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Investigation of the Dynamic Processes of the Excited States of *o*-Hydroxybenzaldehyde and Its Derivatives. 2. Effects of Structural Change and Solvent

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Abstract: We have investigated the structures and dynamic processes of the excited states of *o*-hydroxybenzaldehyde (OHBA) and its derivatives by means of steady-state and picosecond transient emission spectroscopy. From the dependence of the fluorescence decay rate constant of OHBA on the dielectric constant of the solvent, it is shown that the Stokes-shifted fluorescence is likely to originate from the excited state of the enol tautomer. The temperature dependence of the fluorescence decay rate of *o*-hydroxypropiophenone (OHPP) is quite different from that of 7-hydroxy-1-indanone (7HIN) which has a more rigid structure around the carbonyl group. From this result it is suggested that out-of-plane bending and/or torsional motion involving the carbonyl carbon is important in the nonradiative decay processes of OHBA and its derivatives. At 77 K in alcohols the closed conformer of OHPP is converted to the open conformer by UV irradiation changing the fluorescence into phosphorescence. The cause of this change is examined in comparison with that found in OHBA.

1. Introduction

The dynamic process involving the excited state of intramolecularly hydrogen-bonded molecules is a topic of current interest.[1-13] In a preceding paper[2] we have discussed the structures and the dynamic processes of the excited states of *o*-hydroxybenzaldehyde (abbreviated as OHBA) and *o*-hydroxyacetophenone (OHAP) in various solvents studied by emission spectroscopy. Some of the conclusions obtained there are as follows: (1) The Stokes shifted fluorescence originates from the excited states of the proton or hydrogen transferred forms which are considered to be enol tautomers of the closed conformers. (2) The fluorescence decay rate constants are given by the sums of the radiative and nonradiative decay rate constants. The nonradiative decay rate constants are strongly temperature dependent. (3) In the rigid nonpolar solvents at 77 K the fluorescence of OHBA is quickly replaced by the phosphorescence during irradiation which was ascribed to the photochemical isomerization.

Concerning these conclusions, however, there remained important questions. First, enol tautomers were considered for the fluorescing species, but definitive experimental evidences to make this assignment were lacking. This is particularly serious because a zwitterionic structure has been suggested for the excited state of methyl salicylate (MS).[14] Second, the exact mechanism for the temperature-dependent nonradiative decay process has not been established well. In view of the wide occurrence of such a process in the excited states of hydrogen-bonded molecules[3,15,16] it seems desirable to obtain further information about the mechanism of this process. Third, the interesting observation about the change in the luminescence property during irradiation seems to merit further investigations. It seems worthwhile to find other examples for such a change.

In the present work we have attempted to answer these questions. In order to obtain further information about the nature of the fluorescing species, we have examined the dependence of the fluorescence decay rate constant of OHBA on the dielectric constant of the solvent. As to the second question about the mechanism of the temperature-dependent nonradiative decay, there have been suggestions that the bending and/or torsional motion involving the carbonyl group might be crucial.[4,16,17] We have, therefore, compared the temperature dependence of the fluorescence decay rate of *o*-hydroxypropiophenone (OHPP) with that of 7-hydroxy-1-indanone (7HIN) which has a more rigid structure around the carbonyl group. Finally, we have also found a change in the luminescence property of OHPP during irradiation, and we examined its cause in comparison with that found in OHBA.[2] In Figure 1 we give the structures of the molecules studied in this work.

2. Experimental Section

A. Sample Preparation. Commercially obtained OHBA and OHPP were purified by repeated distillation. 7HIN (mp 114–115 °C) was synthesized by the Friedel-Craft reaction of phenyl-β-chloropropionate which was obtained by the Schotten–Bauman reaction of phenol with β-chloropropinyl chloride.[18] The product was extracted with CH_2Cl_2 and purified by recrystallization from CCl_4 followed by column chromatography. 3-Methylpentane (3MP) and decalin (D) used as solvents were purified by column chromatography. *n*-Heptane (H), methanol (MeOH), ethanol (EtOH), isopropyl alcohol (PrOH), isobutyl alcohol (BuOH), acetonitrile (ACN), propionitrile (PCN), butyronitrile (BCN), 1,2-dichloroethane (DCE), *N*,*N*-dimethylformamide (DMF), tetra-

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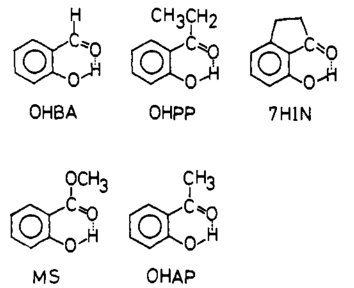

Figure 1. Molecular structures of *o*-hydroxybenzaldehyde (OHBA), *o*-hydroxypropiophenone (OHPP), 7-hydroxy-1-indanone (7HIN), methyl salicylate (MS), and *o*-hydroxyacetophenone (OHAP).

