaw cycles.

Results and Discussion

(1) Energy Levels of $S_1(\pi,\pi^*)$, $S_3(\pi,\pi^*)$, $T_1(\pi,\pi^*)$, and $T_3(\pi,\pi^*)$ of Acridines. Figure 1 shows the absorption and fluorescence spectra of A-d_9 and 9-AA in alkaline water at 296 K, together with the phosphorescence spectrum of A-d_9 in a 1:1 ethanol–methanol mixture at 77 K and the S_0–T_1 absorption spectrum of 9-AA in ethanol at 296 K. The energy level of $S_1(\pi,\pi^*)$ is evaluated from the mirror-image relation of the absorption and fluorescence spectra with an error limit of ±100 cm^{-1}. The extent of the red shift of the $S_1(\pi,\pi^*)$ band parallels the conjugative effect of the substituent: 9-AA > 9-CA > 9-PA, 9-MA > A-h_9, A-d_9. As the energy of $S_3(\pi,\pi^*)$ we adopted the position of the maximum of the ^1L_b band. The energy levels of $T_1(\pi,\pi^*)$ of acridines except for 9-AA are evaluated from the 0–0 band of phosphorescence. Since the phosphorescence of 9-AA was not observed, the energy level of $T_1(\pi,\pi^*)$ was evaluated from the 0–0 band of the oxygen-enhanced S_0–T_1 absorption in ethanol at 296 K: 16 100 cm^{-1}.[15]

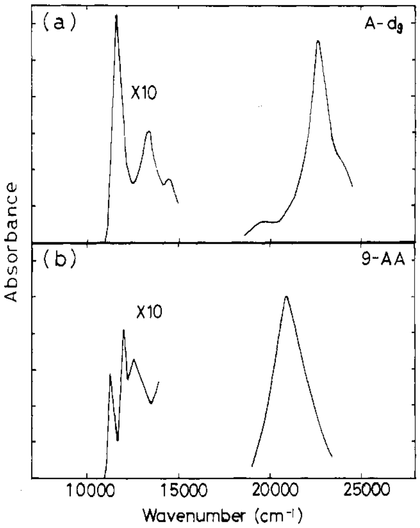

Figure 2. Triplet–triplet absorption spectra of (a) A-d_9 and (b) 9-AA.

Figure 2 shows the T–T absorption spectra of A-d_9 and 9-AA in alkaline water. The T–T absorption spectrum of 9-AA was measured with the triplet energy transfer method using 1,5-naphthalenedisulfuric acid as a sensitizer, because it was hard to observe by the direct excitation. The peak at the lowest wavenumber of the T–T absorption in the near-infrared region is assigned to the 0–0 band of the $T_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition, because no transient absorption is observed below. The energy level of $T_3(\pi,\pi^*)$ is estimated from the phosphorescence or the S_0–T_1 absorption spectrum and the T_1–T_3 absorption spectrum, assuming that the energy level of $T_1(\pi,\pi^*)$ is not much changed from solvent to solvent (e.g., the $T_1(\pi,\pi^*)$ level of A-h_9 is 15 840 cm^{-1} in chloroform[16] and 15 870 cm^{-1} in a 1:1 ethanol–methanol mixture and in a 4:1 methylcyclohexane–n-pentane mixture[7]). The energy levels of $S_1(\pi,\pi^*)$, $S_3(\pi,\pi^*)$, $T_1(\pi,\pi^*)$, and $T_3(\pi,\pi^*)$ are shown in Figure 3.

(2) τ, Φ_F, and the Radiative Transition Probability k_f of Acridines. Table I shows τ, Φ_F, and k_f of acridines in alkaline water at 298 K. The values of τ and Φ_F are larger in the order of 9-CA < 9-MA < 9-PA < 9-AA. It is noted that the values of τ, Φ_F, and k_f of A-d_9 are the same as those of A-h_9.

(3) Temperature Dependences of τ and the Relative Triplet Yield of Acridines. Figure 4 shows the temperature dependence of $1/\tau$. For all of the acridines, $1/\tau$ increases with increasing temperature and the slope is steeper in the order of 9-AA < A-h_9, A-d_9 < 9-CA < 9-PA < 9-MA. It is noticed that the plots of A-h_9 and A-d_9 intersect at room temperature.

