Two-Step Laser Excitation Study on the Proton Transfer and Anion Formation in the Intramolecularly Hydrogen Bonded 7-Hydroxy-1-indanone and the Related Compounds

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Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan, and Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan. Received September 3, 1985

Abstract: We have investigated the structures and the dynamic processes related to the intramolecular proton transfer in 7-hydroxy-1-indanone (7HIN), o-hydroxyacetophenone (OHAP), and salicylamide (SAM) by means of two-step laser excitation (TSLE) and transient absorption techniques. It is concluded that in methylcyclohexane (MCH) and tetrahydrofuran (THF) ground-state enol tautomer exists as a metastable state only in 7HIN among the related molecules. The stability of the tautomer in 7HIN is ascribed to a relatively longer O–H···O distance due to the formation of a five-membered ring. The rate of the reverse proton transfer of 7HIN in MCH was found to be 1.03×10^5 s^{-1} at 300 K with an apparent activation energy of 0.93 kcal/mol. In ethanol (EtOH) and acetonitrile (ACN), the molecules studied here all show TSLE fluorescence. In the case of OHAP and SAM, the TSLE fluorescence is assigned to originate from the anion. In the case of 7HIN, TSLE fluorescences of both the tautomer and the anion were observed. From the analysis of the TSLE fluorescence intensities at variable delay times, it was concluded that the anion is produced from the ground-state tautomer.

I. Introduction

Structures and dynamic processes in the excited states of intramolecularly hydrogen bonded molecules are topics of current interest and have been investigated actively by using various spectroscopic techniques.[1-14] We have recently studied the dynamic processes in the excited states of o-hydroxybenzaldehyde (abbreviated as OHBA) and the related molecules shown in Figure 1 by means of emission and picosecond spectroscopies.[7,8] These molecules are particularly attractive, because they are the simplest among the aromatic molecules in which excited state intramolecular proton transfer takes place. The fluorescence properties of OHBA and the related molecules were discussed in terms of the four-level scheme involving proton transfer given in Figure 2. The S_0' and S_1' states are the ground and excited states of the tautomer which is considered to have a dominantly enol character.[7,8] However, detailed information about the structures and the dynamic processes involved in this four-level scheme is still lacking. For instance, it is not known whether or not the S_0' state exists as a metastable state. The fluorescence properties in alcohols were found rather complex, and possible existence of more than one fluorescing species was indicated,[7] but definitive identification of the species has not been made.

Itoh and co-workers recently demonstrated that two-step laser excitation (TSLE) spectroscopy is a powerful means to investigate the properties of the photoinduced tautomer (S_0') and the kinetics of the reverse proton transfer from S_0' to S_0.[9-14] It can also provide a means to distinguish various fluorescing species with different ground-state lifetimes.[12-14] In this work, we have applied the TSLE fluorescence and transient absorption techniques to study the process of reverse proton transfer and to identify the fluorescing species of 7-hydroxy-1-indanone (7HIN) and the related molecules in polar solvents. The main purpose of the present work is the following.

First, we have tried to determine whether or not the tautomer states exist as metastable states in various solvents. Since the formation of a five-membered ring in 7HIN makes the O–H···O distance longer than in the other related molecules studied here, comparison between 7HIN and others should be useful in finding the effect of the O–H···O distance on the stability of the tautomer. Second, we have attempted to identify various fluorescing species existing in the excitation–relaxation cycle in polar solvents and to clarify the mechanism to produce them. Here we present

conclusive evidence that anions are produced from the ground-state tautomer.

In the present paper, we mainly discuss the results on 7HIN and OHAP. OHAP is taken as the representative example of the three related compounds, OHBA, OHAP, and salicylamide (SAM). Much of the discussion given to OHAP is applicable to the other two, though OHBA in ethanol has its own complexity discussed in the previous paper.[7]

II. Experimental Section

A. Sample Preparation. Commercially obtained OHBA and OHAP were purified by repeated vacuum distillation and by column chromatography on Kiesel gel G (Merck). SAM was recrystallized twice from chloroform. 7HIN is a gift from Professor H. Iwamura of the Institute for Molecular Science, which was synthesized according to the method described elsewhere.[8] Methylcyclohexane (MCH), tetrahydrofuran (THF), ethanol (EtOH), and acetonitrile (ACN) were all of spectroscopic grade and were dried with silica gel or phosphorus pentoxide. Concentrations of the solutions were about 10^{-4} M. Most sample solutions for TSLE measurements were degassed by the repeated freeze–pump–thaw cycles.

