Hysteresis in the Temperature Dependence of Phosphorescence of 4-Hydroxy-3-methoxybenzaldehyde (Vanillin) in Ethanol

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A hysteresis phenomenon was observed in the temperature dependence of the phosphorescence spectra of 4-hydroxy-3-methoxybenzaldehyde (vanillin) in ethanol. Phosphorescence first appeared at 115 K when the temperature (*T*) was decreased from room temperature to 77 K, whereas it lasted until 155 K as *T* was raised from 77 K. Such hysteresis arises from the supercooling of ethanol and is a rather general property of ethanol solution. Moreover, the shape and position of the phosphorescence spectra changed variously in the *T* range of 77−155 K. The unusual spectral changes were explained on the basis of molecular geometries and excitation energies of vanillin calculated by semiempirical molecular orbital methods. Furthermore, two conformations of vanillin were deduced, which give rise to room-temperature phosphorescence for a filter paper and PVA substrate.

1. Introduction

Ionic organic compounds exhibit room-temperature phosphorescence (RTP) when they are adsorbed on a substrate such as filter paper.[1] Though this phenomenon has been widely used in analytical chemistry, the detailed mechanism still remains to be solved.[2,3] To clarify the mechanism of RTP, we have examined the phosphorescence characteristics of several ionic compounds adsorbed on filter paper and also in solution.[4] In the course of the study we observed that 4-hydroxy-3-methoxybenzaldehyde (vanillin) in ethanol showed a peculiar temperature dependence of phosphorescence. As the temperature (*T*) of the solution was decreased from room temperature to 77 K, phosphorescence began to occur at 115 K and was then blue-shifted with reducing *T*. Contrarily, as *T* was raised from 77 K, phosphorescence lasted up to 155 K, varying its spectral shape and position. The phenomenon that the temperature at which phosphorescence first appears on cooling differs from the one at which the phosphorescence last disappears on heating is regarded as hysteresis.

Such hysteresis was also observed for another ionic organic compound, 4-hydroxybenzaldehyde (HBA), and for a nonionic but polar molecule, benzophenone. In all cases, the solvent was ethanol or a mixed one containing ethanol. It was also found that the hysteresis correlates to phase transitions of ethanol, especially its supercooling. We discussed the mechanism of the hysteresis on the basis of the phase transitions of ethanol.

Furthermore, while vanillin showed unusual spectral shifts in the temperature dependence of phosphorescence, HBA, which has a structure similar to that of vanillin except for lack of a methoxyl group, showed no spectral shifts. This indicates that the unusual spectral change of vanillin is caused by interaction of the methoxyl group with the hydroxyl group. To investigate such interactions, we performed semiempirical molecular orbital calculations for vanillin. Conformation analysis provided changes in molecular energies which account for the spectral shift.

2. Experimental Section

4-Hydroxy-3-methoxybenzaldehyde (vanillin) (Koso Chemical) was dissolved into ethanol; the concentration of the solution was varied from 0.05 to 100 mM (1 M = 1 mol dm^{-3}). The solution was kept in a quartz cell and subjected to several freeze−pump−thaw cycles. The cell was set in a cryostat (Oxford DN1754). For the measurements of phosphorescence spectra, light from a 500 W Xe lamp (Ushio) was passed through an excitation monochromator (Spex Minimate) and focused onto the cell through a light chopper. The light chopper gave a light-on time of 0.5 s and a dark time of 1 s. The resulting phosphorescence was filtered by a monochromator (Spex Minimate) and detected by a photomultiplier (Hamamatsu R585 or R649), whose output was processed by a counter (Iwatsu SC-7103) and a personal computer (NEC PC-9801 VM). For lifetime measurements, the sample was irradiated with a flash lamp for photographing (SUNPAK CV-1), whose pulse width was 1 ms, and phosphorescence emitted was detected by a photomultiplier (Hamamatu R585) through an interference filter; the signal was accumulated by a boxcar integrator (NF BX-531).

The temperature, *T*, of the sample was controlled within ±0.5 K and varied between 77 and 295 K. *T* was changed at a slow rate of about 1 K/min, and whenever a new value of *T* was set, the sample stood at the *T* for 20 min before measurement. To assure that *T* was kept constant during measurement, we repeated it until two same spectra were obtained successively.