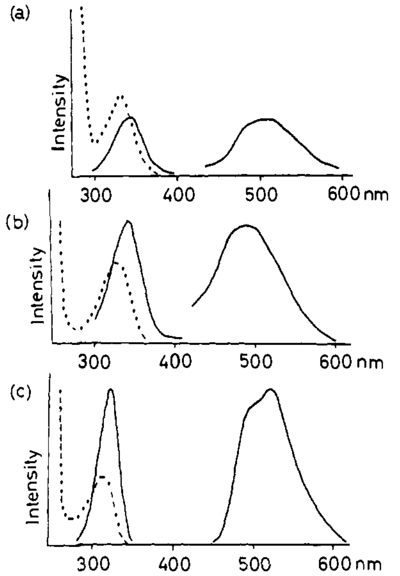

Figure 2. Absorption (---) and fluorescence emission and excitation spectra (uncorrected) (—) of OHBA, OHPP, and 7HIN taken in 3MP at room temperature. The intensity is given in arbitrary units: (a) 10^{-4} M solution of OHBA; (b) 10^{-4} M solution of OHPP; and (c) 10^{-4} M solution of 7HIN.

hydrofuran (THF), and methylene chloride (MC) were all of spectroscopic grade and were used without further purifications.

B. Absorption and Emission Spectroscopy. The absorption spectra were taken with a Shimadzu UV-200 double-beam spectrometer. The fluorescence emission and excitation spectra were taken with a Hitachi MPF-2A fluorescence spectrometer. The phosphorescence spectra were obtained with our zero-field ODMR spectrometer reported previously.[19] In studying the variation of phosphorescence intensity with time, we used the light from a Xenon arc (XBO 900) filtered through a water solution saturated with $NiSO_4$ and a UVD33S Toshiba filter (maximum transmittance at 325 nm). The variation of the phosphorescence was observed by monitoring the emission at 420 nm.

C. Picosecond Measurements. Picosecond measurements were made on the apparatus reported previously[20] with use of the third harmonic (355 nm) of a mode locked Nd:YAG laser as the 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). The lifetime longer than 1 ns was measured with a biplanar photodiode (Hamamatsu R1328-02) and a 1-GHz oscilloscope (Tektronix 7104). The decay signals were handled with suitable programs for obtaining the decay times.

3. Results and Discussion

A. Absorption, Fluorescence, and Excitation Spectra and Fluorescence Decay Scheme. The absorption, fluorescence, and excitation spectra of OHBA, OHPP, and 7HIN taken in 3MP at room temperature are shown in Figure 2. The spectra of OHPP are similar to those of OHBA and OHAP reported in the previous paper.[2] The fluorescence spectra of OHPP and 7HIN both show large Stokes shifts, but the shift is considerably larger in the case of 7HIN. The fluorescence excitation spectra agree reasonably well with the absorption spectra showing that the Stokes-shifted fluorescence originates from the main absorbing species which are considered to be intramolecularly hydrogen-bonded species (closed conformer). As in the case of OHBA and OHAP[2] the Stokes-shifted fluorescence emissions are considered to arise from the proton-transferred forms of the closed conformers. OHPP in 3MP at 77 K exhibits a yellow fluorescence similar to that observed at room temperature, and the fluorescence does not change under UV irradiation. The emission of 7HIN in 3MP at 77 K consists of the superposition of a similar yellow fluorescence and a weak blue phosphorescence. The absorption and fluorescence spectra of OHPP taken in EtOH are also shown in Figure 3. They are similar to those obtained in 3MP suggesting that the fluorescing species is similar to that in 3MP. The luminescence property of OHPP in alcohol at 77 K is discussed in the later section.

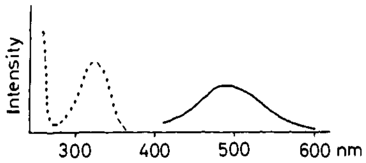

Figure 3. Absorption (---) and fluorescence emission spectra (uncorrected) (—) of a 10^{-4} M solution of OHPP taken in EtOH at room temperature. The fluorescence spectrum was obtained by excitation at 340 nm. The intensity is given in arbitrary units.