B. Absorption, Emission, and Transient Absorption Spectra. 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. Transient

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(1) Weller, A. *Z. Elektrochem.* **1956**, *60*, 1144.
(2) Smith, K. K.; Kaufmann, K. J. *J. Phys. Chem.* **1978**, *82*, 2286.
(3) Goodman, J.; Brus, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 7472.
(4) Brackmann, U.; Ernsting, N. P.; Ouw, D.; Schmitt, K. *Chem. Phys. Lett.* **1984**, *110*, 319.
(5) Mordzinsky, A.; Grabowska, A.; Teuchner, K. *Chem. Phys. Lett.* **1984**, *111*, 383.
(6) Chou, P.; McMorrow, D.; Aartsma, T. J.; Kasha, M. *J. Chem.* **1984**, *88*, 4596.
(7) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K. *J. Am. Chem. Soc.* **1983**, *105*, 4220 and references therein.
(8) Nagaoka, S.; Hirota, N.; Sumitani, M.; Yoshihara, K.; Lipczynska-Kochany, E.; Iwamura, H. *J. Am. Chem. Soc.* **1984**, *106*, 6913 and references therein.
(9) Itoh, M.; Fujiwara, Y. *J. Phys. Chem.* **1983**, *87*, 4558.
(10) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1983**, *105*, 4828.
(11) Itoh, M.; Adachi, T.; Tokumura, K. *J. Am. Chem. Soc.* **1984**, *106*, 850.
(12) Itoh, M.; Adachi, T. *J. Am. Chem. Soc.* **1984**, *106*, 4320.
(13) Itoh, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1561.
(14) Itoh, M.; Yoshida, Y.; Takashima, M. *J. Am. Chem. Soc.* **1985**, *107*, 4819.
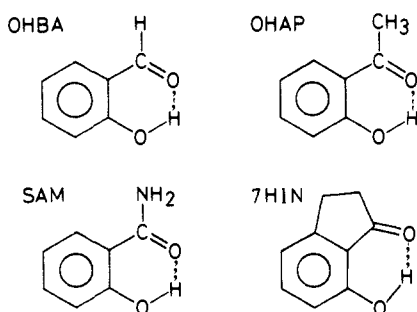
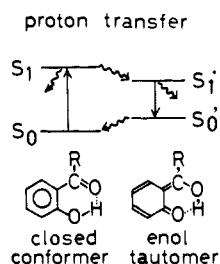Figure 1. Molecular structures of OHBA, OHAP, SAM, and 7HIN.

Figure 2. A schematic energy diagram for the dynamic processes of the major species of OHBA and its derivatives in nonpolar solvents.
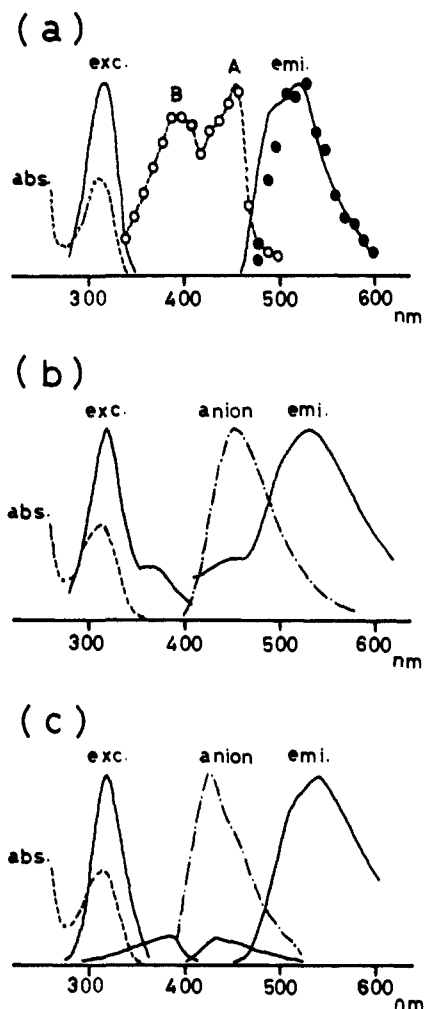