The temperature dependence of phosphorescence for 4-hydroxybenzaldehyde (HBA) (Tokyo Kasei) in ethanol was also examined for comparison. Moreover, room-temperature phosphorescence spectra of vanillin were obtained with the same measurement system; filter paper and poly(vinyl alcohol) (PVA)

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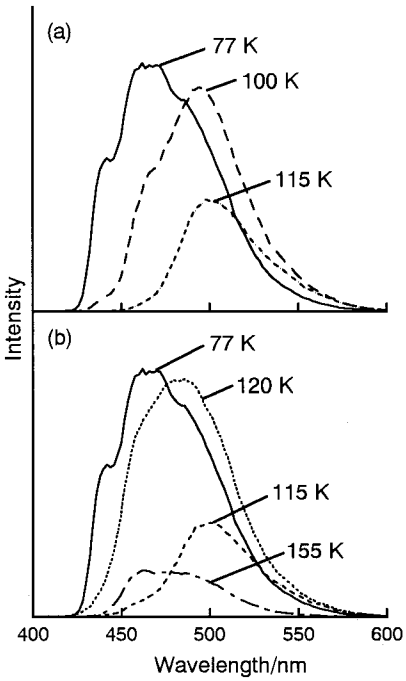

Figure 1. Phosphorescence spectra of vanillin in deoxygenated ethanolic solution (5 mM) as a function of the sample temperature (*T*): (a) with decreasing *T* from room temperature and (b) with increasing *T* from 77 K.

films were used as substrates. The samples with filter paper were prepared by saturating filter paper (Toyo No. 2), cut in a 20 × 25 mm strip, with 0.1 mL of a 1 M NaOH aqueous solution of vanillin and dried;[4] the concentration of vanillin was varied in the range 0.1−100 mM. PVA films doped with vanillin were prepared as follows:[5] PVA powder (Tokyo Kasei) was dissolved in water and heated to produce a thick homogeneous solution containing 5−10% of the polymer. After the polymer solution had been allowed to cool to about 60 °C, vanillin was dissolved in the solution; the concentration was changed from 0.1 to 10 mM. The doped solution was then cast on a glass plate, and the solvent was allowed to evaporate in a dust-free atmosphere over several days. The sheet was peeled off and cut in appropriate size for optical measurements.

In vanillin, various conformations result from rotations (θ) of the methyl group about the C−O bond (see Figure 7). Conformation analysis was performed as follows: the molecular geometries of conformers were first optimized by the modified neglect of overlap method with the PM3 parameters in the MOPAC program, and the energies of the ground state were obtained as a function of θ; then excitation energy was calculated for each optimized conformation by the use of the complete neglect of differential overlap and configuration interaction method with QCPE No. 174.

3. Results

3.1. Temperature Dependence of Phosphorescence for Vanillin in Ethanol. Figure 1 shows the phosphorescence spectra of vanillin in ethanolic solution (5 mM) as a function of the sample temperature (*T*). When *T* was decreased gradually from room temperature, phosphorescence with a broad peak at 500 nm was first observed at 115 ± 1 K, and then its intensity increased with an accompanying change in the spectral shape and peak position (Figure 1a). At 77 K, the maximum peak was blue-shifted by about 40 nm with respect to the peak at 115 K, and a slight vibrational structure also appeared in the short wavelength region. The vibrational structure corresponds to the stretching vibration of the carbonyl group.

