excitation is believed to involve the $v = 0 \rightarrow 1$ transition and thus is a measure of the fundamental vibration for the ion.[3] Although ion-matrix electronic interactions are on the order of 1 eV,[22] differences in interactions between ground and excited vibrational states are probably small, and vibrational spectra of matrix-isolated molecular ions are believed to be representative of the gaseous ion. The fact that argon–krypton matrix differences are small (5–7 cm^{-1}) for such ions as CF_3^+ and $CHBr_2^+$, which are only slightly larger than the 4-cm^{-1} argon–krypton matrix difference for CF_3 and $CHBr_2$ radicals,[1,9,23,24] suggests that the gas-to-argon matrix shift for the vibrational fundamental of the ion is relatively small ($\sim$10 cm^{-1}). This in turn suggests that even the low-intensity IRMPDS may involve higher vibrational manifold excitations and peak at slightly lower energy than the fundamental owing to normal cubic anharmonicity.

Perhaps the most important information from the present study is that C–F vibrational modes in relatively large radical cations absorb at slightly higher frequencies than the corresponding modes of the neutral molecule. The effect on perfluoropropene is relatively small, ca. 29 and 17 cm^{-1} for the two modes. A much larger increase

was found for the antisymmetric C–F stretching modes in $CH_2F_2^+$ (up 176 cm^{-1}), CF_3Cl^+ (up 92 cm^{-1}), and CF_3I^+ (up 53 cm^{-1}).[23] The smaller increase for the C–F stretching modes in $CF_2CFCF_3^+$ as compared to CF_3X^+ and $CH_2F_2^+$ may be due to greater delocalization of the positive charge or "hole" with a corresponding decrease in π-bonding interaction with fluorine lone pairs. It appears reasonable that delocalization of the hole over a larger volume would decrease the effect of the hole on the bonding of atoms adjacent to the hole in the molecular ion.

Conclusions

A reasonable case has been made for the production and trapping of $CF_2CFCF_3^+$ in solid argon using matrix photoionization methods. Excellent agreement with the 1550 $\pm$ 50 cm^{-1} spacing in the first photoelectron band and the 1543-cm^{-1} argon matrix absorption supports assignment of the latter to the C–C π-bond stretching mode. A 1062-cm^{-1} absorption and the 1044 $\pm$ 2 cm^{-1} IRMPDS band are in sufficient agreement to support assignment of these bands to the same vibration. Another absorption at 1414 cm^{-1} is attributed to $CF_2CFCF_3^+$. This study demonstrates the usefulness of the matrix-isolation technique for providing spectral information concerning ions which complements data obtained from other techniques.

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Relaxation Mechanism of Excited Acridine in Nonreactive Solvents

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Electronic relaxation processes of excited acridine have been investigated in water and benzene where the photoreaction does not occur with the irradiation of 365-nm light. In water, the fluorescence yield (Φ_F), the yield (Φ_{ST}) of the lowest triplet state ($T_1(\pi,\pi^*)$), and the fluorescence lifetime (τ) were determined to be 0.34, 0.51, and 11.3 ns at 296 K, respectively, and it was found that Φ_{ST} increases and τ decreases with increasing temperature. In benzene, Φ_F was determined to be $<5 \times 10^{-4}$ at 296 K and Φ_{ST} was found to be 1.0 in the range of 278–336 K. These results indicate the absence of internal conversion in benzene and its presence in water. It was concluded that $S_2(n,\pi^*)$ plays an important role in the deactivation of $S_1(\pi,\pi^*)$ through the $S_1(\pi,\pi^*) \rightleftharpoons (+\Delta E) S_2(n,\pi^*) \rightarrow (k_4) T_3(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$ transition. In water, the energy gap ΔE between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ and the frequency factor k_4 were evaluated to be 1900 cm^{-1} and 5.0×10^{11} s^{-1}, respectively. In benzene, where ΔE is small, the $S_1(\pi,\pi^*) \rightarrow S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$ transition is predominant in the range of 278–336 K.

Introduction

It is well-known that the electronic relaxation of acridine depends on the nature of solvents; the fluorescence is observed in protic solvents such as water and alcohols but not in aprotic solvents such as hydrocarbons at room temperature.[1-3] The solvent dependence of Φ_F was interpreted in terms of the hydrogen bond interaction which causes an interchange of the electronic character in the lowest excited singlet state: π,π^* character in protic solvents and n,π^* character in aprotic solvents.[1,4,5] However, the fluorescence has been observed even in aprotic solvents such as ether–isopentane[6] and n-octane matrixes[7] at 77 K,

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and we observed the fluorescence in benzene at room temperature in the present study. These results indicate that the lowest excited singlet state is of π,π^* character in all solvents.

In a previous work, we investigated the temperature dependences of τ and Φ_{ST} in poly(vinylalcohol) film (PVA) and found that the third excited triplet state $T_3(\pi,\pi^*)$ whose energy level is 420–540 cm^{-1} higher than that of $S_1(\pi,\pi^*)$ is responsible for the temperature-dependent intersystem crossing.[8] However, the deactivation of $S_1(\pi,\pi^*)$ through $S_2(n,\pi^*)$ was not detected.

