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The magnetic field effect induced through the Δg mechanism has been observed above 1200 G for photolysis of the hexane solution of BP.³⁹ The effect, however, is opposite to that actually observed for BP ketyl radical formation in micelles.⁹ This means that the Δg mechanism is not applicable to our reactions. The relaxation mechanism⁴⁰ which is useful for explaining some magnetic field effects upon chemical reactions⁴¹ may be a reasonable

explanation for the discrepancy from the hfc mechanism observed for the SDS solution of BP.

Acknowledgment. The authors thank Dr. Arimichi Minoh, the Institute of Physical and Chemical Research, for his kindness in allowing them to have the digital memory system at their disposal. H.H. is also indebted to Professor Nicholas J. Turro, Columbia University, for his valuable comments.

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Picosecond Fluorescence Lifetimes of Anthraquinone Derivatives. Radiationless Deactivation via Intra- and Intermolecular Hydrogen Bonds

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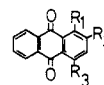
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Radiationless deactivations from the $S_1(^1CT)$ states of seven 1- and 2-substituted aminoanthraquinones were investigated by measuring picosecond fluorescence lifetimes and fluorescence quantum yields in benzene, acetonitrile, and ethanol. The $S_1(^1CT)$ states of all derivatives were largely deactivated in ethanol. Deuterium isotope effects of the solvents on the nonradiative rate constants $k_{nr}(\text{in EtOH})/k_{nr}(\text{in EtOD}) = 9.0$ (1-NH₂ (2)), 2.1 (2-NH₂ (5)), and 1.7 (2-piperidino (7)) were observed. The fluorescence quantum yield in ethanol was not affected by temperature (278–343 K). In benzene the excited 1-aminoanthraquinones were deactivated faster than 2-aminoanthraquinones. These observations were interpreted in terms of the radiationless deactivations of $S_1(^1CT)$ through the intra- and intermolecular hydrogen bonds.

Introduction

Fluorescence quenching by proton transfer or hydrogen-bonding interactions has received special attention as one of the fundamental processes of radiationless deactivation.^{2-13,18-20}

Chart I



Compound	1	2	3	4	5	6	7
R ₁	NHCOCH ₃	NH ₂	NHCH ₃	NHCH ₃	H	H	H
R ₂	-	-	H	H	NH ₂	N(C ₄ H ₉) ₂	
R ₃	H	H	-	Br	-	H	-

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Such quenching is explained either by (1) the intramolecular interactions,³⁻⁸ most of which involve rapid deactivation through a keto-enol tautomeric reaction, or by (2) intermolecular interactions (a) between two π -conjugated systems⁹⁻¹⁹ and (b) between one conjugated molecule and

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TABLE I: Lifetimes of the Excited States of 1-Substituted Anthraquinones

anthraquinones	solvent	$(\bar{\nu}_a - \bar{\nu}_f)/\text{cm}^{-1}$	$10^3 Q_f$	$10^{12} \tau_{\text{obsd}}/\text{s}$	$(10^{-9} Q_f / \tau_{\text{obsd}}) \text{s}^{-1}$	$10^{-9} k_f^{\text{a}} (\text{calcd})/\text{s}^{-1}$	$10^{-9} k_{\text{nr}}/\text{s}^{-1}$
1-NHCOCH ₃ (1)	C ₆ H ₆	4900	1.7	410	0.042	0.047	2.4
	CH ₃ CN	6060	0.82	320	0.026	0.035	3.1
	C ₂ H ₅ OH	6480	0.41	66	0.063	0.036	15
1-NH ₂ (2)	C ₆ H ₆	4320	5.8	1750	0.033	0.040	0.54
	CH ₃ CN	4520	1.0	660	0.015	0.029	1.5
	C ₂ H ₅ OH	4380	0.82	460	0.018	0.030	2.2
1-NHCH ₃ (3)	C ₆ H ₆	3250	0.76	330	0.023	0.039	3.0
	CH ₃ CN	3800	0.16	190	0.0084	0.030	5.3
	C ₂ H ₅ OH	3750	0.14	94	0.015	0.026	11
1-NHCH ₃ -4-Br (4)	C ₆ H ₆	3150	0.32	190	0.017	0.038	5.3
	CH ₃ CN	3570	0.11	190	0.0058	0.031	5.3
	C ₂ H ₅ OH	3610	0.087	53	0.016	0.050	19