Figure 3. Absorption (———) and uncorrected fluorescence emission and excitation spectra (—) taken in nonpolar and polar solvents at room temperature; TSLE fluorescence (●) and transient absorption spectra (O) taken in a nonpolar solvent; uncorrected fluorescence emission spectra (—·—·—) taken in alkaline solutions (containing 10^{-2} M of NaOH). (Exciting and monitoring wavelengths were 320 and 530 nm, and those of the anion were 380 and 430 nm.) (a) 10^{-4} M MCH solution of 7HIN. (b) 10^{-4} M EtOH solution of 7HIN. (c) 10^{-4} M ACN solution of 7HIN.
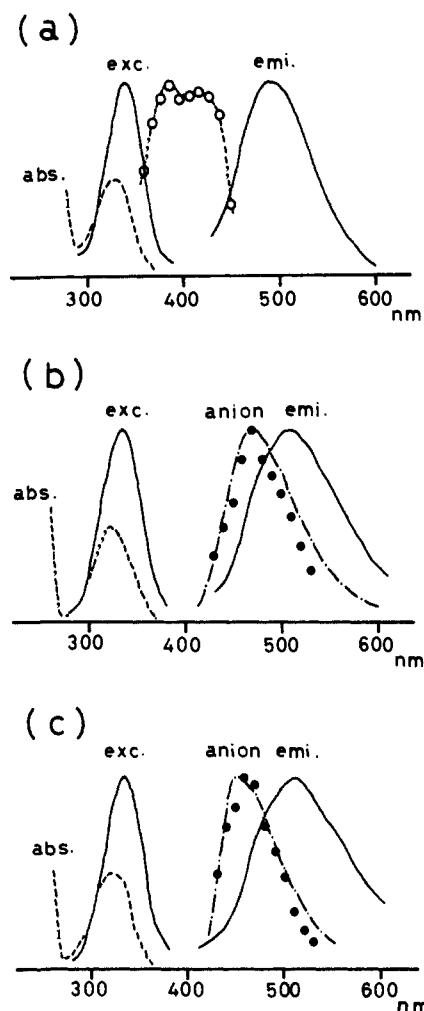

Figure 4. Absorption (———) and uncorrected fluorescence emission and excitation spectra (—) (exciting and monitoring wavelengths were 335 and 500 nm, respectively) and TSLE fluorescence spectra (●) taken in nonpolar and polar solvents at room temperature; transient absorption spectrum (O) taken in a nonpolar solvent; uncorrected fluorescence emission spectra (—·—·—) taken in alkaline solutions (containing 10^{-2} M of NaOH). (a) 10^{-4} M MCH solution of OHAP. (b) 10^{-4} M EtOH solution of OHAP. (c) 10^{-4} M ACN solution of OHAP.

absorption spectra were obtained by using an excimer laser (Lumonics, TE-861M, 308 nm) as an excitation light source and a Xe flash lamp (EG&G, FX-132) as a monitoring light source.

C. Two-Step Laser Excitation (TSLE) Spectroscopy. The detailed procedure for the TSLE measurements was described elsewhere.[12,13] An excimer laser (Lambda physik, EMG-50E, 308 nm) was used as the first excitation light source, and the second nitrogen laser pumped dye laser operating at a desired wavelength (Molectron, UV-12 and DL-14) was synchronously operated with the excimer laser, using a pulse generator and a variable delay circuit. The TSLE fluorescence of the species generated by the first laser excitation was monitored with the second laser pulse delayed for a desired time after the first one. The TSLE fluorescence was detected with a photomultiplier whose output was displayed on an oscilloscope. The oscilloscope was triggered by the second laser pulse detected with a biplaner phototube. The TSLE fluorescence was observed only by the successive laser excitations. The lifetimes of the ground-state transient species were determined from the TSLE fluorescence intensities at variable delay times. In the low-temperature measurements, temperature was controlled by flowing cold nitrogen gas around the sample in a dewar.
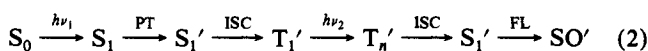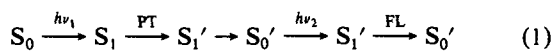
III. Results and Discussion