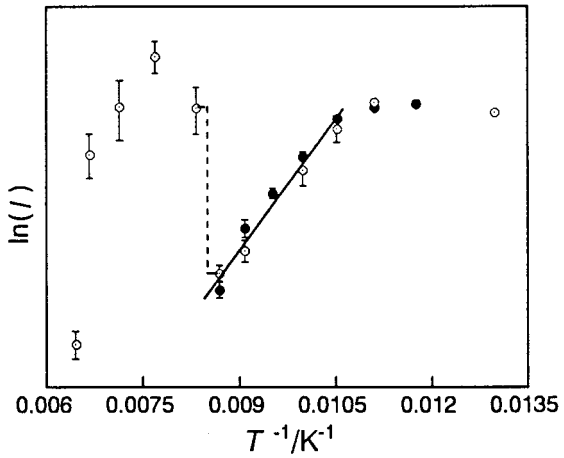

Figure 2. Arrhenius plot of ln *I* against T^{-1}; *I* is the total phosphorescence intensity of vanillin and normalized to the value at 77 K. The filled and empty circles represent the *I* values with decreasing and increasing *T*, respectively. The vertical bars denote probable errors.

On the other hand, as *T* was increased from 77 K, the spectra changed almost reversibly until *T* reached about 115 K (Figure 1b). However, strangely enough, phosphorescence was still observed even when *T* was raised more than 115 K, and the spectra began to change peculiarly. At 118 ± 2 K, the peak was blue-shifted again, accompanied by an increase in the intensity; since the spectra show a broad band with shoulders and have a peak at 482 nm, the shapes are regarded as an intermediate of those at 77 and 115 K. Then the emission weakened by degrees with further increasing *T*. At 160 K no phosphorescence observed. Once phosphorescence was completely disappeared, it did not appear until cooled to 115 K again, and the same phenomenon as described above was repeated by varying *T*. Almost the same results as described above were obtained in the concentration range of 0.05−100 mM in ethanol and also in ethanol−isopentane−ether (EPA) mixed solution.

The change in the spectral intensity during the temperature cycling can be seen more clearly in an Arrhenius plot of T^{-1}− ln *I* (Figure 2), where *I* represents the total phosphorescence intensity, integrated in the 400−600 nm region, and is normalized to the value at 77 K. In the *T* region 95−115 K, ln *I* changes linearly against T^{-1}; the activation energy is calculated to be 6.2 ± 0.5 kJ/mol. A slight decrease at about 77 K probably arises from reduction of the rate of intersystem crossing.[6] When *T* is raised to 118 K, *I* suddenly increases, as described above. The abrupt increase can be related to a phase transition of the solution from a glass to a "snow" (see section 3.3). In fact, the "snow" caused an increase in light scattering and interfered with precise spectral measurements, which gave rise to large errors in *I* above 118 K. It is noted, however, that the spectral shapes are reproduced well in contrast to the intensities.

Figure 3a shows the excitation spectra for phosphorescence at 460 and 500 nm and for fluorescence at 410 nm of vanillin, and they are due to the ground state (S_0) → excited singlet states (S_n, $n \geq 1$) absorption; those due to S_0 → the lowest excited triplet state (T_1) absorption could not be obtained because of weak signal intensity. In the 250−400 nm wavelength region, the excitation spectra for phosphorescence appeared from 350 nm and maximized at 320 nm, while those for fluorescence appeared from 390 nm, maximized at 360 nm, and disappeared

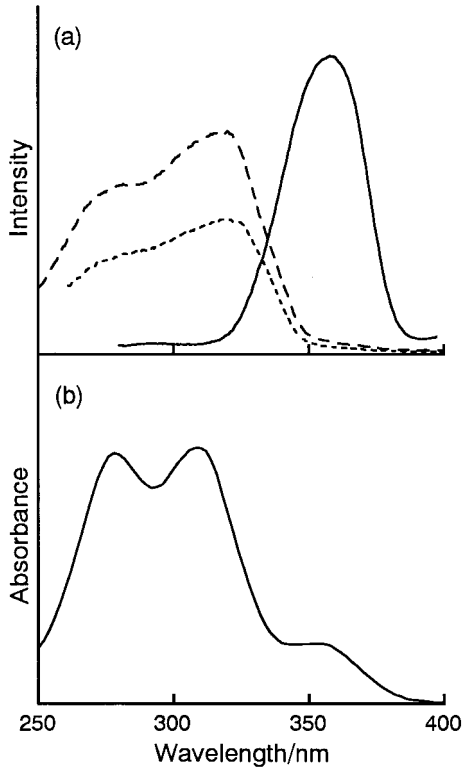

Figure 3. Excitation spectra for fluorescence at 410 nm (solid line) and for phosphorescence at 460 (broken line) and 500 nm (dotted line) at 77 K (a) and absorption spectrum at room temperature (b) of vanillin in deoxygenated ethanolic solution (0.05 mM); they were measured by a Hitachi 850 fluorospectrophotometer and Hitachi U-3210 spectrophotometer, respectively.