Figure 5 shows the temperature dependence of the absorbance D of the T–T absorption immediately after flashing. Figure 6 shows the temperature dependence of D/τ. D/τ is associated with the rate of the intersystem crossing (see section 4). Both $1/\tau$ and D/τ decreases with decreasing temperature and approach the constant values $1/\tau_0$ and D_0/τ_0 at low temperature. When $1/\tau_0$ and D_0/τ_0 are subtracted from $1/\tau$ and D/τ, respectively, the resulting Arrhenius plots are linear as shown in Figure 7 and their slopes are nearly the same. Therefore, the temperature dependence of τ is entirely interpreted by the temperature dependence of the intersystem crossing except for 9-AA. In the case of 9-AA, it is not certain whether

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TABLE I: Physical Constants Related to the Deactivation of Excited Acridines in Water (pH 12.7) at 296 K

	A-h_9	A-d_9	9-CA	9-MA	9-PA	9-AA
ϕ_F	0.33	0.31	0.26	0.38	0.43	0.81
τ, ns	11.1	11.5	6.5	9.5	10.4	15.4
τ_0, ns	20.0	30.3	21.7	22.7	21.7	18.2
$10^{-7}k_f$, s^{-1}	3.0	2.7	4.0	4.0	4.1	5.3
$10^{-7}(k_d + k_1 + k_2)$, s^{-1}	2.0	0.6	0.6	0.4	0.5	$k_d + k_1 = 0.2$
$10^{-12}A$ ($=k_4$), s^{-1}	0.50	0.61	3.9	72	38	$k_2 = 0.08$
ΔE, cm^{-1}	1900	1900	2170	2880	2780	1830
$\Delta E(T_3-S_1)$, cm^{-1}	1760-1990	1820-2020	2180-2280	2310-2410	2250-2350	4360
$\Delta E(S_3-S_2)$, cm^{-1}	≈770	≈770	≈720	250~350	350~450	