^a The lifetime data contain a standard deviation of $\pm 4\%$.

one nonconjugated molecule. The intermolecular interactions of case 2a have been revealed^{9,13} to involve charge-transfer (CT) interactions in their quenching mechanism. On the other hand, details of the quenching mechanism by protic solvents in case 2b have not yet been clear. Recently protic solvents have been supposed to have a specific role in the fluorescence quenching.²⁰ The quenching process is expected to be largely affected by molecular motions of solvent molecules in close proximity to the fluorophores. Information on solute-solvent interaction is most requisite for the elucidation of the quenching mechanism.

Aminoanthraquinones are known to be weakly hydrogen bonded with alcohols in the ground states,²¹ and the fluorescences of the quinones are quenched by alcohols. The lowest excited states have intramolecular charge-transfer characters,²² and the minus charge is mostly localized on the carbonyl oxygen in their CT excited states. A dominant hydrogen-bonding interaction between the carbonyl oxygen with solvent would be expected in the excited state. This interaction might have a distinctive influence on the fluorescence behavior. Studies on a series of N-substituted aminoanthraquinones with widely varying electron-donating character are possible. Hence, aminoanthraquinones are considered to be most suitable for model compounds in the fluorescence quenching of case 2b.

In this paper, radiationless deactivations from the $S_1(^1\text{CT})$ states of aminoanthraquinones are investigated by measuring picosecond fluorescence lifetimes and fluorescence quantum yields in benzene, acetonitrile, and ethanol. All of the results including deuterium isotope effects and temperature effects suggest that the radiationless deactivations from $S_1(^1\text{CT})$ of quinones in ethanol are mainly induced through vibrational modes of the intermolecular hydrogen bond with solvent molecules.

Experimental Section

Materials. 1-(Acetylamino)anthraquinone (1), 1-aminoanthraquinone (2), 2-aminoanthraquinone (5), 2-piperidinoanthraquinone (7), 1-(dimethylamino)anthraquinone (8), and 1-piperidinoanthraquinone (9) were prepared and purified as reported elsewhere²³ (see Chart I). 1-(Methylamino)anthraquinone (3) (Sumitomo Chemical Co.) was purified by repeated recrystallization

from toluene. 1-(Methylamino)-4-bromoanthraquinone (4) was prepared by the bromination of 3 with bromine in acetic acid and purified by repeated recrystallization from benzene. 2-(Dibutylamino)anthraquinone (6) was prepared by the reaction of butyl iodide with 5 treated with potassium hydroxide in dimethyl sulfoxide and purified by repeated recrystallization from benzene. The purities of those anthraquinone derivatives were confirmed by their melting points and elemental analyses. Benzene and acetonitrile (spectrograde, Merck and Co.) were stored under nitrogen and were used without further purification. Ethanol was dried by refluxing over magnesium diethanolate and was fractionally distilled under nitrogen atmosphere. Ethanol-*O-d* (was of 99.9% purity, Merk and Co.) was used.

Measurements. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluorometer. Quinine sulfate was used as a standard ($Q_f = 0.55$ in 0.5 mol/dm³ sulfuric acid aqueous solution)²⁴ for the determination of fluorescence quantum yields. Each anthraquinone derivative (1.0×10^{-5} – 1.0×10^{-4} mol/dm³) in benzene, acetonitrile, or ethanol was excited by the single-pulse third harmonic (355 nm) from a mode-locked picosecond Nd:YAG laser with a pulse width of 15 ps. The picosecond fluorescence apparatus has been described previously.²⁵ Fluorescence of short lifetimes (<1000 ps) were monitored with a streak camera (Hamamatsu C-797 with an S-20 cathode; time resolution ≤ 10 ps and that of the total performance is about 18 ps). Fluorescence of rather long lifetimes (>1000 ps) were monitored with a photomultiplier (Hamamatsu R1328U) connected with a Tektronix 7104 equipped with 7A29 and 7B10 plug-in units (instrumental time resolution, ca. 400 ps). More than five shots were averaged in each experiment. Fluorescence time profiles were computer fitted by a convolution method. The time axis of the streak camera was calibrated by using an etalon. Lifetime measurements by a phase-modulation method were also carried out by means of a Jasco FL-10 phase fluorometer.