Since acridine is photoreduced in hydrogen-donating solvents, the deactivation mechanism is complicated in these solvents.[9-11] The electronic character of the reactive state has been studied in various solvents by several groups, and it was found that the reactive state differs from solvent to solvent.[12-17] In a previous work, we found that Φ_{ST} decreases with increasing temperature in reactive aprotic solvents such as methyl methacrylate (MMA) and poly(methyl methacrylate) (PMMA) and is temperature independent in a nonreactive aprotic solvent, benzene.[18] It was suggested that the photoreduction which occurs in $S_2(n,\pi^*)$ through the thermal activation of $S_1(\pi,\pi^*)$ reduces Φ_{ST}. If the internal conversion of acridine is entirely due to the reaction, it is expected that the internal conversion does not occur in nonreactive solvents such as water and benzene. However, this expectation is contrary to the results of Kellmann showing that the internal conversion occurs in nonreactive solvents such as benzene, *tert*-butyl alcohol, and water.[19]

In the present work, we reinvestigate the intersystem crossing processes in water and benzene in order to compare them with the results of Kellmann. Further, we determine the energy levels of the states through which the deactivation of $S_1(\pi,\pi^*)$ occurs and establish the relaxation mechanism in water and benzene.

Experimental Section

Materials. Acridine (C.P. grade, Tokyo Kasei) was recrystallized from an ethanol–water mixture after pretreatment with activated charcoal in ethanol and dried under vacuum. Benzophenone (G.R. grade, Wako Junyaku) was recrystallized twice from ethanol. G.R. grade ethanol and methanol (Wako Junyaku) and *n*-pentane (S.P. grade, Merck) were used without further purification. Benzene and cyclohexane were purified by ordinary methods.[20] Water was distilled twice.

Apparatus and Procedure. The absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer, and the fluorescence spectra on a modified Hitachi EPU spectrophotometer. The fluorescence spectrum in the benzene
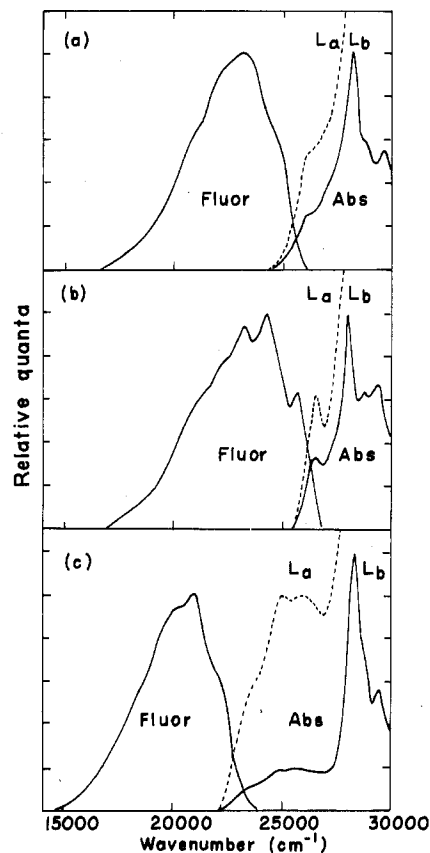
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Figure 1. Absorption and fluorescence spectra of acridine in alkaline water (a) and in benzene (b) and of acridinium ion in acidic water at 296 K (c).

solution and the phosphorescence spectrum were measured with a photon counter NF RC-545A and an Ushio US-H-102D high-pressure mercury lamp as an exciting light source. The photomultipliers used were a HTV-R464 for the fluorescence spectrum in the benzene solution and a HTV-R649 for the phosphorescence spectrum. The T–T absorption spectrum in the visible region was measured with an ordinary flash apparatus (flash tube: xenon, FP-5-100C).[21] The T–T absorption spectrum in the near-infrared region was measured with a HTV-R406 photomultiplier and an Ushio JC-24V-300W halogen lamp as a monitoring light source. Either a Hoya U-2 filter or a Toshiba UVP filter was used for the excitation. An N$_2$ laser was used as an exciting light source for the measurement of τ, and its fwhm was $\sim$7 ns. The fluorescence decay was measured with an RCA 1P 28 photomultiplier and a Tektronix 7904-7S14 sampling oscilloscope, and the decay rate was determined by simulating the decay curve. The error limit is estimated to be 7–8%.

The alkaline aqueous solutions contain 0.02N NaOH, and the acidic aqueous solutions contain 0.06N H$_2$SO$_4$. Sample solutions were degassed by freeze–pump–thaw cycles. The benzene solution, which was used for the measurements of the fluorescence spectrum and yield, was prepared under vacuum without exposing it to air by using benzene dried over a sodium mirror in the same vacuum line.