at 320 nm. The bands in the fluorescence and phosphorescence excitation spectra respectively correspond to the two bands with peaks at 355 and 310 nm in the absorption spectrum (Figure 3b); the longer wavelength band, the $S_0 \rightarrow S_1$ absorption, can be assigned to an $n-\pi^*$ transition and the shorter one, the $S_0 \rightarrow S_2$ absorption, to a $\pi-\pi^*$ transition. These findings indicate that intersystem crossing to triplet states scarcely occurs from S_1, but significantly from S_2, resulting in phosphorescence. The excitation spectra were identical for any observed fluorescence or phosphorescence wavelengths and did not change in the T range of 77−155 K.

Figure 4 shows phosphorescence decay curves of vanillin in ethanol at 100, 77, and 120 K; observed wavelengths were 460 and 520 nm, corresponding to the short and long wavelengths in the spectra. At 100 K, the decay curve depended on the observed wavelength, as can be seen in Figure 4a,b. The curve for 520 nm was approximated by a single exponential with a lifetime of 200 ms, whereas that for 480 nm departed remarkably from a single exponential and could be fitted by a sum of two exponentials with lifetimes of 40 and 170 ms. These features of decay, namely, a wavelength dependence and a double exponential, were observed at $95 \leq T \leq 115$ K both with cooling and with heating. Below 95 K and above 115 K (the "hysteresis" temperatures), phosphorescence provided nearly single-exponential decay curves, which were similar for the two wavelengths; the lifetimes both at 77 K (Figure 4c,d) and at 120 K (Figure 4e,f) were equally 200 ms in spite of a difference in T.

Fluorescence of vanillin also showed hysteresis in its temperature dependence; there was a small difference between the fluorescence intensities on cooling and on heating. Contrary to phosphorescence, spectral shifts were hardly recognized.

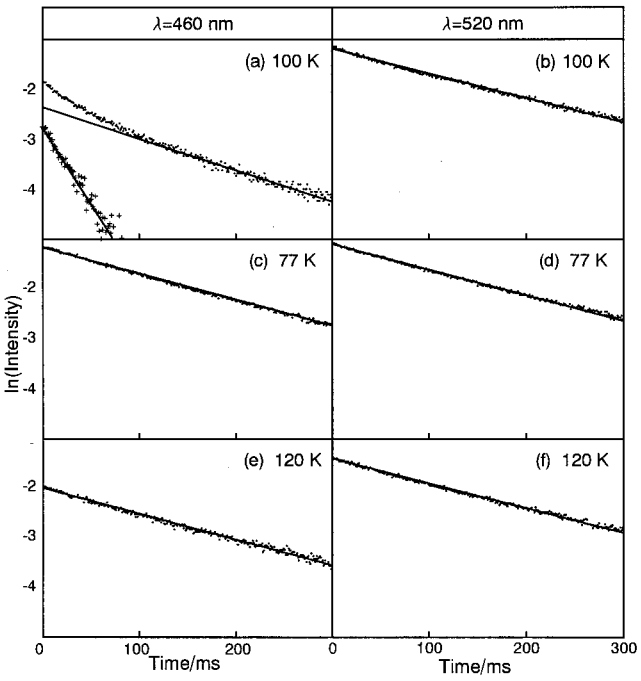

Figure 4. Phosphorescence decay curves of vanillin in deoxygenated ethanolic solution (5 mM) for the emission of 460 nm at 100 K (a), 77 K (c), and 120 K (e) and for the emission of 520 nm at 100 K (b), 77 K (d), and 120 K (f). Crosses in (a) are calculated by subtracting the decay component at the long time from the experimental data.