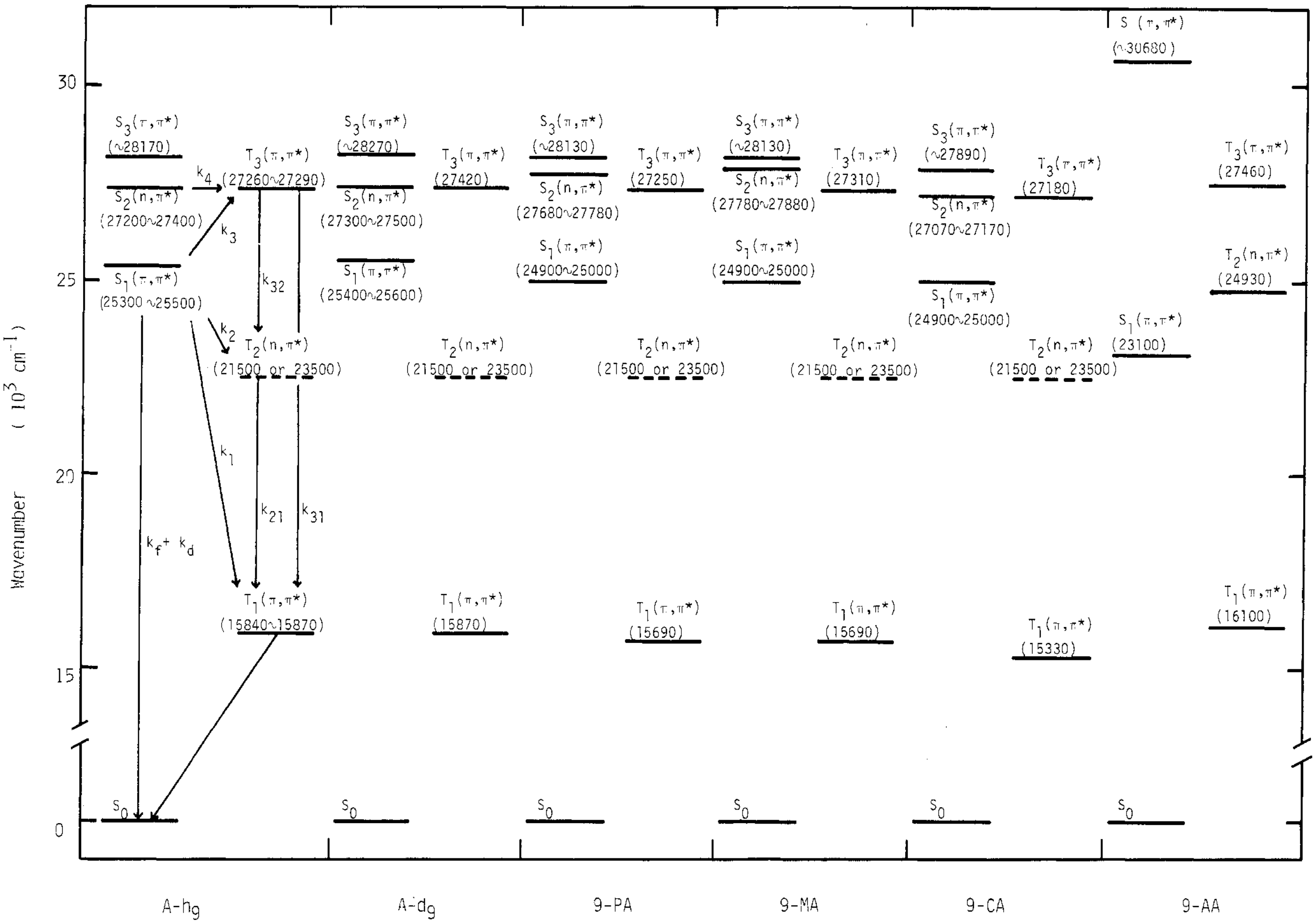

Figure 3. Energy-level diagrams of acridines.

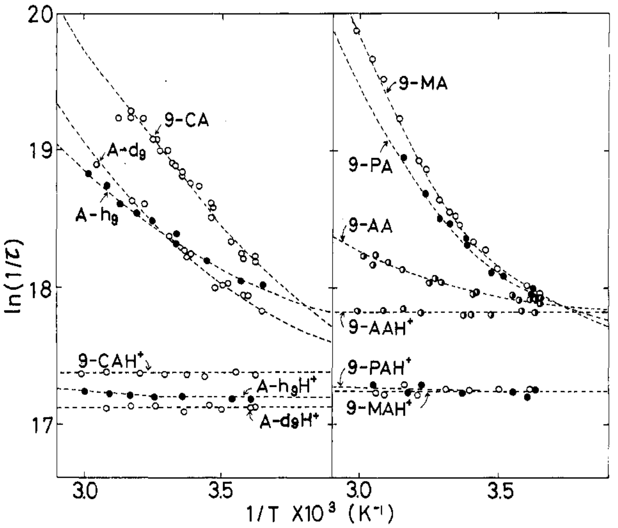

Figure 4. Temperature dependences of fluorescence lifetimes of acridines and acridinium ions.

or not the temperature dependence of τ is associated with that of the intersystem crossing, because it is hard to observe the T–T absorption by the direct excitation. The frequency factor A and the apparent activation energy ΔE obtained from the intercept and the slope of the Arrhenius plots together with τ_0 are listed in Table I.

