Investigation of the Dynamic Processes of the Excited States of *o*-Hydroxybenzaldehyde and *o*-Hydroxyacetophenone by Emission and Picosecond Spectroscopy

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Abstract: We have investigated the structures and dynamic processes of the excited states of *o*-hydroxybenzaldehyde (OHBA) and *o*-hydroxyacetophenone (OHAP) by means of emission and picosecond spectroscopy. It is shown that the main species existing in nonpolar solvents are intramolecularly hydrogen-bonded closed conformers from which proton or hydrogen transfer takes place. The Stokes shifted fluorescences originate from the transferred forms which are likely to be the enol tautomers. The main species in alcohols are intermolecularly hydrogen-bonded open conformers which phosphoresce at low temperatures, but fluorescing species also exist. OHBA in ethanol and methanol shows two different fluorescences with different decay times. It is suggested that one arises from the closed conformer of the enol form of OHBA, and the other is due to the strongly solvated open conformer. At 77 K in nonpolar solvents the closed conformer of OHBA is converted to the open conformer by UV irradiation changing the fluorescence into phosphorescence. The fluorescence decay rate constants are temperature dependent and are given as the sums of the radiative and nonradiative decay rate constants. From the picosecond measurements and the quantum yields of fluorescence we have estimated the rates of the transfer and the nonradiative decay rates of the closed conformers of OHBA and OHAP in nonpolar solvents at 77 K. It is concluded that the proton or hydrogen transfers are relatively slow and the nonradiative decays are dominant in the decay processes of the excited states of the closed conformers of OHBA and OHAP in nonpolar solvents. The slow transfer rates are attributed to the $^1n\pi^*$ characters of the S_1 states.

1. Introduction

In 1956 Weller found that methyl salicylate (abbreviated as MS) exhibits fluorescence with an unusually large Stokes shift.[1] This observation was explained in terms of the proton transfer in the excited state of the intramolecularly hydrogen-bonded MS. Since then the properties of the excited states of MS and related molecules have been investigated extensively.[2-14] In particular, the properties of the excited state of *o*-hydroxybenzophenone (OHBP) have attracted attention because of its use as a polymer-protecting agent.[15-23] More recently dynamic processes involving the excited states of the intramolecularly hydrogen-bonded molecules have been investigated with picosecond spectroscopy.[21-35] In most of the systems so far investigated proton transfer is considered to be complete within the duration of the excitation pulse ($\lesssim$10 ps). It has been also found that nonradiative processes are often important in decays of excited states.[24,29,32] Despite these investigations there seem to remain a number of unsolved questions. For example, in most of the systems rates of proton transfer have not been determined definitely. The exact mechanisms of proton transfer as well as those of nonradiative processes are often not well understood. There is a question about the nature of the fluorescent state of MS, whether it is a zwitterion or a tautomer.[25,32]

In the present work we have studied the emission properties of *o*-hydroxybenzaldehyde (OHBA) and *o*-hydroxyacetophenone (OHAP) by emission and picosecond spectroscopy. OHBA and OHAP are the simplest aromatic molecules with intramolecular hydrogen bonding involving carbonyl groups. The properties of these molecules are interesting in relation to those of MS, OHBP, and related molecules, but they seem to have received less attention. The luminescence properties of OHBA and OHAP are rather different from those of MS and OHBP. OHBA and OHAP fluoresce, but the quantum yields of their fluorescence are much smaller than that of MS.[14] MS shows dual fluorescence in nonpolar solvents, one in the UV and the other in the visible region,[1] but OHBA and OHAP show fluorescence only in the visible region.[14] Furthermore, we have noted that the low-temperature luminescence of OHBA changes from yellow fluorescence to blue phosphorescence upon irradiation of UV light. It was

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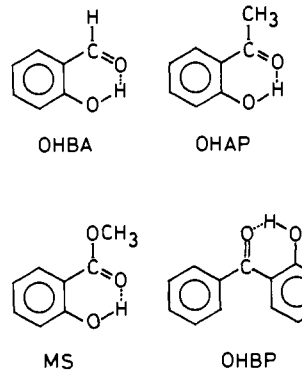

Figure 1. Molecular structures of *o*-hydroxybenzaldehyde (OHBA), *o*-hydroxyacetophenone (OHAP), methyl salicylate (MS), and *o*-hydroxybenzophenone (OHBP).

hoped that a combination of emission spectroscopy with picosecond spectroscopy would provide further useful information concerning the structures and dynamics involving the excited states of OHBA and OHAP.

Here we have studied the emission properties of OHBA and OHAP in different solvents at various temperatures. Their emission properties are very dependent on these factors, and we have tried to identify the species which are responsible for the different emissions. We have also studied the fluorescence decay and rise behavior by picosecond spectroscopy in order to determine the rates of the proton transfer and the nonradiative decays in the excited states of OHBA and OHAP. Here we discuss the decay properties of OHBA and OHAP in comparison with those of MS and OHBP (Figure 1).

2. Experimental Section

A. Sample Preparation. Commercially obtained OHBA and OHAP were purified by repeated distillations. 9,10-Dibromoanthracene and 9,10-diphenylanthracene obtained from Aldrich were used without further purification. Decalin (D) and 3-methylpentane (3MP) used as solvents were purified by column chromatography. Methylcyclohexane (MCH), methanol (MeOH), ethanol (EtOH), isopropyl alcohol (PrOH), isobutyl alcohol (BuOH), and cyclohexane (CH) were all of spectroscopic grade and were used without further purifications. Decalin and methylcyclohexane were mixed in a 1:1 volume ratio to obtain a mixed solvent (D/MCH).[36]

B. Absorption and Emission Spectra. The absorption spectra were taken with a Shimadzu UV-200 double-beam spectrometer and a Hitachi 556 double-wavelength, double-beam spectrophotometer. The fluorescence spectra were obtained with a Hitachi MPF-2A fluorescence spectrophotometer or a Shimdazu RF502 spectrophotometer. The phosphorescence spectra were obtained with our zero-field ODMR spectrometer reported previously.[37]

The fluorescence quantum yields ϕ_f of OHBA and OHAP were measured in comparison with that of 9,10-diphenylanthracene by exciting at the fluorescence maxima of OHBA and OHAP. The value of ϕ_f of 9,10-diphenylanthracene was assumed to be 1.0.[38] All samples were degassed by the freeze–pump–thaw method prior to measurements.