Results and Discussion

Energy Diagrams. Figure 1 shows the absorption and fluorescence spectra of acridine at 296 K in alkaline water, benzene, and acidic water. It is noted that the fluorescence

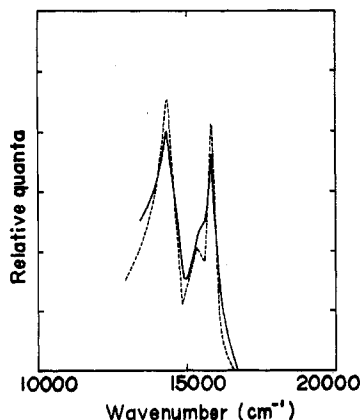(21) K. Kikuchi, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **41**, 1945 (1968).

Figure 2. Phosphorescence spectra in an ethanol–methanol (1:1) mixture (—) and in a methylcyclohexane–*n*-pentane (4:1) mixture (---) at 77 K.

Figure 3. T–T absorption spectra of acridine in alkaline water (—) and in benzene (---) at 296 K.

Figure 4. Energy diagram of acridine in alkaline water.

spectrum in benzene which was not dried over a sodium mirror is similar to that in alkaline water. Although the spectrum shown in Figure 1b differs from that in alkaline water, we cannot exclude the possibility that a trace amount of water is still contained in the benzene solution dried by the sodium mirror. The spectrum shown in Figure 1b is better interpreted as the superposition of the structured spectrum of the free molecules and the broad spectrum of the hydrogen-bonded molecules. The ^1L_a and ^1L_b bands of the absorption spectrum of acridine overlap each other. The energy level of $S_1(\pi,\pi^*)$ is evaluated from the mirror-image relation of the absorption and fluorescence spectra: 25 300–25 500 cm^{-1} in alkaline water and 26 150 cm^{-1} in benzene. As the energy of $S_3(\pi,\pi^*)$, we adopted the location of the peak of ^1L_b: 28 170 cm^{-1} in alkaline water and 27 930 cm^{-1} in benzene. The ^1L_a band of acridinium ion exhibits a red shift of $\sim$2500 cm^{-1}, but the ^1L_b band does not. The energy levels of $S_1(\pi,\pi^*)$ and $S_2(\pi,\pi^*)$ of acridinium ion were evaluated to be 22 900 and 28 250 cm^{-1}, respectively. Figure 2 shows the phosphorescence spectra of acridine in an ethanol–methanol (1:1) mixture and a methylcyclohexane–*n*-pentane (4:1) mixture at 77 K. The 0–0 band of the phosphorescence at 15 870 cm^{-1} and the vibrational progression at 14 300 cm^{-1} in both solvents correspond to the 0–0 band of the $S_0 \rightarrow T_1$ absorption at 15 840 and 17 240 cm^{-1} in chloroform.[22] The poor photomultiplier response for the lower wavenumber region does not allow us to observe the further progressions of the phosphorescence spectrum. The energy level of $T_1(\pi,\pi^*)$ was evaluated to be 15 840–15 870 cm^{-1}.

Although the phosphorescence of acridinium ion has not been observed so far, the energy level of $T_1(\pi,\pi^*)$ of the acridinium ion was determined from the 0–0 band of the oxygen-enhanced $S_0 \rightarrow T_1$ absorption to be 16 100 cm^{-1}, which is close to that of acridine.[23] This is consistent with the prediction from the Förster cycle,[24] since the pK_a value of the ground state (5.5) is close to that of the triplet state (5.6).[25,26]