(*4*) *Deactivation Mechanism of Acridines Other Than 9-AA.* The values of A listed in Table I are much larger than the frequency factor of a temperature-dependent intersystem crossing process in aromatic hydrocarbons which is in the range of 10^6–10^9 s^{-1}.[17] Therefore, the temperature-dependent intersystem crossing of acridines is not attributed to the $S_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. According to the spin–orbit coupling selection rule of El-Sayed,[18] the $^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ and $^1(\pi,\pi^*) \rightarrow {}^3(n,\pi^*)$ transitions are much faster than the $^1(\pi,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ and $^1(n,\pi^*) \rightarrow {}^3(n,\pi^*)$ transitions. The energy differences be-

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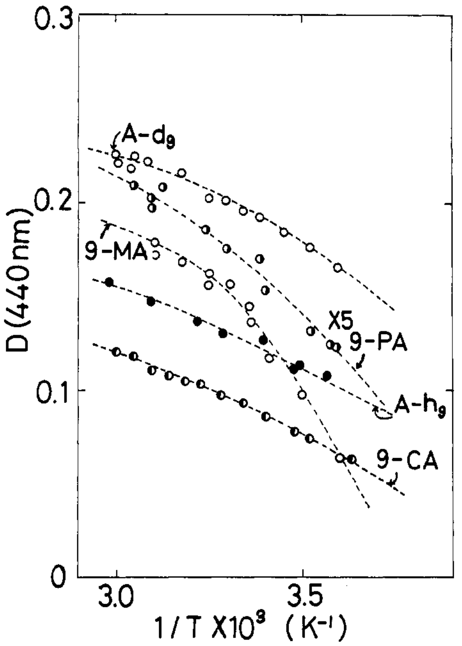

Figure 5. Temperature dependences of relative triplet yields of acridines.

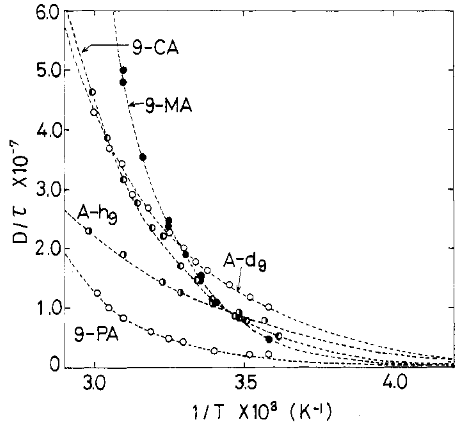

Figure 6. Plots of D/τ vs. $1/T$ for acridines.

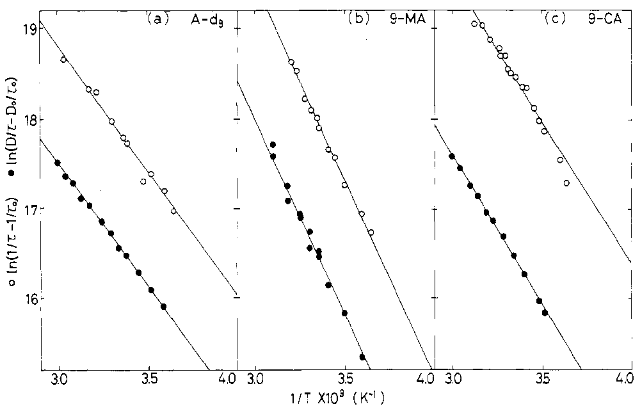

Figure 7. Plots of (○) $\ln(1/\tau - 1/\tau_0)$ vs. $1/T$ and (●) $\ln(D/\tau - D_0/\tau_0)$ vs. $1/T$ for (a) A-d_9, (b) 9-MA, and (c) 9-CA.

tween $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$, $\Delta E(T_3-S_1)$, of acridines are close to their activation energies ΔE. Therefore, the most probable temperature-dependent intersystem crossing is the $S_1(\pi,\pi^*) \rightleftharpoons S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. As the energies of $T_2(n,\pi^*)$ of acridines, we assumed 21 500 or 23 500 cm^{-1}, which were calculated for A-h_9 by Goodman and Harrell.[19]