C. Picosecond Measurements. Picosecond measurements were made on the apparatus reported previously[39] using the third (355 nm) or fourth (266 nm) harmonic of a mode-locked Nd^{3+} YAG laser as a light source. A single pulse was selected and amplified. In order to obtain the decay curves, the fluorescence was observed with a streak camera (Hamamatsu C979) using the third harmonic of the laser. Lifetimes longer than 1 ns were measured with a photodiode (Hamamatsu R1328-02) and a storage oscilloscope (Tektronix 7104 1 GHz). The fluorescence rise curves were obtained by detecting the fluorescence signals with a streak camera (Hamamatsu C1370) and averaging the signals about ten times. The excitation was made with either the third or the fourth harmonic of the laser, and a 532-nm prepulse was used to provide a reference mark on the time axis for signal averaging. The decay and rise signals were processed with a minicomputer system (Hamamatsu C1000) and were handled with suitable programs for obtaining the decay and rise curves. In order to see the wavelength dependence of the fluorescence decay, a particular segment of the emission was selectively detected using Hoya interference filters having band passes of 10 nm.

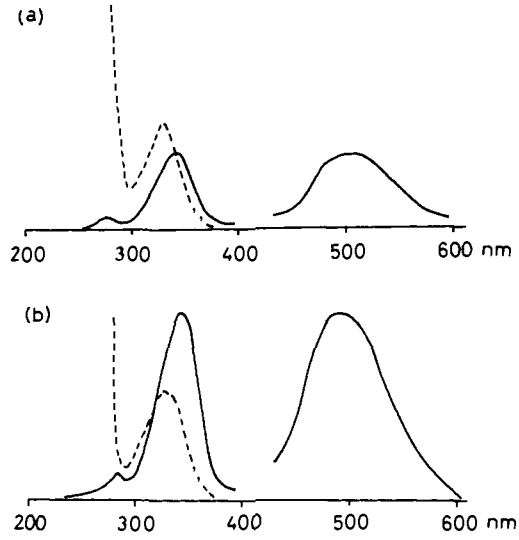

Figure 2. The absorption and emission spectra of OHBA and OHAP taken in nonpolar solvents. The intensity is arbitrary in each case. (a) The absorption (---) and uncorrected fluorescence and excitation spectra (—) of a 10^{-4} M solution of OHBA in D/MCH at room temperature. (b) The absorption (---) and uncorrected fluorescence and excitation spectra (—) of a 10^{-4} M solution of OHAP in D/MCH at room temperature.

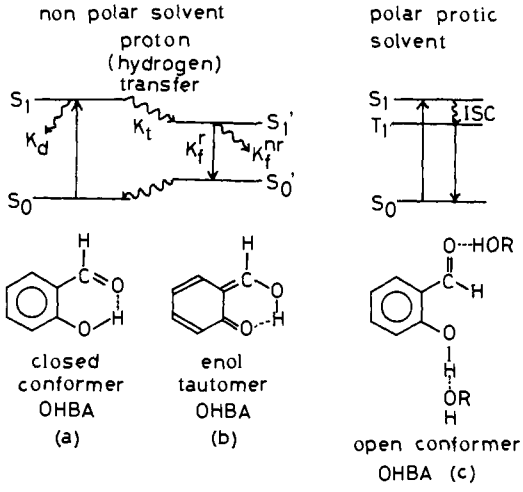

Figure 3. A schematic energy-state diagram for the dynamic processes of the major species of OHBA and related molecules in nonpolar and polar protic solvents. The straight and wavy lines represent radiative and nonradiative processes, respectively.

3. Results and Discussion

A. Absorption and Emission Spectra in Solution. The typical absorption and fluorescence spectra of OHBA and OHAP taken

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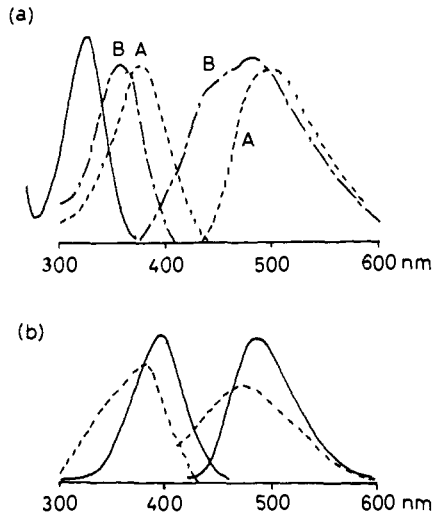

Figure 4. The absorption and emission spectra of OHBA and OHAP taken in alcohol. The intensity is arbitrary in each case. (a) The absorption spectrum (—) and the corrected fluorescence and the excitation spectra (A: ---) and (B: ---) of a 10^{-4} M solution of OHBA in EtOH at room temperature. The fluorescence spectra A and B were obtained by exciting at 415 and 355 nm, and the fluorescence excitation spectra A and B were obtained by monitoring the emissions at 520 and 420 nm, respectively. (b) The uncorrected fluorescence and excitation spectra of a 10^{-4} M solution of OHBA in PrOH (—) and OHAP in EtOH (---) at room temperature.