A. Absorption and Emission Spectra. The absorption and fluorescence spectra of 7HIN and OHAP in MCH at room temperature are shown in Figures 3a and 4a, respectively. The fluorescence spectrum of 7HIN shows a large Stokes shift in which the emission and excitation maxima are separated by 12000 cm⁻¹. The separations in OHBA, OHAP, and SAM are somewhat

smaller, being 9600, 9000, and 7200 cm^{-1}, respectively. 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 keto type closed conformers.[7,8]

The absorption and fluorescence spectra of 7HIN and OHAP in EtOH and ACN are also shown in Figures 3 and 4. As in the cases of MCH large Stokes shifted fluorescence is observed in each case, but in the case of 7HIN in EtOH an additional peak appears with its maximum at 460 nm (Figure 3b). This peak (referred to as a non-Stokes shifted fluorescence) has an excitation spectrum starting at about 400 nm which forms a mirror image. In ACN this peak is very weak but is clearly observable when excited at 380 nm as shown in Figure 3c. Therefore, another fluorescing species is considered to be present in equilibrium with the closed conformer of 7HIN in polar solvents.

We considered the 7HIN anion as a possible candidate for this species. Existence of such an anion was previously suggested for SAM in aqueous solutions.[15-17] We therefore examined the fluorescence spectra of 7HIN in alkaline EtOH and ACN (containing 10^{-2} M of NaOH), in which 7HIN is expected to exist as an anion. As shown in Figure 3, b and c, the anion spectra coincide well with those of the non-Stokes shifted fluorescence, supporting the anion assignment. The intensity of the non-Stokes shifted fluorescence is much stronger in EtOH than in ACN, which seems to indicate that the anion formation is favored by hydrogen bonding with protic solvents. The fact that the anion spectrum of OHAP was not observed in EtOH and ACN indicates that the anion formation is facilitated by weaker intramolecular hydrogen bonding in 7HIN caused by a longer O–H···O distance.

B. TSLE Fluorescence in Nonpolar Solvents. We have attempted to observe the TSLE fluorescence spectra of 7HIN, OHAP, OHBA, and SAM in nonpolar solvents such as MCH and in ethereal solvents such as THF, but only 7HIN showed detectable TSLE fluorescence in these solvents. In Figure 3a, the TSLE fluorescence spectrum obtained in deaerated MCH solution at a delay time of 800 ns between the two lasers is shown. The TSLE fluorescence spectrum agrees quite well with the ordinary Stokes shifted fluorescence spectrum. In this case, the observed fluorescence is due to the species generated by the first laser excitation and the possible species is either the metastable ground state or the triplet state of the tautomer. The possible processes leading to the TSLE fluorescence are then given by

$$S_0 \xrightarrow{h\nu_1} S_1 \xrightarrow{PT} S_1' \rightarrow S_0' \xrightarrow{h\nu_2} S_1' \xrightarrow{FL} S_0' \qquad (1)$$

$$S_0 \xrightarrow{h\nu_1} S_1 \xrightarrow{PT} S_1' \xrightarrow{ISC} T_1' \xrightarrow{h\nu_2} T_n' \xrightarrow{ISC} S_1' \xrightarrow{FL} SO' \qquad (2)$$

Here PT and FL stand for proton transfer and fluorescence, respectively. In order to identify the species responsible for the TSLE fluorescence, we have examined the transient absorption and wavelength dependence of the TSLE fluorescence. Typical examples of the transient absorption spectra are given in Figures 3 and 4. The spectrum of 7HIN in MCH consists of two peaks, A with the maximum at 460 nm and B at 390 nm, which decay with slightly different rate constants. Both peaks are quenched by oxygen. The wavelength dependence of the TSLE fluorescence intensity was examined by using the second laser excitation at 455 and 386 nm. The TSLE fluorescence intensity obtained by the 455-nm excitation was about four times higher than that obtained by the 386-nm excitation after an appropriate correction was made for the difference in the laser power at 455 and 386 nm. When we take account of the overlap of the peaks at 386 nm, this value is reasonably explained by assuming that only peak A gives rise to the TSLE fluorescence. Peak A forms a mirror