The energy diagrams and possible deactivation processes of acridines are shown in Figure 3. According to this mechanism, $1/\tau$ and Φ_{ST} are expressed as follows:

$$1/\tau = k_f + k_d + k_1 + k_2 + k_3 \exp(-\Delta E_3/RT) + k_4 \exp(-\Delta E_4/RT) \quad (1)$$

$$\Phi_{ST} = [k_1 + k_2 + k_3 \exp(-\Delta E_3/RT) + k_4 \exp(-\Delta E_4/RT)]\tau \quad (2)$$

where k_d is the rate constant of the internal conversion from $S_1(\pi,\pi^*)$, ΔE_3 is the energy gap between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$, and ΔE_4 is the total activation energy for the $S_1(\pi,\pi^*) \rightleftharpoons S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. The frequency factor A of the $S_1(\pi,\pi^*) \rightleftharpoons S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition is much larger than that of the direct $S_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. The latter was evaluated to be 3.7×10^8 s^{-1} in PVA.[8] Therefore, the $S_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition is negligible compared with the $S_1(\pi,\pi^*) \rightleftharpoons S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. Hence, eq 1 and 2 are reduced to

$$1/\tau = k_f + k_d + k_1 + k_2 + k_4 \exp(-\Delta E_4/RT) \quad (3)$$

$$\Phi_{ST} = [k_1 + k_2 + k_4 \exp(-\Delta E_4/RT)]\tau \quad (4)$$

At sufficiently low temperature where $k_4 \exp(-\Delta E_4/RT)$ is negligible compared with $k_f + k_d + k_1 + k_2$, the following relations hold:

$$1/\tau_0 = k_f + k_d + k_1 + k_2 \quad (5)$$

$$\Phi_{ST}^0 = (k_1 + k_2)\tau_0 \quad (6)$$

From eq 3 and 5 we obtain

$$1/\tau - 1/\tau_0 = k_4 \exp(-\Delta E_4/RT) \quad (7)$$

The absorbance of the T–T absorption immediately after flashing is expressed as follows:

$$D = \epsilon_T d[T_1] = \epsilon_T d \Phi_{ST} I_{abs} \quad (8)$$

where ϵ_T is the molar extinction coefficient of the T–T absorption, $d = 10$ cm is the optical path length of the sample cell, and I_{abs} is the light quanta absorbed during the flash. From eq 4, 6, and 8 we obtain

$$D/\tau - D_0/\tau_0 = \epsilon_T d I_{abs} k_4 \exp(-\Delta E_4/RT) \quad (9)$$

The results shown in Figure 7 are satisfactorily explained with eq 7 and 9: A and ΔE correspond to k_4 and ΔE_4, respectively. Values for $k_d + k_1 + k_2$ are listed in Table I.

(5) *Deactivation Mechanism of 9-AA.* The deactivation mechanism of 9-AA is rather different from that of other acridines. $\Delta E(T_3-S_1) = 4360$ cm^{-1} is much greater than $\Delta E = 1830$ cm^{-1}, so that the participation of $T_3(\pi,\pi^*)$ to the deactivation of $S_1(\pi,\pi^*)$ is negligible. A purely conjugative substituent causes generally a small-to-moderate blue shift for the n → π^* transition and a large red shift for the $\pi \rightarrow \pi^*$ transition.[20] Since the NH_2 group has a large conjugative effect, it is possible that the energy level of $T_2(n,\pi^*)$ is higher than that of $S_1(\pi,\pi^*)$. The value of $A = 8 \times 10^{10}$ s^{-1} is greater than the frequency factor of a temperature-dependent intersystem crossing processes in aromatic hydrocarbons. Therefore, the temperature dependence of $1/\tau$ of 9-AA may be attributed to the $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ transition and the energy of $T_2(n,\pi^*)$ was evaluated to be 24 930 cm^{-1}. $1/\tau$ is expressed as follows:

$$1/\tau = k_f + k_d + k_1 + k_2 \exp(-\Delta E_2/RT) \quad (10)$$

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TABLE II: Physical Constants Related to the Deactivation of Excited Acridinium Ions in Water (pH 1.2) at 296 K

	A-h_9H$^+$	A-d_9H$^+$	9-CAH$^+$	9-MAH$^+$	9-PAH$^+$	9-AAH$^+$
ϕ_F	0.66	0.73	0.77	0.72	0.73	0.96
τ, ns	33.9	36.5	28.3	32.3	32.3	18.2
$10^{-7}k_f$, s^{-1}	1.9	2.0	2.7	2.2	2.3	5.3
$10^{-7}k_d$, s^{-1}	1.1	0.7	0.8	0.9	0.8	0.2