Figure 3 shows the T–T absorption spectra of acridine in alkaline water and benzene at 296 K. Since no transient absorption was observed below 10 400 cm^{-1} in water and
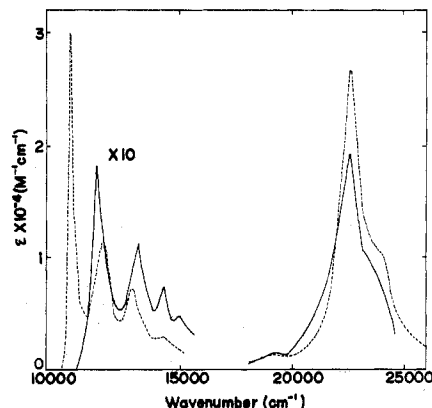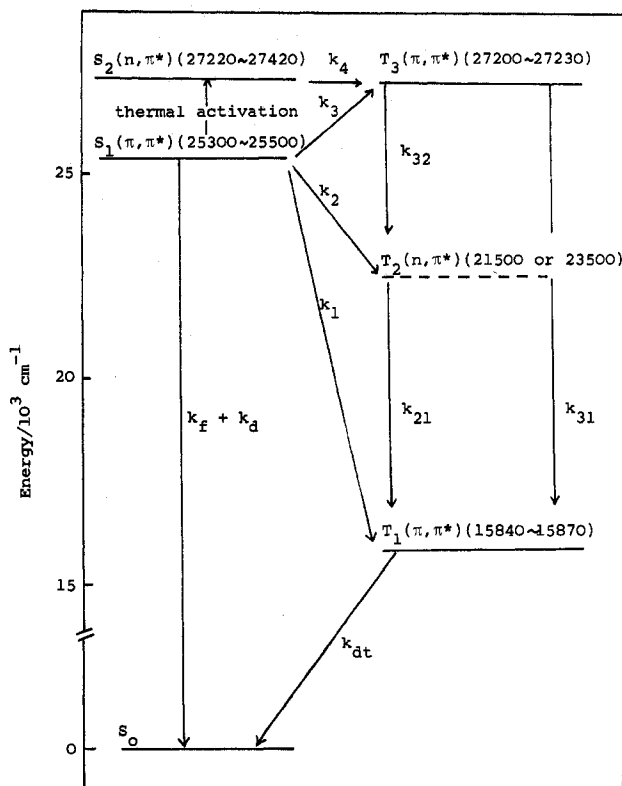
9800 cm^{-1} in benzene, the absorption maxima at 11 360 cm^{-1} in water and 10 100 cm^{-1} in benzene are assigned to the 0–0 band of the $T_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition. The energy level of $T_1(\pi,\pi^*)$ of acridine is not much changed from solvent to solvent. Therefore, the energy level of $T_3(\pi,\pi^*)$ is estimated to be 26 200 $\sim$ 26 230 cm^{-1} in alkaline water and 26 040–26 070 cm^{-1} in benzene. $T_2(n,\pi^*)$ of acridine is not detected experimentally, but its location was predicted theoretically at 21 500 or 23 500 cm^{-1}.[27]

The T–T absorption of acridinium ion was not observed with a direct excitation, so that it was measured with an energy-transfer method using the disodium salt of 1,5-naphthalenedisulfonic acid as a triplet sensitizer.[26] The diffuse nature of the observed T–T absorption spectrum in the red region allows only a rough estimate of the energy level of $T_2(\pi,\pi^*)$ as $\sim$13 000 cm^{-1} above $T_1(\pi,\pi^*)$.

From the above results, the energy diagrams of acridine in alkaline water and benzene are obtained as shown in

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TABLE I: Determination of Φ_{ST} Values in Benzene and Water

| solvent	$D(347)^a$	$D^B(532.5)^b$	$D^A(440 \text{ or } 443)^c$	Φ_{ST} av value	ref 19
benzene	2.0	0.278	0.460	0.50	
	1.0	0.292	0.939	0.98 ⎫	
	0.5	0.204	0.696	1.04 ⎬ 1.00	0.73 ± 0.07
	1.0	0.196	0.620	0.97 ⎭	
	0.5	0.125	0.417	1.0	
water	1.0	0.196	0.244	0.50 ⎫ 0.51	0.39 ± 0.06
	0.5	0.125	0.158	0.51 ⎭	

^{a} Absorbances of benzophenone and acridine at 347 nm. ^{b} Absorbance of triplet benzophenone at 532.5 nm.
^{c} Absorbance of triplet acridine at 440 nm in benzene or at 443 nm in water.
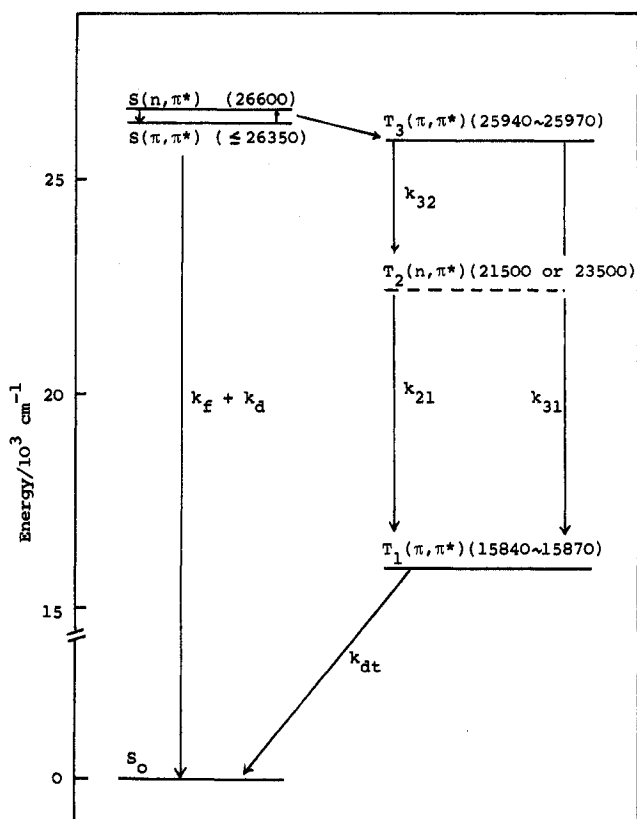
Figure 5. Energy diagram of acridine in benzene.