Results

Emission Spectra. Anthraquinone derivatives have four $\pi\pi^*$ absorption bands in the region of the wavelength between 220 and 350 nm, and an $n\pi^*$ band at the longer wavelength near 400 nm. When an electron-donating substituent such as a hydroxyl or amino group is introduced, a new $\pi\pi^*$ absorption band appears in the visible region, which is assigned to an intramolecular charge-

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TABLE II: Lifetimes of the Excited States of 2-Substituted Anthraquinones

anthraquinones	solvent	$(\bar{\nu}_a - \bar{\nu}_f)/\text{cm}^{-1}$	$10^2 Q_f$	$10^{12} \tau_{\text{obsd}}/\text{s}$	$(10^{-9} Q_f / \tau_{\text{obsd}})/\text{s}^{-1}$	$10^{-9} k_f^{\text{calcd}} (\text{calcd})/\text{s}^{-1}$	$10^{-9} k_{\text{nr}}/\text{s}^{-1}$
2-NH ₂ (5)	C ₆ H ₆	5810	21	6500	0.032	0.030	0.12
	CH ₃ CN	6780	0.80	850	0.0094	0.021	1.2
	C ₂ H ₅ OH	8930	0.059	54	0.011	0.024	19
2-N(C ₄ H ₉) ₂ (6)	C ₆ H ₆	3990	15	9800	0.015	0.039	0.087
	CH ₃ CN	4790	0.33	680	0.0049	0.027	1.5
	C ₂ H ₅ OH	4650	0.021	76	0.0028	0.031	13
2-piperidino (7)	C ₆ H ₆	4760	8.5	7700	0.011	0.035	0.095
	CH ₃ CN	5590	0.12	300	0.0040	0.024	3.3
	C ₂ H ₅ OH	5150	0.012	40	0.0030	0.029	25

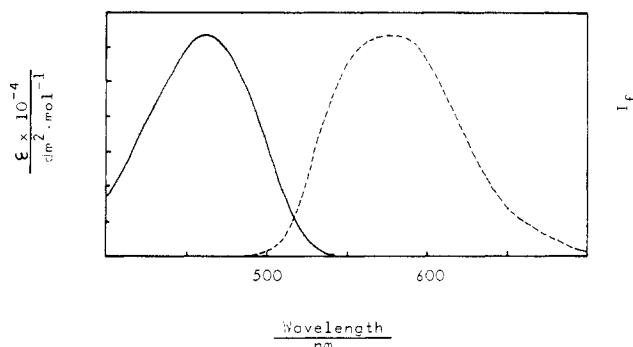


Figure 1. Absorption (—) and fluorescence (---) spectra of 2 in benzene at 294 K.

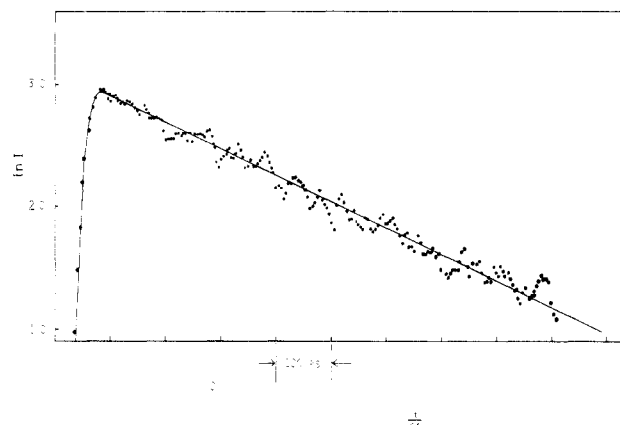
transfer band between the substituent and the carbonyls.²² Aminoanthraquinones (1–9) used in this study have their CT bands between 400 and 520 nm according to the electron-donating characters of the substituents. Fluorescence emissions were observed in the region of the wavelengths between 520 and 630 nm, and their excitation spectra coincided well with their absorption spectra in all derivatives. The absorption and fluorescence spectra of 2 as a typical example are shown in Figure 1. As indicated in Tables I and II, larger Stokes shifts are observed in polar solvents than in a nonpolar solvents, indicating that the excited states of these aminoanthraquinones are more stabilized by polar solvents in accord with their intramolecular CT natures. Though the position of the intramolecular CT state is affected by the substituent, the ¹CT is always the lowest excited singlet state in all aminoanthraquinones.²⁶ No phosphorescence emission was observed in each derivative. The absence of the photoamination and the photocycloaddition via the triplet mode by direct irradiation^{27,28} strongly indicates that the triplet yield of the aminoanthraquinones is negligibly small. No photochemical reaction was observed when an aminoanthraquinone derivative alone in benzene, acetonitrile, or ethanol was excited to its ¹CT level. Hence, the major deactivations from the S₁(¹CT) states are limited to the radiative and nonradiative deactivations. This indicates that measurements of fluorescence quantum yields and lifetimes of the aminoanthraquinones afford significant information about the nonradiative deactivations from their excited states.