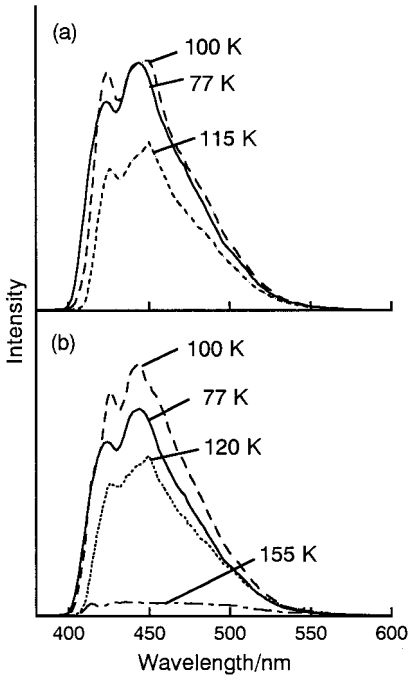

Figure 5. Phosphorescence spectra of HBA in deoxygenated ethanolic solution (5 mM) as a function of the sample temperature (T): (a) with decreasing T from room temperature and (b) with increasing T from 77 K.

3.2. Temperature Dependence of Phosphorescence for HBA in Ethanol. Figure 5 shows the T dependence of phosphorescence of HBA. With cooling, phosphorescence first appeared at 115 K as a structured band in the wavelength region of 400−600 nm, and the intensity reached a maximum at 100 K. On the contrary, with heating from 77 K, phosphorescence varied nearly reversibly until 115 K and then lasted up to 155 K as in the case of vanillin. However, the spectral shape and

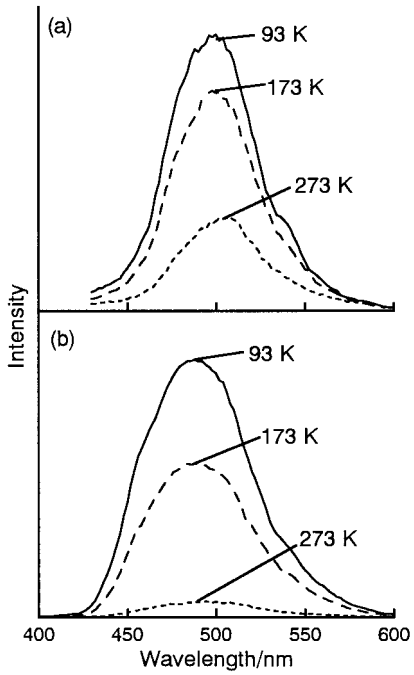

Figure 6. Phosphorescence spectra of vanillin adsorbed on filter paper (a) and embedded in PVA films (b) as a function of the sample temperature (*T*).

peak position changed only slightly during the variation of *T*, which was distinctly different from the results in vanillin.

3.3. Phase Transition of Ethanol. We observed carefully the state change of degassed pure ethanol in the cryostat as temperature was varied. The ethanol was supercooled inevitably to become a rigid glass, though temperature was decreased as slowly as possible (1 K/min); crystallization of ethanol did not occur. It remained in a transparent solid between 77 and 115 K, regardless of the changing direction of *T*. At about 93 K, ethanol lost fluidity, showing the occurrence of glass transition.[7] As *T* returned to 115 K with heating, microcrystals of ethanol began to separate out and grew with *T*; eventually the whole solution became a white solid like a snow at 120 K. The solid fused at 160 K. Ethanol solution of vanillin also exhibited the same phase transition as pure ethanol.

3.4. Room-Temperature Phosphorescence (RTP) of Vanillin. Figure 6 shows phosphorescence spectra of vanillin adsorbed on filter paper (a) and embedded in PVA films (b). At room temperature, both the spectra appeared as a broad band in the wavelength region of 430−600 nm. The RTP spectra for filter paper substrates were red-shifted slightly compared to those for PVA substrates; the former has a peak position of 500 nm and the latter of 485 nm. It is also noticed that the spectra for PVA substrates are a little more structured. When *T* was decreased, the intensities of the spectra increased, but the spectral shape and position remained almost constant. Though the concentration of vanillin was varied from 0.1 to 50 mM, no changes in the spectral shape were observed for both the substrates.