Figures 4 and 5, respectively. The energy levels of $S_2(n,\pi^*)$ in benzene and $T_2(n,\pi^*)$ are those calculated by Goodman and Harrell.[27]

Determination of Φ_F, Φ_{ST}, and τ at 296 K. Φ_F of acridine was determined to be 0.34 in alkaline water at 296 K in comparison with quinine sulfate in 1.0 N sulfuric acid (Φ_F = 0.546 at 298 K[28]) as a standard solution. Φ_F in benzene was determined to be 5 × 10⁻⁴ at 296 K for the spectrum shown in Figure 1b. Since its spectrum might not entirely be attributed to the free molecules, the above Φ_F value may be regarded as the upper limit of the intrinsic one. Φ_F of acridinium ion was determined to be 0.66 in acidic water at 296 K.

Φ_{ST} was determined by the use of benzophenone in benzene (Φ_{ST} = 1.0 at room temperature[29] as an actinometer. Acridine and benzophenone solutions were prepared in such a way that they have the same absorbance at 347 nm ($D(347)$) and irradiated by a frequency-doubled ruby laser. Table I shows the absorbances of the T–T absorptions immediately after laser excitations of benzophenone at 532.5 nm and acridine at 440 nm in benzene and at 443 nm in alkaline water. The molar extinction coefficients

of the T–T absorptions in benzene were reported to be 7630 M⁻¹ cm⁻¹ for benzophenone at 532.5 nm (ref 30) and 24 300 (ref 30) or 25 000 M⁻¹ cm⁻¹ (ref 31) for acridine at 440 nm. The molar extinction coefficients of T–T absorption of acridine in water were reported to be 19 000 M⁻¹ cm⁻¹ at λ_{max} (=443 nm)[19] by a light-saturation method[31] and 14 500 M⁻¹ cm⁻¹ at 443 nm by a triplet energy transfer method[26] in which proflavin was used as an energy acceptor. The discrepancy is not small, so we tried to determine the molar extinction coefficients of the T–T absorptions of acridine and proflavin by a light-saturation method with a high-intensity flash tube (FP-5-100C) instead of a modified UF-693 flash tube. Measurements were made on the solutions in the initial concentration range of 0.5–1.5 μM for acridine and 0.2–0.8 μM for proflavin with an input energy of 200 J. A Toshiba UV-31 filter was used to excite proflavin. The molar extinction coefficient of proflavin was determined to be $(8.0 \pm 0.8) \times 10^3$ M⁻¹ cm⁻¹ at 549 nm, from which the molar extinction coefficients of acridine and acridinium ion were evaluated to be $(2.0 \pm 0.2) \times 10^4$ M⁻¹ cm⁻¹ at 443 nm and $(7.7 \pm 0.8) \times 10^3$ M⁻¹ cm⁻¹ at 490 nm, respectively. Since no filter was used to excite acridine, the permanent fading of acridine (ca. 25%) was observed after flashing.[32] The triplet concentration of acridine was estimated from the ground-state concentration after flashing. The molar extinction coefficient of the T–T absorption of acridine was estimated to be $(1.94 \pm 0.14) \times 10^4$ M⁻¹ cm⁻¹ at 443 nm, which agrees with the one evaluated above. In the present study we used 19 000 M⁻¹ cm⁻¹ as the molar extinction coefficient of the T–T absorption in alkaline water. As seen in Table I, Φ_{ST} obtained for the benzene solution with the largest $D(347 \text{ nm})$ is one half of the others, and hence it was excluded in the calculation of the averaged value. This method of Φ_{ST} determination may give some errors when $D(347 \text{ nm})$ is too large.

Since no T–T absorption of acridinium ion in acidic aqueous solution was observed, it is concluded that Φ_{ST} of acridinium ion is very small (presumably <10⁻²).

The values of Φ_{ST} determined by us are larger than those reported by Kellmann. According to our results the internal conversion from $S_1(\pi,\pi^*)$ is negligible in benzene but not in alkaline and acidic aqueous solutions.

The fluorescence lifetimes (τ) of acridine and acridinium ion in water were determined to be 11.3 ± 0.8 and 33.9 ± 0.3 ns at 296 K, respectively. The fluorescence lifetime in alkaline water at 298 K measured with an N₂ laser is 11.0 ± 0.8 ns, which agrees with a previous value of 10.3 ns by the phase-shift method.[33] From τ and Φ_F, the rate constants of fluorescence emission k_f of acridine and