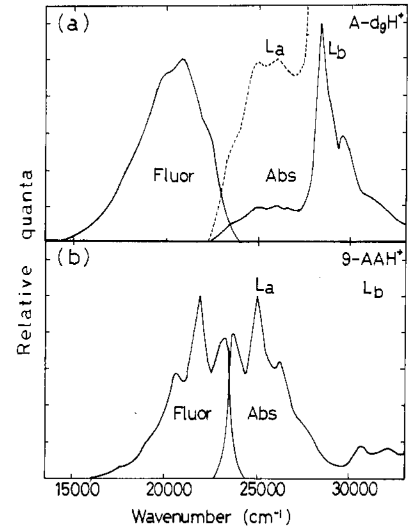

Figure 8. Absorption and fluorescence spectra of (a) A-d_9H$^+$ and (b) 9-AAH$^+$.

where ΔE_2 is the energy gap between $S_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$. At low temperature where $k_2 \exp(-\Delta E_2/RT)$ is negligible compared with $k_f + k_d + k_1$, eq 10 is reduced to

$$1/\tau_0 = k_f + k_d + k_1 \tag{11}$$

From eq 10 and 11 we obtain

$$1/\tau - 1/\tau_0 = k_2 \exp(-\Delta E_2/RT) \tag{12}$$

Hence, A and ΔE of 9-AA correspond to k_2 and ΔE_2, respectively. $k_d + k_1$ is listed in Table I. It is noteworthy that the T–T absorption of 9-AA is hard to observe by the direct excitation even at 330 K where $k_2 \exp(-\Delta E_2/RT) = 3 \times 10^7$ s^{-1}; that is, the deactivation process $k_n{}^T$ from $T_2(n,\pi^*)$ may be much faster than the $T_2(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$ transition: $k_n{}^T \gg k_{21}$. The details of $k_n{}^T$ are not clear. When the deactivation process from $T_2(n,\pi^*)$ participates also in acridines other than 9-AA, k_2 in eq 4 and 6 should be corrected as $k_2k_{21}/(k_{21} + k_n{}^T)$.

(6) *Deactivation Mechanism of Acridinium Ions.* Figure 8 shows the absorption and fluorescence spectra of A-d_9H$^+$ and 9-AAH$^+$ in acidic water at 296 K, from which the energy levels of $S_1(\pi,\pi^*)$ and $S_2(\pi,\pi^*)$ are determined. The phosphorescence could not be observed for the acridinium ions. But the $T_1(\pi,\pi^*)$ energy levels of A-h_9H$^+$, 9-MAH$^+$, and 9-AAH$^+$ were determined to be 16180, 15870, and 18730 cm^{-1}, respectively, from the 0–0 bands of the oxygen-enhanced $S_0 \rightarrow T_1$ absorption spectra.[21]

The values of Φ_F, k_f, and τ of acridinium ions in water at 296 K are listed in Table II. Figure 4 shows the temperature dependence of $1/\tau$. It is obvious that values of $1/\tau$ for acridinium ions depend scarcely on temperature in contrast to those of acridines. Since the T–T absorptions of acridinium ions are not observed by direct excitation, the rate constant k_d of the internal conversion from $S_1(\pi,\pi^*)$ can be evaluated with the relation $k_d = (1 - \Phi_F)\tau$. Values for k_d are listed in Table II.

From Table II it is noticed that (i) k_d of A-h_9H$^+$ is greater than that of A-d_9H$^+$ while k_f of A-h_9H$^+$ is the same as that of A-d_9H$^+$ and (ii) k_d of A-h_9H$^+$ is also greater than k_d values of the other acridinium ions. These results may be explained on the basis of the energy-gap law:[22] in the weak coupling limit the transition probability of the nonradiative decay process is dominated by the accepting modes with the highest vibrational frequency; that is, the C–H stretching mode and thus a marked isotope effect will be revealed. Since k_d is remarkably affected by substitution at the 9 position, it is expected that the C–H vibration at the 9 position plays an important role in the $S_1(\pi,\pi^*) \rightarrow S_0$ nonradiative decay process.