(15) Schulman, S. G.; Kovi, P. J.; Young, J. F. *J. Pharm. Sci.* **1973**, *62*, 1197.
(16) Thistlethwaite, P. J.; Woolfe, G. J. *Chem. Phys. Lett.* **1979**, *63*, 401.
(17) Woolfe, G. J.; Thistlewaite, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 6917.
(18) Saitoh, T.; Mori, K.; Itoh, R. *Chem. Phys.* **1981**, *60*, 161.

Table I. Temperature Dependence of the Lifetimes

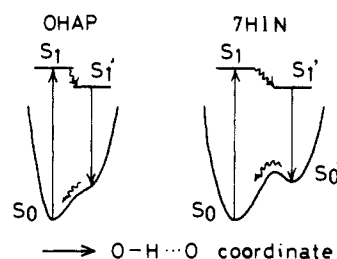| T (K)	τ (μS)
(a) Ground-State Tautomer of 7HIN in MCH	
296	9.7
267	12
247	13.4
214	14.6
186	20.3
(b) Ground-State Anion of OHAP in EtOH	
297	50.5
272	57
243	125.5
214	286
183	950

Figure 5. Schematic potential energy surfaces for the motion of the hydrogen bonded protons of 7HIN and OHAP in MCH.

image of the fluorescence as shown in Figures 3a. On the basis of these observations, we assign the species A to the ground-state tautomer, which exhibits TSLE fluorescence by process 1 and the species B to the triplet state. It is considered that the $T_n' \rightarrow T_1'$ internal conversion is much more efficient than the $T_n' \rightarrow S_1'$ intersystem crossing making process 2 inefficient. Transient absorption was also observed in the case of OHAP in MCH as shown in Figure 4a, but no TSLE fluorescence was observed. Therefore, only the triplet state is produced by the first laser excitation and the $T_1' \rightarrow T_n'$ absorption does not produce the TSLE fluorescence.

The TSLE fluorescence intensity was measured at variable delay times between the two laser pulses in order to determine the lifetime of the ground-state tautomer. The log plots of the TSLE fluorescence intensities vs. the decay times provide straight lines from which the lifetimes of the ground-state tautomer were estimated to be 9.7 μs in MCH and 5.3 μs in THF at room temperature. The TSLE fluorescence of 7HIN disappears in aerated solution of MCH. The difference in aerated and deaerated solutions is attributed to a quenching reaction of the ground-state tautomer, because the lifetime of the excited state of the tautomer is too short for such a reaction to be effective. However, the exact mechanism of this quenching process is not known at present.

The decay rate constant of the tautomer is considered to be determined by the reverse proton transfer from S_0' to S_0. In order to determine the activation energy for this process, we have measured the temperature dependence of the lifetime of the tautomer in MCH. The result is given in Table I. It is seen that temperature dependence is rather small. Use of the Arrhenius equation gives rise to an apparent activation energy of 0.93 kcal/mol and a preexponential factor of 5 × 10^5 s^{-1}. It is noted that the preexponential factor is remarkably small. However, such small preexponential factors have also been found in other proton transferring systems such as 6-(2'-hydroxy-5'-methylphenyl)-*s*-triazines studied by Sizuka et al.[19] and 3-hydroxyflavone studied by Fujiwara et al.[20]

Failure to observe the TSLE fluorescence of OHBA, OHAP, and SAM in nonpolar solvents suggests that the tautomers of these molecules are likely to be unstable (lifetime must be less than 100