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(32) Acridine is not practically photobleached in water by the irradiation at 365 nm, but at <300 nm.
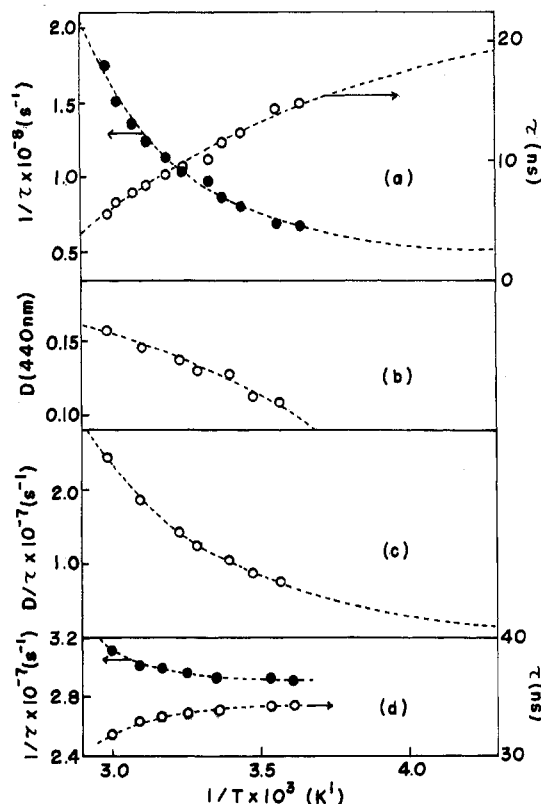(33) H. Kokubun, *Bull. Chem. Soc. Jpn.*, **42**, 919 (1969).

Figure 6. For acridine in alkaline water, the temperature dependences of (a) the fluorescence lifetime, (b) the absorbance of the T–T absorption immediately after flashing at 440 nm, and (c) their ratio; (d) temperature dependence of the fluorescence lifetime of acridinium ion in acidic water.

acridinium ion in water were estimated to be 3.0×10^7 and 1.9×10^7 s^{-1}. If k_f of acridine in benzene is the same as that in alkaline water, the lifetime of $S_1(\pi,\pi^*)$ is evaluated to be <16.7 ps.

Deactivation Mechanism. From the energy-level diagrams, it should be noticed that (i) the energy level of $T_3(\pi,\pi^*)$ is higher than that of $S_1(\pi,\pi^*)$ in alkaline water and vice versa in benzene and (ii) the energy levels of $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ lie close to each other in benzene. If $T_3(\pi,\pi^*)$ plays an important role in the intersystem crossing, it is expected that Φ_{ST} increases with increasing temperature in alkaline water and is independent of temperature in benzene. These expectations agree with our previous results in PVA.[8] Furthermore, the fact that Φ_F is very small ($<5 \times 10^{-4}$) and $\Phi_{ST} = 1.0$ in benzene seems to be consistent with the energy diagram shown in Figure 5, because the participation of $S_2(n,\pi^*)$ on the deactivation of $S_1(\pi,\pi^*)$ enhances extremely the intersystem crossing according to the El-Sayed[34] and extended El-Sayed[35] rules. In PVA, such participation of $S_2(n,\pi^*)$ was not observed in the range of 77–296 K.

In order to obtain further information about the deactivation mechanism, we first studied the temperature dependences of τ and Φ_{ST} in alkaline water. Figure 6 shows the temperature dependences of τ, the absorbance D of the T–T absorption immediately after flashing, and the ratio (D/τ). τ increases and D decreases with decreasing temperature. D/τ, which is associated with the rate of intersystem crossing, decreases with decreasing temperature and approaches a constant value, D_0/τ_0, at low temperature. Therefore, it is supposed that τ and D attain

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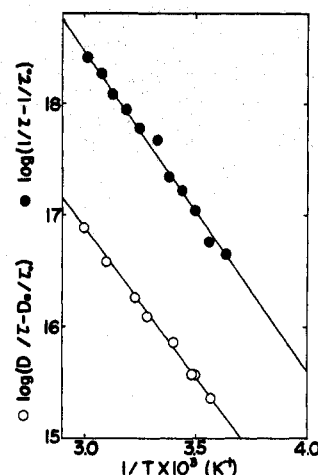(35) N. Shimakura, Y. Fujimura, and T. Nakajima, *Chem. Phys.*, **19**, 155 (1977).

Figure 7. Arrhenius plots of $(1/\tau - 1/\tau_0)$ and $(D/\tau - D_0/\tau_0)$ vs. temperature in alkaline water.

the respective constant values τ_0 and D_0 at low temperature. When $1/\tau_0 = 5.0 \times 10^7$ s^{-1} and $D_0/\tau_0 = 1.6 \times 10^6$ s^{-1} 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 above extrapolated values are appropriate, and the temperature dependence of τ seems to be entirely interpreted with the temperature dependence of the intersystem crossing. The apparent activation energy, $\Delta E = 1900$ cm^{-1}, agrees with the energy difference between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$, 1700–1900 cm^{-1}. From the intercept of the Arrhenius plot for $1/\tau - 1/\tau_0$, we obtain the frequency factor of the rate of the temperature-dependent process, 5.0×10^{11} s^{-1}. This value is much larger than that for the intersystem crossing from $S_1(\pi,\pi^*)$ to $T_3(\pi,\pi^*)$ in PVA, 3.7×10^8 s^{-1}. The frequency factor of a temperature-dependent intersystem-crossing process in aromatic hydrocarbons is in the range of 10^6–10^9 s^{-1}.[36] According to the spin–orbit coupling selection rule of El-Sayed, the $^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ transition is much easier than the $^1(\pi,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ transition. Therefore, it is concluded that $S_2(n,\pi^*)$, although there is no spectroscopic evidence, plays an important role in the intersystem crossing in alkaline water in contrast to PVA. Further, the apparent activation energy may be attributed to the energy difference between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$, because it is the upper limit of the estimated energy difference between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$.