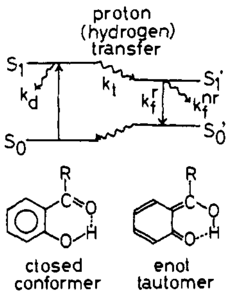

Figure 4. A schematic energy-state diagram for the dynamic processes of OHBA and the related molecules in nonpolar solvents. The straight and wavy lines represent radiative and nonradiative processes, respectively.

We consider the excitation and the decay process using the scheme given in Figure 4, though the exact natures of the S_1, S_1', and S_0' states are not well established in the case of the present system.[21]

B. Fluorescence Decay in Nonpolar Solvents. The fluorescence decays observed in 3MP are all well characterized by single exponential decays. As in the cases of OHBA and OHAP studied previously,[2] the fluorescence decay rate constant (k_f) is given by the sum of the temperature-dependent nonradiative decay rate constant ($k_f^{nr}(T)$) and the temperature-independent decay rate constant k_f^0,

$$k_f(T) = k_f^0 + k_f^{nr}(T) \qquad (1)$$

In the case of OHBA and OHPP in 3MP at room temperature, $k_f^{nr}(T)$ is much larger than k_f^0 and the room-temperature decay rate constants (k_f) represent the decay rate constants of the nonradiative processes.

a. Solvent Dependence of the Room-Temperature Decay Rate Constant. In Table I we give the decay rate constants of OHBA observed in various solvents[23,24] at room temperature. In Figure 5 we show the relationship between k_f and the dielectric constant (ϵ) of the solvent. The dependence seems to be rather different depending on whether the solvent is an alcohol or nonalcoholic. In nonalcoholic solvent k_f seems to increase very slightly with the increase of ϵ, whereas in alcohols k_f appears to increase more with the increase of ϵ. In Figure 6 we give the correlation between k_f

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Table I. Fluorescence Lifetime of OHBA Closed Conformer at Room Temperature

solvent	$10^{-10}k_f$, s	viscosity,[a] cP	dielectric constant[a]
3MP	1.9	0.307	1.895
H	2.0	0.4370	1.924
D	1.4	2.415	2.1542
MeOH	1.9	0.5506	32.70
EtOH	1.6	1.078	24.58
PrOH	1.1	2.859	19.92
BuOH	1.0	4.210	16.56
THF	2.0		7.58
ACN	2.3	0.345	37.5
PCN	2.4	0.454	27.2
BCN	2.2	0.624	20.3
DMF	2.0		36.71
MC	2.1	0.449	8.93
DCE	2.1	0.887	10.36

[a] References 23 and 24.

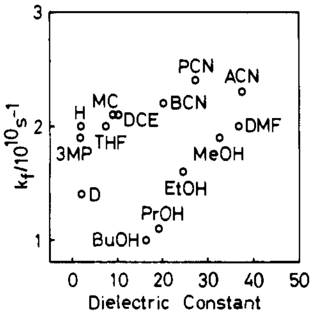


Figure 5. Plot of k_f vs. the dielectric constant of the solvent.

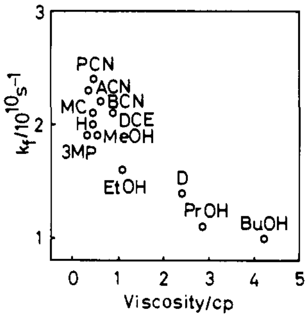


Figure 6. Plot of k_f vs. the viscosity of the solvent.

and the viscosity of the solvent. Though the points are somewhat scattered, k_f seems to increase as the viscosity of the solvent decreases. Therefore, the large increase of k_f with ϵ in the case of alcohol is likely to be due, at least partly, to the decrease of the viscosity. From the results given in these two figures we conclude that k_f is dependent on ϵ only very slightly and that the viscosity of the solvent affects k_f considerably. Since k_f is due, to a large extent, to the nonradiative decay, this conclusion is applicable to k_f^{nr}.