(19) Shizuka, H.; Machii, M.; Higaki, Y.; Tanaka, M.; Tanaka, I. *J. Phys. Chem.* **1985**, *89*, 320.
(20) Fujiwara, Y.; Itoh, M.; Sumitani, M.; Yoshihara, K. 50th Annual Meeting of the Chemical Society of Japan, 1985; Abstract I, p 208.
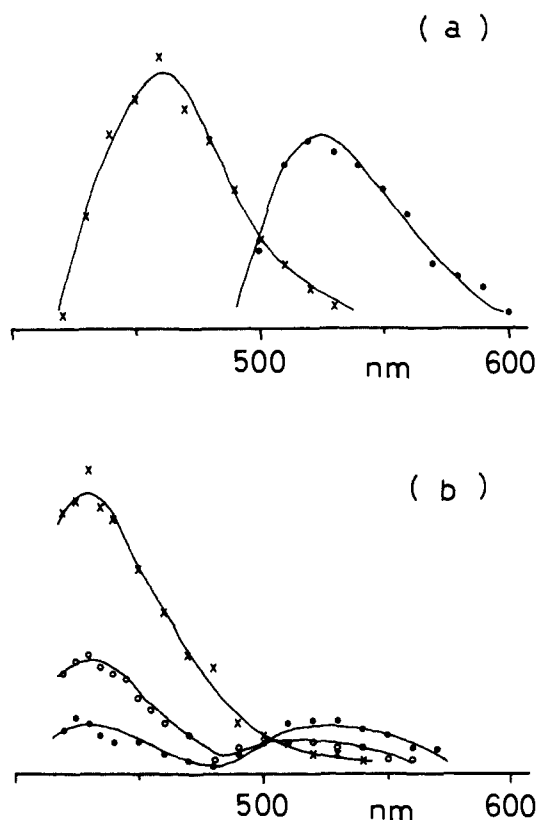
Figure 6. Time resolved TSLE fluorescence spectra at room temperature. (a) 5×10^{-4} M EtOH solution of 7HIN. (Delay times were 1 μs (●) and 12 μs (X), respectively.) (b) 5×10^{-4} M ACN solution of 7HIN. (Delay times were 0.8 μs (●), 1.8 μs (O), and 12 μs (X), respectively.)

Figure 7. Plots of log intensities of the TSLE fluorescence vs. delay times. (a) 5×10^{-4} M ACN solution of 7HIN. (Monitoring wavelengths were 540 nm (X) and 460 nm (O).) (b) 5×10^{-4} M EtOH solution of OHAP. (Monitoring wavelength was 460 nm.)

Figure 8. A schematic energy diagram for the dynamic processes of the major ground-state species of 7HIN in EtOH.

ns). Thus among the related molecules studied here, only 7HIN has a double minimum character along the O–H···O hydrogen bonding coordinate. Since the O–H···O distance in 7HIN is slightly longer than in others studied here, elongation of the O–H···O distance seems to stabilize the tautomer state significantly. Schematic potential energy curves for the motion of the hydrogen bonded proton in 7HIN and OHAP in nonpolar solvents are shown in Figure 5. Evidence for a drastic change in the potential energy on going from OHAP to 7HIN is provided by the results of the low-temperature spectroscopic studies.[21]

A model calculation using the Lippincott–Schroeder potential function predicts a double minimum potential for an O···O distance from 2.45 to 2.60 Å.[18] The barrier for the reverse proton transfer becomes higher as the O···O distance increases. This trend is qualitatively in agreement with the observed results, but the predicted height is much too higher, showing that such a simple model cannot account for the real situation. The scheme shown in Figure 1 assumes that the change from S₀' to S₀ involves the isomerization from the enol to the keto form. Such an isomerization must accompany a considerable geometrical rearrangement of the entire molecule in the course of proton transfer. The observed low activation energy in 7HIN and the absence of a barrier in OHAP and others may be the consequence of the extensive geometrical rearrangement. The exact cause for the remarkably small preexponential factor found here is not certain. If this result is correct, it seems to suggest that among numerous vibrational states accessible by thermal excitation only very specific states compatible with the required geometrical change can lead to isomerization. However, the transfer rate may be affected by the tunneling process which gives rise to an apparent low activation energy. Further investigation is needed to clarify this point.