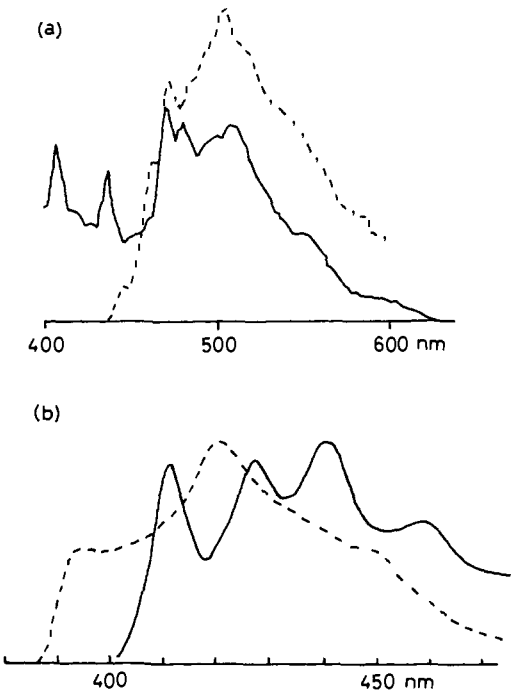

Figure 5. The emission spectra in rigid media at 77 K. The intensity is arbitrary in each case. (a) The solid curve represents the uncorrected fluorescence spectrum of a 10^{-5} M solution of OHBA in 3MP at 77 K. The spectrum is contaminated with the phosphorescence spectrum. The broken curve shows the corrected fluorescence spectrum of a 10^{-5} M solution of OHAP in 3MP at 77 K. (b) The solid and broken curves represent the emission spectra of a 10^{-4} M solution of OHBA and OHAP in EtOH at 77 K, respectively.

in nonpolar solvents at room temperature are shown in Figure 2. The fluorescence spectra are similar to those reported recently by Catalán et al.[14] The first absorption band covers the range 375–280 nm with $\epsilon_{max} \sim 4000$. This relatively large ϵ indicates that the absorption is due to a $S_0 \rightarrow {}^1\pi\pi^*$ transition as previously pointed out by Seliskar.[40] The $S_0 \rightarrow {}^1n\pi^*$ absorption of the aromatic carbonyls commonly observed in the range 370–340 nm are blue shifted because of hydrogen bonding and are presumably hidden by the stronger $S_0 \rightarrow {}^1\pi\pi^*$ absorptions. The fluorescence spectra show large Stokes shifted emissions with the maxima at ~510 nm for OHBA and ~490 nm for OHAP, respectively. The fluorescence spectra did not change with concentration in the range of $\sim 10^{-2}$–10^{-5} M. The fluorescence excitation spectra agree reasonably well with the absorption spectra showing that the Stokes shifted fluorescence originates from the main absorbing species. The main species existing in nonpolar solvents are considered to be intramolecularly hydrogen-bonded species (closed conformer in Figure 3). In analogy with the fluorescence of MS[1], the large Stokes shifted fluorescence spectra may be considered to originate from the proton-transferred forms of OHBA and OHAP, but the characters of these species will be discussed later.

The absorption spectra of OHBA and OHAP in polar protic solvents are similar to those obtained in nonpolar solvents as shown in Figure 4, but the fluorescence spectra are rather complicated. The fluorescence spectrum of OHBA in EtOH is dependent on the excitation wavelength, and the excitation spectra obtained by monitoring the emissions at 420 and 520 nm are different as shown in Figure 4a. This observation clearly indicates that there are at least two fluorescing species, one with the emission maximum at longer wavelength (species A) and the other at shorter wavelength (species B). The fact that the excitation spectra given in Figure 4a are different from the absorption spectrum indicates that the main absorbing species is not fluorescent. A similar result was obtained in MeOH, but in PrOH only the A species is dominant. In the case of OHAP and EtOH the A species seems to be dominant as shown in Figure 4b. The nature of these species is discussed in a later section.

B. Emission Spectra in Rigid Media at 77 K. The emission spectra of OHBA and OHAP in 3MP at 77 K are shown in Figure 5a. The OHAP spectrum is a Stokes shifted fluorescence spectrum with the 0–0 band at 445 nm. The emission spectrum of OHBA consists of the superposition of a similar Stokes shifted fluorescence spectrum and a phosphorescence spectrum. The origin of the phosphorescence spectrum is discussed in the next section. The quantum yields of the fluorescence were determined to be 0.024[41] and 0.081 for OHBA and OHAP, respectively, at 77 K. These values are very small compared with that of MS, but are larger than those reported for these molecules in gas and nonpolar solvents at room temperature by Catalán et al.[14] The Stokes shifted fluorescence is considered to arise from the species which are responsible for the solution fluorescence at higher temperatures.

The emission spectra of OHBA and OHAP in alcohols at 77 K consist only of phosphorescence spectra as shown in Figure 5b. The phosphorescence lifetimes were determined to be 58 and 85 ms for OHBA and OHAP, respectively. The OHBA spectrum in EtOH shows a band due to the CH out-of-plane wag, which is characteristic of a ${}^3\pi\pi^*$ aromatic carbonyl of the benzaldehyde type. This type of spectrum is usually found for benzaldehydes which are intermolecularly hydrogen bonded.[42-44] Therefore, the phosphorescence spectra of OHBA and OHAP in alcohols are likely due to the intermolecularly hydrogen-bonded conformers such as shown in Figure 3. This is in agreement with the suggestion previously made by Lamola and Sharp.[16] The phosphorescence excitation spectra agree well with the absorption spectra, indicating that the main species existing in polar protic solvents are intermolecularly hydrogen-bonded open conformers.

The open conformer of MS shows UV fluorescence,[1] but the open conformers of OHBA and OHAP rather show phosphorescence because the intersystem crossings in these carbonyls

(40) C. J. Seliskar, *J. Mol. Spectrosc.*, **53**, 140 (1974).