The present result on the solvent dependence of k_f^{nr} of OHBA is very different from that observed for MS by Smith and Kaufmann.[14] They found that there is a good correlation between the dielectric constant of the solvent and k_f^{nr} and that k_f^{nr} does not depend on the viscosity of the solvent. On the basis of these results they suggested a zwitterionic structure for the fluorescing state of MS. The present result, on the other hand, shows that the fluorescing state of OHBA is likely to be less ionic, perhaps more like an enolic tautomer as suggested in the previous paper.[2] The viscosity dependence seems to show that the internal motion of OHBA is also important in the nonradiative decay process, but this point is further discussed in the later section. It is interesting to note that the solvent dependence of k_f^{nr} of OHBA is rather different from that of MS in spite of the similarity of the molecular structure. Replacement of the hydrogen atom of the formyl group by a methoxy group seems to change the nature of the fluorescence state significantly.

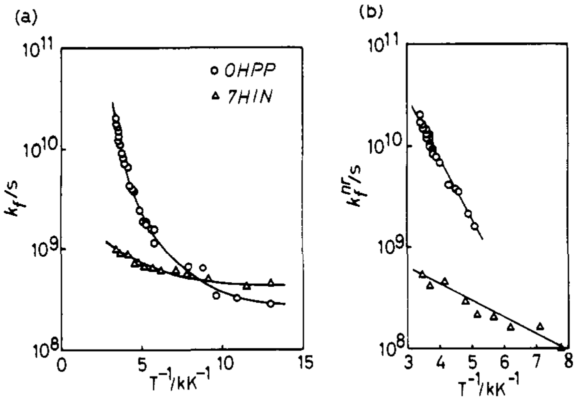


Figure 7. (a) Plot of log k_f vs. $1/T$ for OHPP and 7HIN in 3MP. (b) Plot of log k_f^{nr} vs. $1/T$ for OHPP and 7HIN in 3MP.

b. Temperature Dependence of the Nonradiative Decay Rate Constants of OHPP and 7HIN. The nonradiative decay rate constants (k_f^{nr}) of MS, OHBA, OHAP, and 2-(2′-hydroxyphenyl)benzothiazole and 2-(2′-hydroxy-5′-methylphenyl)benzothiazole are known to be strongly temperature dependent[2,3,15,16] and are given by approximately by

$$k_f^{nr}(T) = k_f^{nr}(\infty)\exp(-E_a/RT) \tag{2}$$

where E_a denotes an apparent activation energy. In Figure 7 we give the temperature dependence of k_f and $k_f^{nr}(T)$ for OHPP and 7HIN. It is seen that the temperature-dependent nonradiative decay process is strongly suppressed on going from OHPP to 7HIN. The plots of $k_f^{nr}(T)$ vs. $1/T$ give satisfactory straight lines for both molecules, but the values of $k_f^{nr}(\infty)$ as well as E_a are remarkably different. In OHPP we obtain E_a = 2.7 ± 0.3 kcal/mol and $k_f^{nr}(\infty) = 1.6 \times 10^{12}\ s^{-1}$, which are similar to those obtained for OHAP. On the other hand, for 7HIN we obtain E_a = 0.8 ± 0.2 kcal/mol and $k_f^{nr}(\infty) = 2.0 \times 10^{9}\ s^{-1}$, which are much smaller than those obtained for the other molecules in this series.[2,3,15,16]

Temperature dependence of the nonradiative decay of MS in solution has been discussed recently in connection with the increase of the nonradiative decay rate of the excited MS in the supersonic nozzle beam.[4,17] It was found by Felker et al.[17] that the threshold of the decrease of the lifetime of MS in the gas phase is in excellent agreement with E_a determined for MS by Smith and Kaufmann[15] suggesting that the increase in the nonradiative decay rate of MS in solution is caused by the thermal excitation to the higher vibrational levels with larger nonradiative decay rate constants. Felker et al. consider that the out-of-plane bending motion of the ring including the intramolecular hydrogen bond is involved in this process.[17] Heimbrook et al. also found that the S_1 state of MS is strongly coupled to a nonradiative decay channel, when the vibrational energy exceeds about 1500 cm^{-1}. They considered that this process is induced by a large-amplitude out-of-plane vibration in the ring containing the hydrogen bond. Barbara and co-workers suggested that the nonradiative decay processes in the derivatives of benzothiazole involve the torsional motion.[16] As in the case of MS and benzothiazoles, out-of-plane bending and/or torsional motion involving the carbonyl carbon would also be important in the nonradiative decay process of OHPP. Presence of a rigid five-membered ring in 7HIN makes such out-of-plane motions much more difficult than in OHPP suppressing the nonradiative decay drastically. Furthermore, the viscosity of the solvent would also affect such motions making k_f^{nr} viscosity dependent. Therefore, the present results seem to provide a further support for the suggestion that the out-of-plane bending and/or torsional motion involving the carbonyl carbon is important in inducing the nonradiative decay.[4,16,17]