Fluorescence Quantum Yields and Lifetimes. Fluorescence quantum yields (Q_f) and lifetimes (τ_{obsd}) of seven 1- and 2-aminoanthraquinones (1–7) at 294 K were

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Figure 2. Fluorescence time profile of 2 (1.00×10^{-4} M) by 355-nm excitation in ethanol at 294 K. The solid line is the simulated curve with a rise time of 0 ps and a decay constant of 460 ps.

measured in benzene, acetonitrile, and ethanol (Tables I and II). 1-Substituted (dialkylamino)anthraquinones 8 and 9 were weakly fluorescent ($Q_f < 10^{-5}$) in every solvent. The fluorescence time profile of 2 in ethanol as a typical case is shown in Figure 2. The fluorescence of the long-wavelength region ($\lambda > 600$ nm) was monitored by a streak camera. A pulse-limited rise and a single-exponential decay with a time constant of $\tau_{\text{obsd}} = 460$ ps were observed. This agreed well with the value of $\tau_{\text{obsd}} = 400 \pm 100$ ps obtained in the measurement by a phase-shift method in which a weak steady-state exciting light source was used. These results indicate that the fluorescence kinetics are not due to nonlinear optical phenomena. All other derivatives exhibited similar fluorescence time profiles in every solvent. As indicated in Tables I and II, the fluorescence behavior of the aminoanthraquinones is largely dependent on the nature of the solvents.

From the data of the fluorescence quantum yields (Q_f) and lifetimes (τ_{obsd}), the radiative rate constant, $k_f(\text{obsd})$, and the nonradiative one, k_{nr} , are obtained by eq 1 and 2.

$$k_f(\text{obsd}) = Q_f / \tau_{\text{obsd}} \quad (1)$$

$$k_{\text{nr}} = k_{\text{isc}} + k_d = 1 / \tau_{\text{obsd}} - k_f(\text{obsd}) \quad (2)$$

where k_{isc} and k_d denote the rate constants of intersystem crossing to T₁ and direct radiationless deactivation to the ground state. The radiative rate constant can also be calculated by the following relation:²⁹

$$k_f(\text{calcd}) = (2.880 \times 10^{-9}) \frac{n_f^3}{n_a} \frac{\int F(\bar{\nu}) d\bar{\nu}}{\int F(\bar{\nu}) / \bar{\nu}^3 d\bar{\nu}} \int \frac{\epsilon(\bar{\nu})}{\bar{\nu}} d\bar{\nu} \quad (3)$$

where n_f and n_a denote the mean values of the refractive

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TABLE III: Deuterium Isotope Effects on the Fluorescence Lifetimes

anthra-quinones	solvent	$10^{12} \times 10^2 Q_f$	τ_{obsd}/s	$(10^{-9} Q_f / \tau_{\text{obsd}})/s^{-1}$	$10^{-9} k_{\text{nr}}/s^{-1}$
Temperature = 294 K					
1-NH ₂ (2)	EtOH	0.82	460	0.018	2.2
	EtOD	4.98	3030	0.016	0.31
2-NH ₂ (5)	EtOH	0.059	54	0.011	19.0
	EtOD	0.14	109	0.013	9.2
2-piperidino (7)	EtOH	0.012	40	0.003	25.0
	EtOH	0.016	68	0.002	14.7
Temperature = 77 K					
1-NH ₂ (2)	EtOH		1980		0.48
	EtOD		9600		0.082
2-NH ₂ (5)	EtOH		4930		0.19
	EtOD		12700		0.068
2-piperidino (7)	EtOH		14600		0.065
	EtOD		15300		0.062

indexes of solvent in the region of the fluorescence and the absorption, $F(\bar{\nu})$ is the fluorescence spectrum, and $\epsilon(\bar{\nu})$ is the absorption spectrum in units of the molar extinction coefficient.