Since values for $k_d + k_1 + k_2$ of acridine derivatives are not greater than k_d values of their acridinium ions, it may be concluded that the vibronic coupling between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ in acridines does not cause a remarkable increase of the $S_1(\pi,\pi^*) \rightarrow S_0$ internal conversion. The fact that values for $k_d + k_1 + k_2$ of A-h_9 are greater than $k_d + k_1 + k_2$ values of other acridines may also be attributed to the C–H vibration at the 9 position as in the case of k_d of acridinium ions.

(7) *Consideration of the Temperature-Dependent Intersystem Crossing.* The energy levels $S_1(\pi,\pi^*)$, $S_2(n,\pi^*)$, $S_3(\pi,\pi^*)$, and $T_3(\pi,\pi^*)$ of A-d_9 are ~100 cm^{-1} lower than those of A-h_9, but the relative energy gaps of these levels are not essentially changed. On the other hand, the frequency factor 5.0×10^{11} s^{-1} of A-h_9 is not so different from 6.1×10^{11} s^{-1} of A-d_9. These results show the absence of a deuterium effect on the $S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition.

In the case of 9-MA and 9-PA, the activation energy is greater than the energy gap between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$ so that the activation energy is attributed to the energy gap between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$. In the case of A-h_9, A-d_9, and 9-CA, on the other hand, the activation energy is the same as the energy gap between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$ so that the energy level of $S_2(n,\pi^*)$ is close to $T_3(\pi,\pi^*)$. Therefore, the energy gap $\Delta E(S_3\text{–}S_2)$ between $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$ is evaluated as listed in Table I. Judging from the spectral shift shown in Figure 1, $\Delta E(S_3\text{–}S_2)$ of 9-CA seems to be less than $\Delta E(S_3\text{–}S_2)$ values of A-h_9 and A-d_9.

It should be noticed from Table I that k_4 increases with decreasing $\Delta E(S_3\text{–}S_2)$. This fact shows that the vibronic interaction between $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$ causes the remarkable increase of intersystem crossing from $S_2(n,\pi^*)$ to $T_3(\pi,\pi^*)$. If $\Delta E(S_3\text{–}S_2)$ is relatively small, $S_2(n,\pi^*)$ will be strongly distorted along out-of-plane vibrational coordinates.[23,24] This distortion can lead to a large increase in the vibrational factor for intersystem crossing. On the other hand, the electronic factor for the $S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition decreases slowly with decreasing $\Delta E(S_3\text{–}S_2)$ on account of the mixing of $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$.[17] Consequently, the product of the electronic and vibrational factors increases with decreasing $\Delta E(S_3\text{–}S_2)$.

Lim et al. have studied the substitution effect of the $T_1(\pi,\pi^*) \rightarrow S_0$ phosphorescence in monocyclic diazine.[25] They found that, upon methyl substitution of monocyclic

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(21) The $S_0 \rightarrow T_1$ absorption spectra of acridines and acridinium ions will be published elsewhere.

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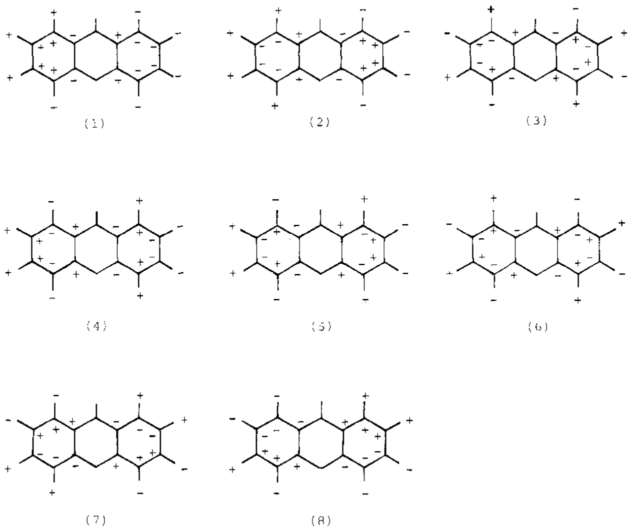