On the basis of the above information, we propose the deactivation pathways in water as shown in Figure 4. If the frequency factor of the $S_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition in alkaline water is the same as that in PVA, 3.7×10^8 s^{-1},[8] the rate constant of this transition is estimated to be 5.7×10^5 s^{-1} at 296 K; the contribution of the direct $S_1(\pi,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition on the temperature-dependent intersystem crossing is neglected. Therefore, it is concluded that the temperature-dependent intersystem crossing occurs essentially through the $S_1(\pi,\pi^*) \rightleftharpoons (\Delta E) S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$ transition.

When k_d represents the rate constant of the internal conversion from $S_1(\pi,\pi^*)$ to the ground state, τ and Φ_{ST} are expressed as follows (see Figure 4 and 5):

$$1/\tau = k_f + k_d + k_1 + k_2 + k_4 \exp[-\Delta E/(RT)] \quad (1)$$

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

At sufficiently low temperature, where $k_4 \exp[-\Delta E/(RT)]$

(36) J. B. Birks, "Organic Molecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley, London, 1973, p 41.

TABLE II: Rate Constants of the Deactivation of
Excited Acridine in Alkaline Water

$$k_f = 3.0 \times 10^7 \text{ s}^{-1}$$
$$k_1 + k_2 = 1.0 \times 10^7 \text{ s}^{-1}$$
$$k_d = 1.0 \times 10^7 \text{ s}^{-1}$$
$$k_3 = 5.7 \times 10^5 \text{ s}^{-1} \text{ (at 296 K)}$$
$$k_4 = 5.0 \times 10^{11} \text{ s}^{-1} \quad \Delta E = 1900 \text{ cm}^{-1}$$
$$k_{dt} = 6.5 \times 10^3 \text{ s}^{-1} \text{ (at 296 K)}$$

is neglected in comparison with $k_f + k_1 + k_2$, the following relations hold:

$$1/\tau_0 = k_f + k_d + k_1 + k_2 \tag{3}$$

$$\Phi_{ST}^0 = (k_1 + k_2)\tau_0 \tag{4}$$

The T–T absorbance, D, is related to Φ_{ST} according to eq 5, where ϵ_T is the molar extinction coefficient of the T–T

$$D = \epsilon_T d[T_1] = \epsilon_T d\Phi_{ST}I_{abs} \tag{5}$$

absorption, $[T_1]$ the triplet concentration immediately after flashing, $d = 100$ mm the optical path length of a sample cell, and I_{abs} the light absorbed during flashing. From eq 1–5 we obtain eq 6 and 7, where $D_0 = \epsilon_T d I_{abs}\Phi_{ST}^0$. Analyzing

$$1/\tau - 1/\tau_0 = k_4 \exp[-\Delta E/(RT)] \tag{6}$$

$$D/\tau - D_0/\tau_0 = \epsilon_T d I_{abs} k_4 \exp[-\Delta E/(RT)] \tag{7}$$

lyzing the results shown in Figure 7 by eq 6 and 7, we obtain eq 8–11. From eq 8–11 and $k_f = 3.0 \times 10^7 \text{ s}^{-1}$, we

$$k_4 = 5.0 \times 10^{11} \text{ s}^{-1} \tag{8}$$

$$\epsilon_T d I_{abs} k_4 = 7.7 \times 10^7 \text{ s}^{-1} \tag{9}$$

$$D_0/\tau_0 = 1.6 \times 10^6 \text{ s}^{-1} \tag{10}$$

$$1/\tau_0 = 5.0 \times 10^7 \text{ s}^{-1} \tag{11}$$

obtained $k_1 + k_2 = 1.0 \times 10^7 \text{ s}^{-1}$ and $k_d = 1.0 \times 10^7 \text{ s}^{-1}$. The value of $k_1 + k_2$ is consistent with that in PVA, 1.4×10^7 s^{-1}. The value of k_d agrees satisfactorily with another estimate, 1.3×10^7 s^{-1}, which was calculated from $\tau = 11.3$ ns and $\Phi_{ic} = 1 - (\Phi_F + \Phi_{ST}) = 0.15$ at 296 K. All of the rate constants involved in the scheme shown in Figure 4 are summarized in Table II. From eq 1 and 2, the relation $\Phi_F = k_f\tau$, and the rate constants cited in Table II, Φ_F and Φ_{ST} at 296 K are calculated to be 0.31 and 0.59, respectively, which agree moderately with their experimental values, $\Phi_F = 0.34$ and $\Phi_{ST} = 0.51$.