In benzene $k_f(\text{obsd})$'s agree well with $k_f(\text{calcd})$'s in the derivatives bearing rather weak electron-donating substituents such as 1, 2, and 5. On the other hand, rather strong electron-donating substituents cause a deviation of $k_f(\text{obsd})$ from $k_f(\text{calcd})$ as seen in the cases of 3, 4, 6, and 7. In polar solvents, large deviations of $k_f(\text{obsd})$ from $k_f(\text{calcd})$ are observed in all derivatives. The tendency is more distinct in 2-aminoanthraquinones than in 1-substituted derivatives (Tables I and II).

The rate constant of the radiationless deactivation from the $S_1(^1\text{CT})$ to the ground state, k_{nr} , also suffers considerable solvent effects. They are observed to be accelerated in acetonitrile and by far the larger in ethanol as compared with those in benzene. In 2-substituted aminoanthraquinones, k_{nr} 's are 1 order of magnitude larger in acetonitrile and 2 orders of magnitude larger in ethanol than in benzene. These striking solvent effects strongly suggest the possibility that ethanol not only acts as a polar medium to stabilize the CT excited states as in the case of acetonitrile but also plays a specific role as a molecule in the radiationless deactivations from the $S_1(^1\text{CT})$ of the aminoanthraquinones. These results prompted us to investigate further the deuterium isotope effect in order to clarify the role of ethanol molecule in the radiationless deactivations of the excited aminoanthraquinones.

Deuterium Isotope Effect. Fluorescence quantum yields and lifetimes of three aminoanthraquinones, 2, 5, and 7, were measured in ethanol-*O-d* at 294 and 77 K. The obtained results are compared with those in ethanol in Table III and Figure 3.

In fluid solvent at 294 K, values of both Q_f and τ_{obsd} of each derivative increase dramatically in ethanol-*O-d* as compared with ethanol. Since the values of $k_f(\text{obsd})$ and $k_f(\text{calcd})$ are insensitive to the deuteration of the solvent, the observed deuterium effects on Q_f and τ_{obsd} are due to the effects on the nonradiative deactivation process. That is, the rates of the radiationless deactivations are much slower in deuterated ethanol than in ethanol.

In rigid ethanol at 77 K, where the reorientational motion of the surrounding solvent of the excited molecule is inhibited, no deuterium effect on the radiationless deactivation is observed in the case of 7, which has no N-H bond in the substituent. This gives a striking contrast to the fluid media at 294 K. On the other hand, large deu-

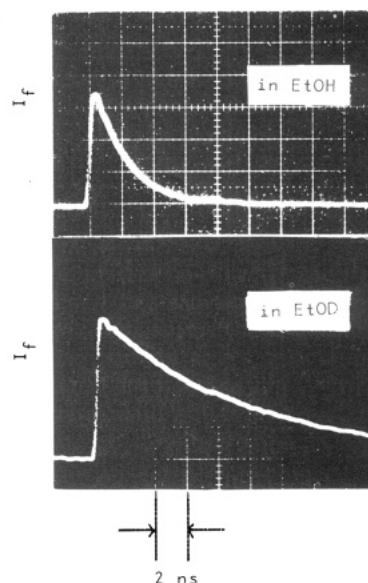


Figure 3. Deuterium isotope effect on the fluorescence time profile of 2 (1.00×10^{-4} M) by 355-nm excitation at 77 K in ethanol (EtOH) and ethanol-*O-d* (EtOD), monitored with a photomultiplier (Hamamatsu R1328U) connected with a Tektronix 7104 equipped with 7A29 and 7B10 plug-in units.