Figure 9. Vibrational modes of a_2 symmetry.

diazine, the energy level of $T_2(\pi,\pi^*)$ becomes lower while that of $T_1(n,\pi^*)$ becomes higher; that is, the energy gap between $T_1(n,\pi^*)$ and $T_2(\pi,\pi^*)$ in methylated diazines is much smaller than that of parent diazine. With decreasing of the energy gap between these states, both the quantum yield and the lifetime of the phosphorescence decreases remarkably; that is, the $T_1(n,\pi^*) \rightarrow S_0$ nonradiative decay is enhanced. This result is consistent with our result.

Acridine and 9-substituted acridines have C_{2v} symmetry. The symmetries of $S_1(\pi,\pi^*)$, $S_2(n,\pi^*)$, and $S_3(\pi,\pi^*)$ are ${}^1A_1$, ${}^1B_1$, and ${}^1B_2$, respectively. Therefore, the inducing vibrational mode of the vibronic coupling between $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$ is the out-of-plane vibrations of a_2 symmetry as shown in Figure 9. On the basis of the resonance Raman scattering study of pyrazine,[26] it was concluded that the bending vibrations such as 1, 2, 4, and 5 shown in Figure 9 contribute selectively to the vibronic coupling between $S_2(n,\pi^*)$ and $S_3(\pi,\pi^*)$.

As regards 9-AA, the temperature-dependent intersystem crossing was attributed to the $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ transition. However, it is still unknown why the deactivation process from $T_2(n,\pi^*)$ is much faster than the $T_2(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$ internal conversion. In order to make clear the deactivation mechanism of excited 9-AA, further studies are in progress.

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Electronic Energy Transfer from Organic Triplet States to Chromium(III) Complexes. The Role of Steric Effects, Spectroscopically Forbidden Excited States, and "Plateau Regions" for Quenching

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Rate constants have been measured for quenching by chromium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), $Cr(dpm)_3$, of the triplet states of organic donors as a function of the donor triplet energy. A non-diffusion-controlled "plateau" region has been established for quenching of low-energy donors consistent with quenching via exothermic energy transfer to low-lying nondistorted doublet states. A sudden rise in quenching efficiency when the singlet–triplet transition in the donor reaches 2 μm^{-1} is attributed to energy transfer to produce the higher nondistorted ${}^2T_{2g}$ state of $Cr(dpm)_3$, confirming previous theoretical estimates for the energy of this state. The reduction in quenching efficiency of $Cr(dpm)_3$ compared to that of chromium(III) tris(acetylacetonate), $Cr(acac)_3$, is shown to be due to lower transmission coefficients for exchange energy transfer due to the steric effect of the *tert*-butyl groups in $Cr(dpm)_3$.

Introduction

Recently Balzani et al.[1] have applied their general classical treatment for vertical and nonvertical energy transfer[2] to literature data for the rate constants (k_q) for quenching of the triplet states of anthracene, acridine, and naphthalene by 11 Cr(III) complexes. They point out that each complex has approximately the same value of k_q independent of the triplet being quenched. Since all of these complexes have lowest excited states with energy $E({}^2E_g)$ lying well below $E({}^3D^*)$, the energy of the triplet donor being quenched, this indicates that low values of k_q are associated with low transmission coefficients for energy transfer to give metal-centered states. Some years ago[3] we showed that tris(acetylacetonato)iron(III), $Fe(acac)_3$, quenches organic triplet states with different efficiencies and, when the logarithms of the measured quenching constants are plotted against the energy of the triplets being quenched, there is a good correlation, with the quenching efficiency rising in a series of steps as the energy of each known excited state is reached. This effect was also observed for quenching due to energy transfer to tris(dipivaloylmethanato)iron(III), $Fe(dpm)_3$, but with the "plateau" values being much lower because of the increased steric blocking by the *tert*-butyl groups as opposed to the methyl groups in the ligand which reduces the overlap of orbitals on the donor and acceptor thereby resulting in less

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