(41) This value is probably somewhat smaller than the real value because of contamination due to phosphorescence.

(42) A. J. Duben, L. Goodman, and M. Koyanagi in "Excited State", Vol. 1, E. C. Lim, Ed., (Academic Press, New York, 1974, p 295.

(43) E. C. Lim in "Excited State", Vol. 3, E. C. Lim, Ed., (Academic Press, New York, 1977, p 305.

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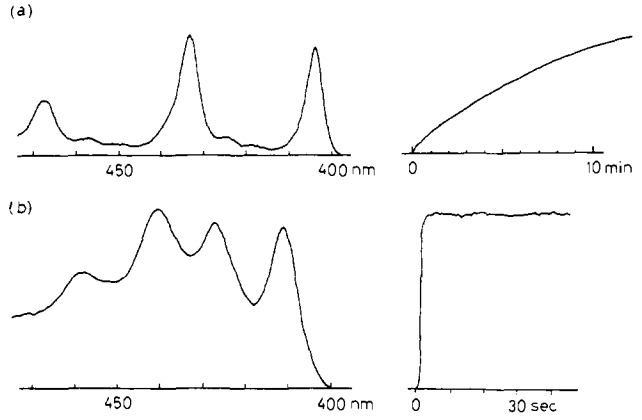
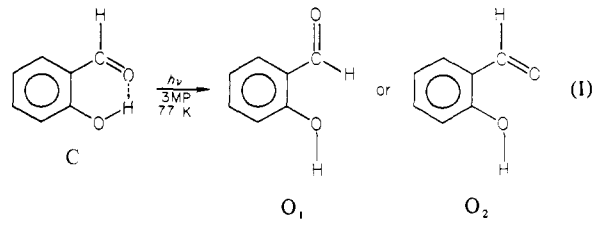


Figure 6. The phosphorescence spectra of OHBA at 77 K with the variations of the phosphorescence intensities with time. The intensity is arbitrary in each case. The excitation was made using a 900-W xenon lamp whose output was filtered with a $NiSO_4$ solution and a UV transmitting filter and was focused by a quartz lens: (a) OHBA in 3MP, (b) OHBA in EtOH.

are very efficient. As the temperature is raised the phosphorescence intensities and lifetimes gradually decrease because of the phosphorescence quenching and only fluorescence is observed at room temperature. However, the open conformers are considered to be dominant in solution at higher temperatures. The existence of such an open conformer was previously suggested for OHBP in ethanol from the T–T absorption at room temperature.[21]

C. Low-Temperature Emission and Photoisomerization. The fluorescence of OHBA in nonpolar solvents is quickly replaced by the phosphorescence upon irradiation. In Figure 6a we show the phosphorescence spectrum of OHBA in 3MP at 77 K together with the intensity change with time. It is seen that the phosphorescent species of OHBA in 3MP is produced by irradiation. This situation is in contrast to the case of OHBA in alcohols in which the phosphorescence intensities do not change with time as shown in Figure 6b and the phosphorescent species exists before irradiation. The phosphorescence spectrum in 3MP is characterized only by a progression of the C=O stretching mode, which is characteristic of a $^3n\pi^*$ aromatic carbonyl of the benzaldehyde type. The short lifetime ($\lesssim$3 ms) is also consistent with this assignment. The T_1 states of benzaldehyde and some substituted benzaldehyde in nonpolar solvents are $^3n\pi^*$ in character.[42,43] Thus benzaldehyde without hydrogen bonding is likely to be produced by irradiation. The conversion of the fluorescence spectrum into the phosphorescence spectrum is extremely slow in the case of OHAP.

The most plausible explanation for these observations is the following. The low-temperature fluorescence of OHBA in 3MP is due to the intramolecularly hydrogen-bonded closed conformer, and this is the main species existing in 3MP before irradiation but is quickly converted into an open conformer by irradiation as shown by eq I.



(I)

Both of the open conformers O_1 and O_2 can give rise to the $^3n\pi^*$-type phosphorescence in nonpolar solvents, but very slow conversion of the fluorescence into the phosphorescence in OHAP indicates that the above process is strongly suppressed by the larger size of the methyl group attached to the C=O group. This seems to indicate that rotation of the carbonyl group is involved. Thus the open conformer O_1 is favored. In polar protic solvents phosphorescence intensities do not change because the open conformers are the main species existing before irradiation.

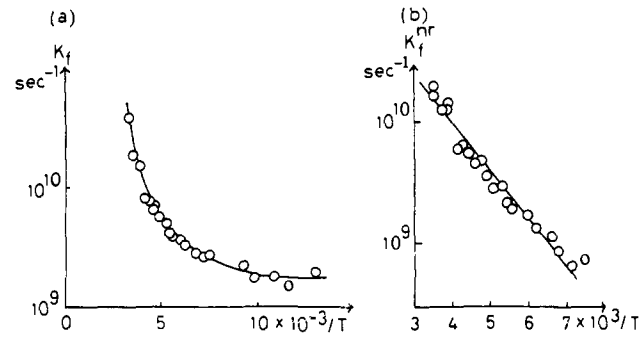


Figure 7. (a) Plot of log k_f vs. $1/T$. (b) Plot of log k_f^{nr} vs. $1/T$.

Nishimura et al. previously reported the phosphorescence spectra of OHBA in a number of mixed crystals at 4.2 K and discussed the spectra in terms of the intramolecularly hydrogen-bonded structures.[45] We have, however, found similar conversions of the fluorescence spectra into the phosphorescence spectra even in the mixed crystals. Therefore, we think that the phosphorescence spectra observed in the mixed crystals are also due to the photoinduced open conformers as in the case of 3MP glass.