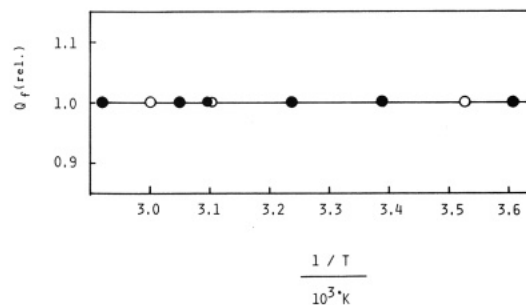


Figure 4. Effect of temperature on the fluorescence quantum yield of 2 in (●) ethanol and (○) ethanol-*O-d*.

terium effects are observed in 2 and 5, which have N-H bonds in their substituents.

Effect of Temperature on Fluorescence. The effect of temperature on the fluorescence quantum yield of 2 was investigated in ethanol and deuterated ethanol. As shown in Figure 4, the fluorescence quantum yield of 2 was independent of temperature in the range of 278–343 K in both solvents. The negligibly smaller value of the radiative rate constant (k_f) than the radiationless one (k_{nr}) in ethanol (Table I) indicates that the fluorescence quantum yield can be expressed by $Q_f = k_f/k_{\text{nr}}$. It is reasonable to assume that k_f is independent of temperature; thus, the results of Figure 4 strongly indicate that k_{nr} is not affected by temperature at all. The nonradiative process in ethanol does not require any appreciable activation energy (0 ± 1.7 kJ/mol).

Discussion

Deactivation in Benzene. Since $k_f(\text{obsd})$'s agree quite well with $k_f(\text{calcd})$'s for compounds with relatively weak electron-donating substituents (1, 2, and 5), the nuclear configurations of the fluorescent states are similar to those of the excited Franck-Condon states. The fluorescent states of the derivatives with relatively strong electron-donating substituents (3, 4, 6, and 7) have different nuclear configurations from those of the excited Franck-Condon states. These are well correlated with the CT natures of the excited states of the aminoanthraquinones; the higher degree of charge transfer in the excited state may cause

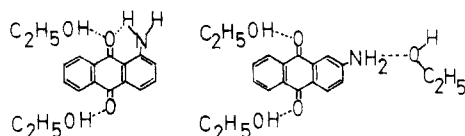


Figure 5. Hydrogen-bonded forms of 2 and 5 in the ground states in ethanol.

the larger alteration of the nuclear configurations.

As indicated in Table II, the nonradiative rate constants of 6 and 7, which have no N-H bond, are smaller than that of 5. Moreover, in rigid ethanol at 77 K deuterium isotope effects are observed in the cases of 2 and 5, which have N-H bonds, but not in the case of 7. Since the amino groups of 2 and 5 are supposed to be almost deuterated in ethanol-*O-d*, these results suggest that the N-H bond of the substituent plays a significant role in the inherent radiationless deactivation. The larger k_{nr} of 1-aminoanthraquinones than those of 2-amino derivatives in benzene also suggest that the intramolecular hydrogen bond between the carbonyl oxygen and the hydrogen atom of the amino group at position 1 accelerates the radiationless deactivation.

Deactivation in Polar Solvents. The larger deviations of $k_f(\text{obsd})$'s from $k_f(\text{calcd})$'s in polar solvents clearly indicate that all the excited aminoanthraquinones fluoresce from the states largely apart from the excited Franck-Condon states. A sudden appearance of a giant dipole by an intramolecular charge transfer in the excited state would induce a large reorientation of the surrounding solvent molecules from the Franck-Condon environmental configurations. By far the larger deactivation (k_{nr}) in ethanol than in acetonitrile and deuterium isotope effects also indicated that the O-H bond of ethanol plays a specific role in the radiationless deactivation of the excited aminoanthraquinones. In ethanol aminoanthraquinones are known to form hydrogen bonds in the ground states with solvent molecules. Fully hydrogen-bonded forms of 2 and 5 are shown in Figure 5.²¹ The oxygen atoms of the carbonyl groups of 2 interact with the hydrogen atom of ethanol and the hydrogen atoms of the amino group of 5 also interact with the oxygen atom of ethanol.²¹ The possibility that the hydrogen bond at the amino group participates in the deactivation processes is clearly eliminated by the observations that 6 and 7, which have no N-H bond, also suffer large deactivations in ethanol. Thus, the hydrogen bonds at the carbonyl groups of quinones are supposed to accelerate the nonradiative deactivation in ethanol. It is also suggested that reorientational motions of ethanol have an important role in the deactivation, since any deuterium isotope effect is not observed in the case of 7 in rigid matrix at 77 K in contrast to the result in the fluid media at 294 K. The pulse-limited rise of fluorescence indicates that reorientation of surrounding solvents is completed within the pulse duration and the fluorescence arises from a fully relaxed state at 294 K. After the rapid relaxation including environmental solvent configurations, the nonradiative dissipation (k_{nr}) of the electronic energy competes with the radiative decay (k_f). Thus, the observed data in ethanol are best rationalized as depicted in Figure 6. The excitations of hydrogen-bonded aminoanthraquinones to their ¹CT levels would induce reorientation of surrounding solvent molecules. In the relaxed fluorescent state, the hydrogen bonds between the hydroxyl groups of ethanol and the carbonyl groups of aminoanthraquinones would be strengthened considerably