The above examinations support the validity of the deactivation scheme shown in Figure 4 and the rate constants cited in Table II.

The temperature dependence of τ of acridinium ion is much smaller than that of acridine, as shown in Figure 6, which shows the little importance of the temperature-dependent relaxation process of $S_1(\pi,\pi^*)$. Since $\Phi_F = 0.66$ and Φ_{ST} is very small ($<10^{-2}$), the rate constant of the internal conversion k_d from $S_1(\pi,\pi^*)$ to the ground state is evaluated to be 1.1×10^7 s^{-1}. This value is almost equal to that of acridine in alkaline water, $k_d = 1.0 \times 10^7$ s^{-1}.

Figure 8 shows the temperature dependence of D at 440 nm in benzene. D does not vary in the range of 278–336 K. Since $\Phi_{ST} = 1.0$ and $\Phi_F < 5 \times 10^{-4}$ at 296 K in benzene, the deactivation of $S_1(\pi,\pi^*)$ is essentially due to the intersystem crossing in the range of 278–336 K. When $k_f = 3.0 \times 10^7$ s^{-1} is used, the decay rate constant of $S_1(\pi,\pi^*)$ is estimated to be $<6 \times 10^{10}$ s^{-1} at 296 K. The decay rate constants of $S_1(\pi,\pi^*)$ in hydrocarbons have been determined by the measurement of the growth of the T–T ab-
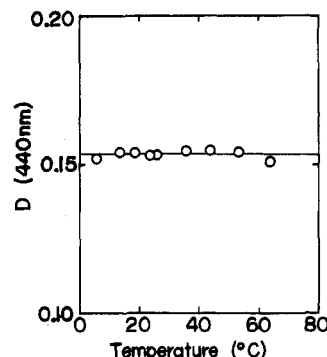

Figure 8. Temperature dependence of the absorbance of the T–T absorption immediately after flashing in benzene.

sorption by the use of a ps laser technique: 8×10^{10} s^{-1} in isooctane[4] and 3×10^{10} s^{-1} in *n*-hexane[5] at room temperature. These decay rate constants are of the same order as that estimated in benzene, so that k_f might not change from solvent to solvent. Assuming that both the rate constants of the temperature-independent processes and the frequency factor of the temperature-dependent process do not depend on the solvent, we obtain eq 12. From eq

$$\Phi_F \approx 3.0/\{5.0 + (3.7 \times 10) + (5.0 \times$$
$$10^4) \exp[-\Delta E/(RT)]\} < 5 \times 10^{-4} \quad \text{(at 296 K)} \tag{12}$$

12, we obtain $\Delta E < 440$ cm^{-1}, and hence the energy level of $S_2(n,\pi^*)$ is estimated to be $<26\,600$ cm^{-1}. It is concluded that the energy gap of $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ is very small and that the results in benzene can be qualitatively accounted for by the deactivation scheme shown in Figure 5 and the rate constants and frequency factor cited in Table II.

In the present study, it was found that the internal conversion of acridine is negligible in benzene but not in alkaline water. This fact, however, does not indicate that k_d in benzene is smaller than 1.3×10^7 s^{-1} in alkaline water, because τ is much smaller in benzene than in alkaline water. Even if the yield Φ_{ic} of the internal conversion is no more than 1%, k_d in benzene is estimated to be $<6 \times 10^8$ s^{-1}. Consequently, we cannot comment on the enhancement of k_d from alkaline water to benzene due to the vibronic interaction between $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$.[37]

The fact that the sum of Φ_F, Φ_{ST}, and the yield of the photoreduction in hydrogen-donating solvents such as alcohols and *n*-hexane is less than the sum of Φ_F and Φ_{ST} in nonreactive solvents such as water and benzene suggests the existence of a trivial deactivation caused by the hydrogen abstraction reactions followed by the back-reaction. Noe et al. have measured Φ_{ST} of acridine in ethanol, 2-propanol, acetonitrile, and hexane and concluded that k_d increases in that order.[38] However acridine in these solvents exhibits the hydrogen abstraction reaction. The estimation of the intrinsic rate constant of internal conversion is hard to carry out as long as reactive solvents are employed.

The reason that $S_2(n,\pi^*)$ does not contribute to the deactivation of $S_1(\pi,\pi^*)$ in PVA but does in alkaline water and benzene may be explained by the difference of the energy gap between $S_1(\pi,\pi^*)$ and $T_3(\pi,\pi^*)$ in these solvents: 420–540 cm^{-1} in PVA and 1900 cm^{-1} in water. Above room temperature, $S_2(n,\pi^*)$ may contribute to the deactivation of $S_1(\pi,\pi^*)$ even in PVA.

(37) R. Lin and E. C. Lim, *J. Chem. Phys.*, **57**, 605 (1972).
(38) L. J. Noe, E. O. Degenkolb, and P. M. Rentzepis, *J. Chem. Phys.*, **68**, 4435 (1978).