D. Fluorescence Rise and Decay. We analyze the fluorescence rise and decay assuming the scheme given in Figure 3. The S_1 state of the closed conformer decays via the nonradiative decay process and the proton- or hydrogen-transfer process with the decay rate constants k_d and k_t, respectively. The transferred state (S_1') decays by radiative and nonradiative processes with decay rate constants k_f^r and k_f^{nr}, respectively. The fact that the quantum yield of the fluorescence is very small indicates that the nonradiative processes are dominant.

a. Fluorescence Decays in Nonpolar Solvents. The fluorescence decays in nonpolar solvents are well characterized by exponential decays. Figure 7a shows the temperature dependence of the fluorescence lifetime of OHBA in 3MP. The lifetime increases as the temperature is lowered and approaches a constant value at $\sim$100 K. The lifetime depends neither on the concentration in the range of $\sim 10^{-1}$–10^{-4} M nor on the wavelength at which the measurement was made. The fluorescence intensity also increases with increase of the lifetime as the temperature is lowered. Similar behavior was found for OHAP in 3MP. The behavior described here is very similar to that observed for the fluorescence decay of MS studied by Smith and Kaufmann.[24]

The fluorescence decay rate constant (k_f) is analyzed in terms of the sum of the temperature-independent radiative decay rate constant (k_f^r) and the temperature-dependent nonradiative decay rate constant ($k_f^{nr}(T)$):

$$k_f(T) = k_f^r + k_f^{nr}(T) \qquad (1)$$

k_f^r is estimated to be 1.9×10^9 s^{-1} for OHBA from the value of k_f at 77 K. This value is one order of magnitude larger than $k_f^r = 1.2 \times 10^8$ s^{-1} found for MS.[24] In Figure 7b the plot of log $k_f^{nr}(T)$ vs. $1/T$ is shown. It gives a satisfactory straight line and $k_f^{nr}(T)$ is given by $k_f^{nr}(T) = k_f^{nr}(\infty) \exp(-\Delta E/RT)$. An apparent activation energy (ΔE) of 1.7 $\pm$ 0.3 kcal/mol and a preexponential factor $k_f^{nr}(\infty)$ of 2.5×10^{11} s^{-1} were obtained. This activation energy is smaller than the 3.7–4.7 kcal/mol obtained for MS.[24] k_f^{nr} at room temperature is considerably larger than that for MS. Similar results were obtained in other nonpolar solvents as well as in the case of OHAP. The results are summarized in Table I.

It is shown that this ΔE's for OHAP are somewhat larger than those for OHBA. Preliminary results on a series of the related molecules show that ΔE depends considerably on the group attached to the carbonyl, which may indicate the importance of the carbonyl torsion in the nonradiative decay. However, further

(45) K. A. Martin, G. Moller, and A. M. Nishimura, *J. Phys. Chem.*, **80**, 2778 (1976).

Table I. Fluorescence Decay[a]

solute	solvent	τ_{298K} (ps)	τ_{77K} (ps)	ΔE (kcal/mol)	log $k_f^{nr}(\infty)$
OHBA	3MP	52	520	1.7 ± 0.3	11.4 ± 0.3
	D/MCH	75	780	1.9 ± 0.4	11.4 ± 0.3
	EtOH A	63	600	2.0 ± 0.6	11.4 ± 0.5
	B	~200	(≳5600)	8.9 ± 0.7	16.3 ± 0.5
OHAP	3MP	64	2500	2.8 ± 0.1	12.2 ± 0.1
	EtOH	83	2400	2.2 ± 0.2	11.7 ± 0.1
MS[b]	MCH	280	8330	3.7–4.7	

[a] τ denotes the fluorescence lifetime. $k_f^{nr}(\infty)$ is the extrapolated value of k_f^{nr} in the limit $T \to \infty$. [b] Taken from ref 24.

investigation is needed to establish the mechanism of the nonradiative decay.

b. Fluorescence Rise in Nonpolar Solvents. The representative examples of the fluorescence rises obtained by the excitation at 266 nm are shown in Figure 8. Similar rise curves were obtained by the excitation at 355 nm. The fluorescence rise of OHBA in D/MCH at 77 K is distinctly slower than those of 9,10-dibromoanthracene in CH and of OHBA at room temperature. We analyze the rise curves using the scheme given in Figure 3. The decay rates of S_1 and S_1' are given by

$$d[S_1]/dt = -(k_t + k_d)[S_1] \quad (2)$$

$$d[S_1']/dt = k_t[S_1] - k_f[S_1'] \quad (3)$$

where $[S_1]$ and $[S_1']$ denote the populations of S_1 and S_1', respectively. Integration of (2) and (3) yields

$$[S_1'] = [S_1]_0 \frac{k_t}{k_f - k_t - k_d}[\exp(k_f - k_t - k_d)t - 1] \exp(-k_f t) \quad (4)$$

where $[S_1]_0$ is the initial population of S_1. The fluorescence intensity $I(t)$ is then given by[46]

$$I(t) \propto \int_0^t \frac{k_t}{k_f - k_t - k_d} P_0(\tau)[\exp(k_f - k_t - k_d) \times (t - \tau) - 1] \exp(-k_f(t - \tau))\, d\tau \quad (5)$$

where $P_0(\tau)$ is the intensity of the excitation pulse at $t = \tau$. We have simulated the fluorescence rise and decay curves with different values of $k_t + k_d$ and the laser pulse shape. In order to ascertain that the observed slower rise of OHBA in D/MCH is genuine and not due to an artifact, we have simulated the fluorescence rise and decay curves of dibromoanthracene in CH at room temperature which is known to fluoresce with no delay time and expected to show the fluorescence rise due to the apparatus function. Taking the fluorescence decay rate constant as k_f, $I(t)$ is given as

$$I(t) \propto \int_0^t P_0(\tau) \exp[-k_f(t - \tau)]\, d\tau \quad (6)$$

As is shown in Figure 8 the simulated rise curve agrees very well with the experimental rise curve of dibromoanthracene. On the other hand, the rise curves of OHBA at 77 K cannot be simulated with eq 6, but are simulated well with eq 5. The simulation yields $k_t + k_d = 5.0 \times 10^{10}$ and 1.4×10^{11} s^{-1} for OHBA in D/MCH and OHAP in 3MP at 77 K, respectively. $k_t + k_d$ increases with temperature and the fluorescence rise was not observed clearly at room temperature ($k_t + k_d \gtrsim 2 \times 10^{11}$ s^{-1}).