C. Low-Temperature Emission and Photoisomerization in Alcohol. Though the low-temperature yellow fluorescence of OHPP in 3MP is not changed by prolonged UV irradiation, the fluorescence of OHPP is replaced by a blue phosphorescence in EtOH at 77 K. In Figure 8 we show the change of the phos-

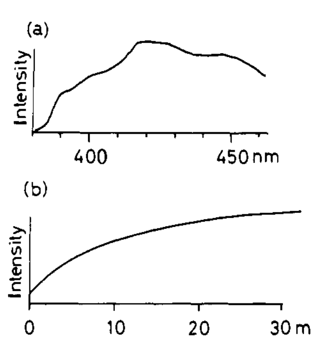
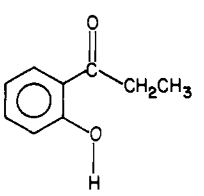
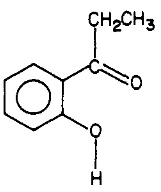


Figure 8. (a) Phosphorescence spectrum (uncorrected) of OHPP taken in EtOH at 77 K. (b) Variation of the phosphorescence intensity of OHPP with time by the irradiation at 325 nm. The intensity is given in arbitrary units.

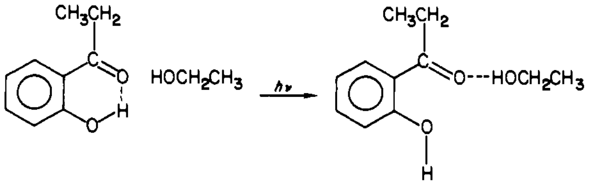
phorescence intensity with time obtained by continuous irradiation at 325 nm.

In analogy with the result on OHBA reported in the previous paper,[2] the yellow fluorescence is considered to originate from the intramolecularly hydrogen-bonded species (closed conformer), while the blue phosphorescence is due to the intermolecularly hydrogen-bonded species (open conformer). For the open conformer two different structures (O_1 or O_2) can be considered.[2]


O_1


O_2

In the case of OHBA in 3MP at 77 K the change from fluorescence to phosphorescence takes place by the rotation of the formyl group.[2] This process, however, does not seem to take place in OHPP in 3MP at 77 K, since no change from the fluorescence to the phosphorescence was observed. Therefore it is highly unlikely that such a process takes place in alcohols. The most plausible explanation of the change is given by the conversion from the closed conformer to the hydrogen-bonded open conformer O_2 shown by the scheme



This process involves the switching of the hydrogen bond from the intra- to intermolecular one.

Because of the coexistence of the open and closed conformers, OHPP in EtOH at 77 K shows phosphorescence even in the beginning of irradiation. Neither the phosphorescence decay rate nor the spectrum changes with irradiation, but the phosphorescence intensity increases with irradiation. This means that the species produced by irradiation is the same as the open conformer existing before irradiation. The phosphorescence spectrum is rather broad and its lifetime is 150 ms, which are characteristics of a $^3\pi\pi^*$ aromatic carbonyl.[25,26] These characteristics are consistent with the T_1 state of the hydrogen-bonded open conformer (O_2) of OHPP.

We have examined the conversion of the fluorescence of OHPP to the phosphorescence in a series of alcohols: MeOH, EtOH, PrOH, and BuOH. The conversion is fast in MeOH and EtOH, but it is extremely slow in PrOH and BuOH. Thus strong solvation of alcohol with a strong intermolecular hydrogen bond seems to accelerate the conversion. This observation is consistent with the above scheme. It should be noted also that such a change of the hydrogen bond from an intra- to intermolecular bond has been mentioned by Graf et al. to interpret the photochemical hole burning of quinizarin in a matrix of alcohol.[27] The present scheme shows that the switching of the hydrogen bond takes place in the excitation and decay cycle shown in Figure 4, but it does not say whether the switching occurs in S_1' or in S_0'. Further investigation is needed to clarify more details.

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Registry No. OHBA, 90-02-8; OHPP, 610-99-1; 7HIN, 6968-35-0.

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(21) It was indicated that the S_1 state of MS is a distorted excited state which is created simultaneously with the absorption of a photon,[17,22] but in the case of the present system the exact nature of the S_1 state is not well understood.

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