3.5. Conformation Analysis. Figure 7 shows the energies of the ground state (S_0), the lowest excited singlet state (S_1), and triplet state (T_1) for conformers as a function of θ. Two typical cases can be distinguished in view of the energy of S_0: (1) $\theta = 90°$ and 270°, where the methyl group is "perpendicular" to the plane of the benzene ring, and (2) $\theta = 0°$ and 180°, where the methyl group is "parallel" to the plane. The "perpendicular" and "parallel" conformations give the energy minima and maxima, respectively; in particular, the energy is highest at $\theta = 180°$ due to steric repulsion between the methoxyl and hydroxyl groups. The difference between the maximum and minimum energies, 0.19 eV, suggests that the methyl group is practically "perpendicular", especially at low *T*.

The energies of S_1 show the same θ dependence as those of S_0. However, T_1 gives two more maxima and minima than the singlet states; it is noticed that the "perpendicular" conformation in S_0 provides high energies for T_1. On the basis of the energy differences between S_0 and T_1 of each conformer, the wavelength of phosphorescence emission can be determined; phosphorescence from the T_1 conformations with $\theta = 45°$ and 90° predicted to occur at around 520 and 480 nm, respectively.

4. Discussion

4.1. Hysteresis in the *T* Dependence of Phosphorescence for Vanillin and HBA. As described in the Results section, the hysteresis is observed in solution containing ethanol; the solution is supercooled with cooling and then undergoes an irreversible phase transition with heating. These findings indicate that the hysteresis arises from the supercooling of the solution, which leads to irreversible interactions between the phosphorescent molecules and ethanol. We will discuss only the hysteresis of vanillin since the same discussion holds in the case of HBA.

Molecules in solution are generally not isolated but are solvated by solvent molecules.[8] In particular, when both solute and solvent are polar, the solvent is oriented around the solute by dipole−dipole interactions. This is the case for vanillin in ethanol. At low temperatures, especially, both molecules interact so strongly via hydrogen bonding that vanillin is completely trapped in a solvent cage.[8] This cage structure immobilizes vanillin and prevents intermolecular collisional deactivation of its triplet state. In fact, phosphorescence of vanillin begins to occur at 115 K, and its intensity (*I*) increases with decreasing *T* until about 90 K (Figure 2); the Arrhenius plot gives an activation energy of 6.2 kJ/mol. This value is close to the activation energy of 10.3 kJ/mol, which was obtained from the temperature dependence of RTP of vanillin adsorbed on filter paper and was explained as the energy necessary for vanillin to be held rigidly.[4] By analogy, the energy of 6.2 kJ/mol is considered as the one necessary for cages to be formed. Further cooling of the solution to 77 K leads to its contraction; as a result, the solvent cavities are also compressed, which causes a large spectral shift (see section 4.2).

Conversely, with increasing *T* from 77 K, the ethanol molecules forming a cage gain freedom to move and the cage begins to relax. At $T = 118$ K, however, ethanol undergoes a phase transition to crystals, and the phosphorescence intensity abruptly increases (Figure 2). This means that the cages are compressed again due to decrease in the volume of the solution, and vanillin in the cages is held strongly. Thus, phosphorescence emission lasts even above 115 K, as far as vanillin is trapped in the solvent cage.

4.2. Spectral Changes of Vanillin with *T*. While vanillin showed an unusual spectral shifts in the *T* dependence of phosphorescence, HBA exhibited no spectral shifts. It is natural to consider that such difference between the two molecules is ascribed to their structural difference; namely, vanillin has one more polar substituent, the methoxyl group, which enables it to take various conformations. The conformational analysis indeed demonstrated that different conformers provide different wavelengths of phosphorescence, as described in section 3.5. Therefore, it is concluded that the spectral change with *T* arises