If we consider that the low-temperature limiting values of the decay rate constants are due to the radiative process, the small values of the quantum yields indicate that the decays of the S_1 states are predominantly nonradiative, namely, $k_d \gg k_t$. The fluorescence quantum yield ϕ_f is given by

$$\phi_f = k_t k_f^r/(k_t + k_d)k_f \quad (7)$$

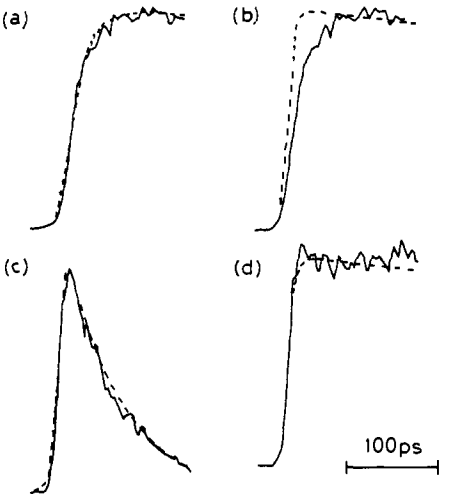


Figure 8. The fluorescence rise and decay curves. For each figure the solid lines are the observed ones obtained after averaging and the broken ones are the simulated ones. The curves shown here were obtained with the excitation at 266 nm, but similar results were obtained with the 355-nm excitation in all cases. (a) OHBA in D/MCH at 77 K simulated by eq 5; $k_t + k_d = 5.0 \times 10^{10}$ s^{-1}. (b) OHBA in D/MCH at 77 K simulated by eq 6. (c) OHBA in D/MCH at room temperature simulated by eq 6. (d) Dibromoanthracene in CH at room temperature simulated by eq 6.

where k_f and k_f^r are the total and radiative decay rate constants of the fluorescent state, respectively. With the assumption that $k_f^r/k_f = 1$, $\phi_f = 0.024$ for OHBA, and $\phi_f = 0.081$ for OHAP at 77 K, we obtain $k_t = 1.2 \times 10^9$ s^{-1}, $k_d = 4.9 \times 10^{10}$ s^{-1} and $k_t = 1.1 \times 10^{10}$ s^{-1} and $k_d = 1.3 \times 10^{11}$ s^{-1} for OHBA in D/MCH and OHAP in 3MP at 77 K, respectively. k_t's estimated in this way are much smaller than the rate constant for the proton transfer in 6-(2-hydroxy-5-methylphenyl)-*s*-triazine (abbreviated as triazine) ($k_t > 5 \times 10^{11}$, $\sim 10^{12}$ s^{-1}) and MS ($k_t \geq 10^{11}$ s^{-1}).[24] Whether $k_f^r/k_f \simeq 1$ is true is not certain here, but $k_d > k_t$ should still hold, even if k_f contains a large nonradiative decay rate constant. Therefore, it is concluded that the nonradiative deactivation process dominates over the transfer process, and the transfer rates in OHBA and OHAP are relatively slow. This is a characteristic which is quite different from that found for MS.[24] We discuss the possible reasons for this below.

It is considered that the intramolecular hydrogen bonding causes a blue shift of the $^1n\pi^*$ state, and the $^1n\pi^*$–$^1\pi\pi^*$ separation becomes small. However, the S_1 state may still be dominantly $^1n\pi^*$ in character for the following reasons. The absence of the UV fluorescence at ~77–300 K in spite of the relatively small value of $k_t + k_d$ indicates that the emission efficiency of the S_1 state is rather small. This seems to be in favor of the $^1n\pi^*$ character of the S_1 state of OHBA and OHAP in contrast to the $^1\pi\pi^*$ character of the S_1 state of MS. In the $^1n\pi^*$ state the oxygen atom becomes more positive by promoting a nonbonding electron to a more delocalized π^* orbital. Then the basicity of the carbonyl group is decreased and the proton transfer will be more difficult. On the other hand, it is well known that hydrogen abstraction takes place easily in the $n\pi^*$ carbonyl. Therefore, in the $^1n\pi^*$ state of the closed conformer of OHBA, the hydrogen atom rather than proton may be transfered from the OH group to the carbonyl group, yielding the enol tautomer of OHBA (Figure 3b). If this is the case, the process to produce the fluorescent state is more properly called hydrogen transfer. We think that the difference in the transfer rates between MS and OHBA is mainly due to the difference in the characters of the S_1 states.

The present result shows that the nonradiative deactivation process from the S_1 state is dominant. Rapid nonradiative deactivation of the S_1 state has been noted in the cases of OHBP,[21] triazine,[48,49] and 2-(2′-hydroxy-5′-methylphenyl)benzotriazole

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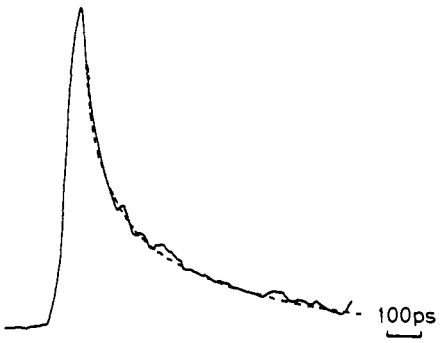

Figure 9. The fluorescence decay of OHBA in EtOH, monitoring the emission at 463 nm at room temperature. (---) represents the simulated curve.