C. TSLE Fluorescence in Polar Solvents. In polar solvents TSLE fluorescence was observed not only in 7HIN but also in OHAP, OHBA, and SAM as shown in Figures 3 and 4. However,
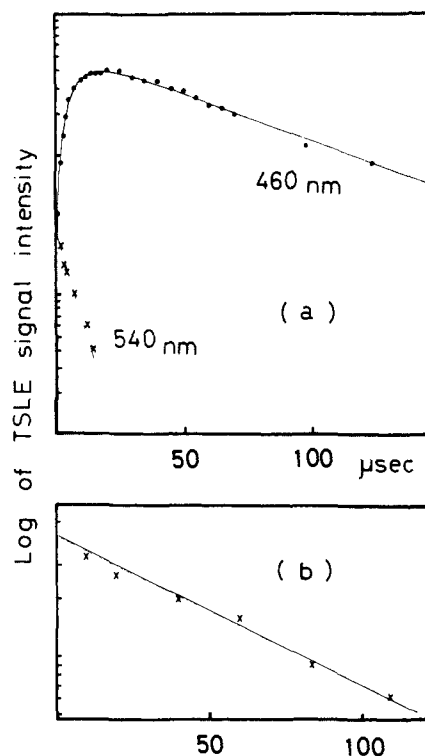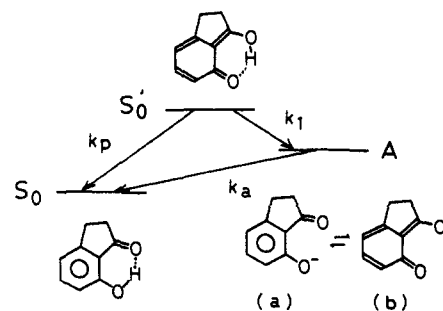
the TSLE fluorescence spectra of OHAP and SAM do not coincide with those of the Stokes shifted fluorescence. The TSLE fluorescence spectra of 7HIN in deaerated EtOH and ACN at various delay times are shown in Figure 6. In both cases, the spectra consist of two components, one with the maximum at 520 nm and the other at 460 nm in EtOH (430 nm in ACN). The 520-nm spectra agree with the ordinary Stokes shifted and the TSLE fluorescence spectra of the tautomer in nonpolar solvents, and the 460-nm (430-nm) spectra agree with the fluorescence spectra of the anions. Therefore, it is reasonable to assign the former to the tautomer and the latter to the anion. The 520-nm spectra rapidly decay, while the 460-nm (430-nm) spectra first rise and then gradually decay. This is clearly seen from the plots of the intensities of both peaks vs. the delay times given in Figure 7. These results show that the anion is generated at the expense of the tautomer. In order to obtain kinetic parameters, we have simulated the rise and decay curves by the scheme given in Figure 8. Here A stands for the anion. The TSLE fluorescence intensities of the tautomer (S_0') and the anion (A) are given by the following equations

$$I(S_0') = [S_0'] \exp(-(k_p + k_1)t)$$

$$I(A) = \frac{k_1[S_0']}{k_p + k_1 - k_a} (\exp(-k_a t) - \exp(-(k_p + k_1)t))$$

(21) Nishiya, T.; Yamauchi, S.; Hirota, N.; Baba, M.; Hanazaki, I., to be published.

From the simulation of the data given in Figure 7, we estimated the rate constants. The lifetimes of the tautomers in EtOH and ACN are 6.5 and 7.2 μs, respectively. These values are similar to those found in nonpolar solvents. The lifetimes of the anions are 60 and 76 μs, respectively.

In addition to the process shown in Figure 8 the anion may be formed from the intermolecularly hydrogen bonded species, but the present result seems to indicate that such a process is not major.

The TSLE spectra of OHAP in deaerated EtOH and ACN at a delay time of 5 μs at room temperature coincide well with the fluorescence spectra of the anions obtained in the alkaline EtOH and ACN solutions as shown in Figure 4. Therefore, the TSLE fluorescence spectra of these systems are also assigned to the anions. However, different from the case of 7HIN, these TSLE spectra were independent of the delay time without showing the fluorescence of the tautomer. A typical example of the decay of the TSLE fluorescence intensity is shown in Figure 7. The log plots of the TSLE fluorescence intensity vs. the delay times give a nearly linear relation at the initial stage of the decay, but at longer delay times the plots seem to deviate from the linearity. The linear portion of the plots gives a lifetime of 50 μs for OHAP in EtOH at room temperature. Temperature dependence of the lifetime gives an activation energy of 3.0 kcal/mol for the decay process of the anion. The lifetime of the OHAP anion in deaerated ACN was estimated to be 32 μs. The fact that the TSLE fluorescence of the tautomer was not observed in OHAP, OHBA, and SAM in polar solvents indicates that the tautomers also do not have metastable states in polar solvents as in nonpolar solvents, although relatively stable anions are formed in the relaxation processes of the excited-state tautomers.