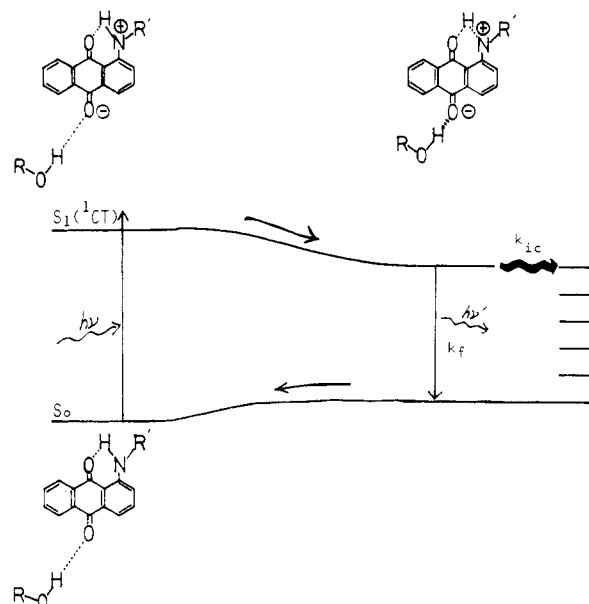


Figure 6. Radiationless deactivation via the intermolecular hydrogen bond with solvent.

by the increased electron density on the carbonyl oxygen because of the intramolecular CT nature of the excited state. That is, a weakly hydrogen-bonded ethanol molecule in the excited Franck-Condon state is supposed to be attached more closely to the carbonyl oxygen in the relaxed fluorescent state. Then the excited energy is mostly dissipated through the intermolecular hydrogen bond of $-\text{OH}\cdots\text{O}=\text{C}$. Taking the weakly hydrogen-bonded form as the initial state, the vibrational modes of the intermolecular hydrogen bonds are considered to act as accepting modes in the radiationless transition between the $S_1(^1\text{CT})$ and the ground state of aminoanthraquinone. The deuterium isotope effects may reflect the difference of the Franck-Condon factors in the radiationless transition. This is also supported by an absence of an appreciable activation energy in the nonradiative process (k_{nr}) (Figure 4); the observed deuterium effect can arise from the variation of the preexponential term of k_{nr} in deuterated ethanol from those in ethanol.

Dominant Modes of Radiationless Deactivation. The excited aminoanthraquinones are understood to have at least the following three modes of radiationless deactivation as predominant processes: deactivation (A) through the N-H bond, (B) through the intramolecular hydrogen bond, and (C) through the intermolecular hydrogen bond with solvent. The rate constant of the deactivation of mode A in 5 may be estimated to be on the order of $0.1 \times 10^9 \text{ s}^{-1}$. The deactivation of mode B in 2 is on the order of $0.5 \times 10^9 \text{ s}^{-1}$. These inherent deactivations of modes A and B are accelerated in acetonitrile to the extent of the order of $1.5 \times 10^9 \text{ s}^{-1}$. Mode C in ethanol has by far the larger contribution (3×10^9 – $25 \times 10^9 \text{ s}^{-1}$) to the radiationless deactivation than the others, and the fluorescence of aminoanthraquinones are almost quenched.

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