(abbreviated as triazole).[50] In OHBP Merritt et al. considered that proton transfer in the S_1 state and/or intersystem crossing (ISC) from the S_1 state to the triplet state are (is) responsible for the decay of the S_1 state. In the case of triazine, Sizuka et al. seem to be in favor of the internal conversion (IC) of the S_1 state associated with the out-of-plane vibration of the hydroxy group, while Huston et al. suggested the importance of the rapid proton transfer tautomerization between the vibrationally unrelaxed S_1 and S_1' (tautomer) states with the internal conversion of the S_1 state in the case of triazole. Since proton-transfer rates are slow in the present system, nonradiative deactivation must take place from the S_1 states. An important characteristic of the present system is that the $^1n\pi^*$ and $^1\pi\pi^*$ states are close to each other. Therefore, rapid internal conversion due to the distortions of the molecules caused by the pseudo-Jahn–Teller effect may be important.[51] However, ISC to the triplet states can be effective for the following reasons.

In the intramolecularly hydrogen-bonded OHBA and OHAP, the T_1 states are probably $^3\pi\pi^*$ states as in the cases of intermolecularly hydrogen-bonded OHBA and OHAP. In such aromatic carbonyls ISC processes

$$\text{(a)}\quad {}^1\pi\pi^* \overset{IC}{\rightsquigarrow} {}^1n\pi^* \xrightarrow{ISC} {}^3\pi\pi^*$$

$$\text{(b)}\quad {}^1\pi\pi^* \xrightarrow{ISC} {}^3n\pi^* \overset{IC}{\rightsquigarrow} {}^3\pi\pi^*$$

are expected to occur effectively. Indeed $k_d = 5 \times 10^{10}\ s^{-1}$ is in the same order of magnitude as the ISC rates determined for a number of aromatic carbonyls,[52-55] and it does not seem unreasonable to assume that the ISC rates of OHBA and OHAP are of this magnitude.

If the ISC process is also taking place effectively, we may expect to see the phosphorescence of the closed conformer in the rigid matrices. The observation that the phosphorescence of OHBA is due only to the open conformer produced by irradiation and that OHAP does not phosphoresce in nonpolar rigid matrices seems to contradict this expectation. A possible way to resolve this contradiction is to assume that proton transfer also takes place in the T_1 state and no phosphorescence of the closed conformer is observed. The possibility of such a proton transfer in the triplet state has been discussed recently by Merritt et al.[22] to explain the transient absorption spectrum of OHBP. However, further investigation including the triplet–triplet absorption spectroscopy is needed to confirm this possibility.

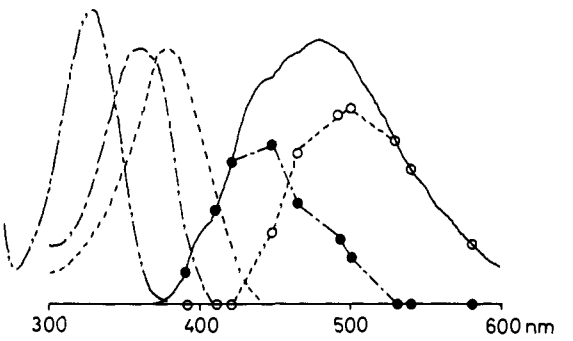

Figure 10. The absorption (—·--·—) and the corrected fluorescence spectra (—) of a 10^{-4} M solution of OHBA in EtOH obtained by exciting at 355 nm. Open circles and solid circle show $A_1f(\lambda)I_0(\lambda)$ and $A_2(1 - f(\lambda))I_0(\lambda)$ at room temperature, respectively. (---) and (—·—) give the corrected excitation spectra obtained by monitoring the emission at 520 and 420 nm, respectively.

c. Fluorescence Decays in Polar Protic Solvents and the Characteristics of the Fluorescing Species. The fluorescence of OHBA in EtOH shows decays with two different decay times. We have studied decay curves by observing the emissions at different wavelengths at room temperature. A representative decay curve is shown in Figure 9 together with the simulated one. The simulation was made with the double exponential decay,

$$I(t,\lambda) = A_1f(\lambda)\exp(-t/\tau_1) + A_2(1 - f(\lambda))\exp(-t/\tau_2) + B \tag{8}$$

where τ_1 and τ_2 are the lifetimes of the two components which give rise to different decays. f refers to the fraction of the component with the lifetime τ_1. A_1 and A_2 denote the amplitude parameters and B is the baseline one. The obtained decay curves can be fitted very well by eq 8. The fraction of each component to fit the observed decay depends on the wavelength at which the emission was detected. We have attempted to resolve the fluorescence spectrum into those of A and B species by plotting $A_1f(\lambda)I_0(\lambda)$ and $A_2(1 - f(\lambda))I_0(\lambda)$ vs. wavelength λ. $I_0(\lambda)$ denotes the steady-state fluorescence intensity obtained by excitation at 355 nm. The result is shown in Figure 10. The spectrum of the A species has a maximum at ~500 nm and is very similar to those of the Stokes shifted fluorescence spectra of OHBA in nonpolar solvents. The lifetime of the A species is also similar to the fluorescence lifetimes of OHBA in nonpolar solvents. On the other hand, the spectrum of the B species has a maximum at ~430 nm and its lifetime is much larger. The results are summarized in Table I. At present we cannot make an unambiguous assignment of the A and B species, but we suggest possible explanations in the following.