On the basis of these observations, we discuss the process of the anion formation and possible structures of the anions. In the case of 7HIN, the first laser excitation generates the excited-state tautomer which relaxes vertically to the metastable ground-state tautomer. Then the proton is abstracted by the solvents forming

the anion. Whether the anion is ion paired or dissociated is not known definitely, but the nearly exponential decay of the anion at the initial stage of the decay may be attributed to the ion paired anion with the dissociated anion contributing to the slower decay at a later time. Though we were not able to detect the ground-state tautomers of OHAP, OHBA, and SAM in polar solvents, the anions are likely to be formed similarly from the ground-state tautomers after they relax from the excited states. The fact that anions formed from the enol tautomers and those formed from the keto forms in the alkaline EtOH have the same absorption spectra means that these anions are identical. The absorption spectra of the anions are blue-shifted from those of the tautomers. The anion structure compatible with those observations may be given by a resonance between structures a and b shown in Figure 8.

IV. Summary and Conclusions

Among 7HIN, OHBA, OHAP, and SAM, only 7HIN shows TSLE fluorescence due to the metastable enol tautomer. The stability of the tautomer is ascribed to a relatively longer O–H⋯O bond length in 7HIN caused by the five-membered ring formation. Temperature dependence on the lifetime of the tautomer gave an apparent activation energy of 0.93 kcal/mol.

In polar solvents, not only 7HIN but also OHBA, OHAP, and SAM show TSLE fluorescence. In 7HIN the TSLE fluorescences of the tautomer and the anion were detected, but in others only the TSLE fluorescence of the anion was detected. The analysis of the delay time dependence of the TSLE fluorescence reveals that the anion of 7HIN is formed at the expense of the ground-state tautomer.

Chemistry of Acetylene Exposed to Alumina and Alumina-Supported Rhodium Catalysts

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Contribution from the Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444, Japan. Received October 28, 1985

Abstract: Raman spectroscopy and mass analysis of desorption products were used to obtain information about the chemistry of acetylene exposed to alumina, thermally activated alumina, and alumina-supported rhodium catalysts. For the three catalyst systems, the chemistry is similar. High-mass species appear in the mass spectra that are characteristic of polymers containing mixtures of single, double, and triple bonds. For the supported catalyst, the trapping of acetylene trimers correlates with a decrease in the Raman intensity.

The interaction between hydrocarbons and metals and metal oxides is important in many processes of heterogeneous catalysis. We have used Raman spectroscopy and mass analysis of desorption products to obtain information about the chemistry of acetylene exposed to alumina and alumina-supported rhodium catalysts. Our principle interest is to characterize the species that is responsible for the Raman spectrum and to assess whether Raman spectroscopy can serve as a useful probe for chemical species on catalytic surfaces under technologically relevant conditions.

In previous work on these systems, different assignments of similar Raman spectra were made. In one case, the Raman spectrum was assigned to $\sigma_2\pi$-C_2H_2 bonded to supported rhodium with the C–C bond parallel to the surface.[1] In another case, involving acetylene exposed only to alumina, the assignment was to polyacetylene with a mean chain length of about 30 carbons.[2,3]

(1) Parker, W. L.; Siedle, A. R.; Hexter, R. M. *J. Am. Chem. Soc.* **1985,** *107,* 264–266.

(2) Heaviside, J.; Hendra, P. J.; Tsai, P.; Cooney, R. P. *J. Chem. Soc., Faraday Trans. 1* **1978,** 2542–2549.

(3) Tsai, P.; Cooney, R. P.; Heaviside, J.; Hendra, P. J. *Chem. Phys. Lett.* **1978,** *59,* 510–513.

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