The fact that the fluorescence spectra and lifetime of the A species are very similar to those obtained in nonpolar solvents seems to indicate that the A species are the closed conformers which are responsible for the fluorescence in nonpolar solvents. Existence of the closed conformer also has been suggested for OHBP in ethanol.[21] However, the closed conformer shown in Figure 3 cannot explain the excitation spectra of the A species which are red shifted from the absorption spectra of OHBA in nonpolar solvents by ~50 nm. This observation shows that the structure of the ground state of the A species is not the same as that of OHBA in nonpolar solvents. These observations can be explained if the closed conformers of OHBA in polar protic solvents exist as the enol form (shown in Figure 3b) in the ground state. In this connection the work by Migirdicyan et al.[56] on *o*-methylbenzaldehyde is suggestive. Upon irradiation *o*-methylbenzaldehyde in durene develops coloration due to absorption, with the maximum at 405 nm. This absorption was attributed to the enol created from *o*-methylbenzaldehyde by hydrogen transfer from the methyl group to the carbonyl group.[56] The enol forms of OHBA and OHAP are expected to have ab-

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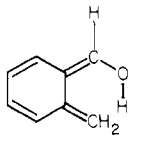

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sorptions similar to enol I. The observed excitation spectra of OHBA and OHAP are indeed similar to the absorption spectrum of I.

The B spectrum has no large Stokes shift and its excitation spectrum is only slightly shifted from the absorption spectrum, which seems to be in favor of the open conformation. This spectrum is seen for OHBA in EtOH and MeOH, not in PrOH and BuOH. Thus strong solvation of alcohol seems to be needed for the appearance of this spectrum. In the strongly solvating protic solvents OHBA may exist in differently solvated structures. In the more strongly solvated species the $^1n\pi^*$ state of OHBA is further blue shifted and its $^1\pi\pi^*$ state may become the S_1 state. The B fluorescence may come from the S_1 state of such a species.

4. Summary

The Stokes shifted fluorescence of OHBA and OHAP in nonpolar solvents take place from the excited states of the proton or hydrogen-transferred forms (S_1') of the closed conformers which are likely to be the enol forms. At 77 K the transfer rates are rather slow and the nonradiative decays are dominant in the decay processes of the excited states (S_1). The decay rate constants of the transferred form (S_1') are given by the sums of the temperature-independent radiative decay rate constants and the temperature-dependent nonradiative decay rate constants. The main species of OHBA and OHAP in alcohols are open conformers which phosphoresce at low temperature. However, fluorescence spectra similar to those found in nonpolar solvents are also obtained in alcohols. It is suggested that the fluorescence originates from OHBA and OHAP which exist in the enol forms in the ground state and the strongly solvated open conformers of OHBA. The closed conformer of OHBA is converted into the open conformer by UV irradiation in nonpolar solvents at 77 K.

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Registry No. OHBA, 90-02-8; OHAP, 118-93-4; MS, 119-36-8; OHBP, 117-99-7.

Effect of Solvation on the Acid/Base Properties of Glycine

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Abstract: The gas-phase acidity and basicity of glycine and several of its methyl-substituted isomers have been measured by pulsed ion cyclotron resonance (ICR) mass spectrometry. The amino acids were introduced into a heated, ultra-high-vacuum chamber using a direct insertion probe. Their partial pressures were measured directly, and these values were used in calculating equilibrium constants for gas-phase proton-transfer reactions. The proton affinity of glycine ($\Delta H°$ for $GlyH^+ \rightarrow H^+ + Gly$) is 213 kcal/mol, and the heterolytic bond dissociation energy ($\Delta H°$ for $Gly \rightarrow H_2NCH_2CO_2^- + H^+$) is 342 kcal/mol. Glycine is a zwitterion in the crystalline state and in aqueous solution, but the pulsed ICR experiments indicate that it is not a zwitterion in the gas phase. Thermodynamic cycles have been constructed for transfer of the protonated and deprotonated forms of glycine from the gas phase to aqueous solution. The heat of solvation for $^+H_3NCH_2CO_2H$ is −87.1 kcal/mol, and the heat of solvation of $H_2NCH_2CO_2^-$ is −90.7 kcal/mol.

It is widely known that in aqueous solution and in the crystalline state α-amino acids have the structure of a dipolar ion, or zwitterion. They are appreciably soluble only in water and do not melt until they decompose at almost 300 °C, which is consistent with the "salt-like" dipolar ion structure. There are two ionizable groups in aqueous solution having pK_a values around 2 and 9. Taking glycine as an example, the first pK_a at 2.3 is what one expects for ionization of a carboxyl group.

$$^+NH_3CH_2CO_2H = H^+ + {}^+NH_3CH_2CO_2^- \qquad \Delta G°_{aq} = 3.2 \text{ kcal/mol} \quad (1)$$

This pK_a value is consistent with that of acetic acid ($pK_a = 4.8$) and the presence of a strong electron-withdrawing effect of the positive ammonium group which stabilizes the glycine dipolar ion.[1] The second acid dissociation for glycine has a pK_a of 9.6 and corresponds to the reaction:

$$^+NH_3CH_2CO_2^- = H^+ + NH_2CH_2CO_2^- \qquad \Delta G°_{aq} = 13.3 \text{ kcal/mol} \quad (2)$$

This is similar to the ethylammonium ion which has a pK_a of 10.7. Thus, in aqueous solution the basicity of glycine (the reverse of reaction 1) is similar to that of acetate ion, and its acidity (reaction 2) is similar to that of an alkylammonium ion.

Little is known about the acid/base properties of the α-amino acids in the gas phase, yet comparisons of the gas-phase and solution-phase data would be of fundamental importance. It would be interesting to know if zwitterions exist in the gas phase and how the hydration enthalpies of the protonated and deprotonated α-amino acids compare with simpler analogues.

Recently we reported the first measurements of the gas-phase acidity and basicity of glycine.[2] Using a pulsed ion cyclotron resonance (ICR) mass spectrometer with an ultra-high-vacuum

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