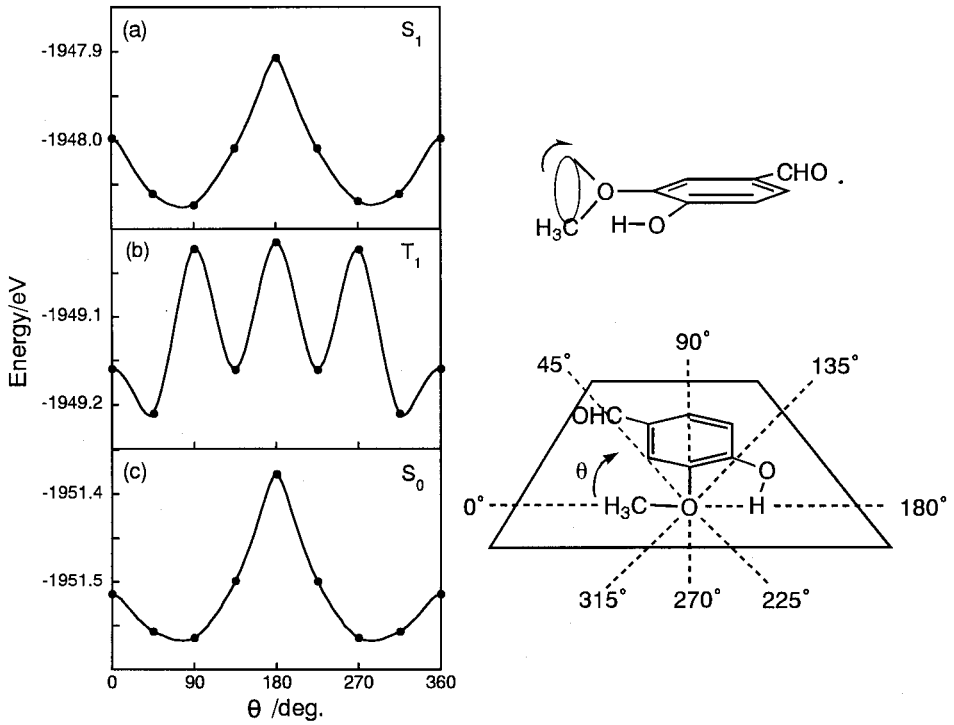

Figure 7. Energies of conformers of vanillin as a function of rotation (θ) of the methoxyl group about the C−O bond for S_0, S_1, and T_1; the hydroxyl group is located toward the methoxyl group due to a weak internal hydrogen bonding between them.

from corresponding conformational changes in S_0 and T_1. Then the peculiar T dependence of the spectra can be explained as follows.

At 115 K, above the glass transition temperature of about 93 K, the solution is not yet completely frozen, and the methoxyl group of vanillin can still rotate considerably freely in a solvent cage. In such a situation conformations of vanillin are populated according to Boltzmann statistics in both the ground and excited states. On irradiation, vanillin molecules are excited to T_1 via S_2. Then the molecules in T_1 rearrange to the energy-minimum conformations, having $\theta = 45°$, 135°, 225°, and 315° (see Figure 7), by thermal energy; these conformers are referred to as "oblique" ones. Phosphorescence occurs from the "oblique" conformations as shown in Figure 8a; it appears at the longer wavelength region, i.e., around 520 nm. At 77 K, however, the glass transition has occurred; the solution is completely frozen, causing the solvent cages to be compressed. Then most vanillin molecules in S_0 are held in the "perpendicular" conformation. Since the movement of the methoxyl group is significantly restricted, the "perpendicular" conformation is preserved during the photophysical processes. Accordingly, phosphorescence appears at the shorter wavelength region around 460 nm, as illustrated in Figure 8b.

The T dependence of the movement of the methoxyl group, assumed in the above discussion, is supported by the wavelength dependence of the phosphorescence lifetime at $95 \leq T \leq 115$ K. The decay curve for 460 nm emission at 100 K is clearly different from that for 520 nm (Figure 4); the former is reproduced by a sum of two exponentials with lifetimes of 40 and 170 ms, whereas the latter is fitted by a single exponential with a lifetime of 200 ms. This means that there exists a certain nonradiative process that competes with the 460 nm emission and accounts for the fast decay with a lifetime of 40 ms. It is generally known that rotational motion of molecules in a viscous environment occurs in the milliseconds time range.[9] Thus, the most likely nonradiative process is the conformational change in T_1 from the "perpendicular" conformation, which is predicted

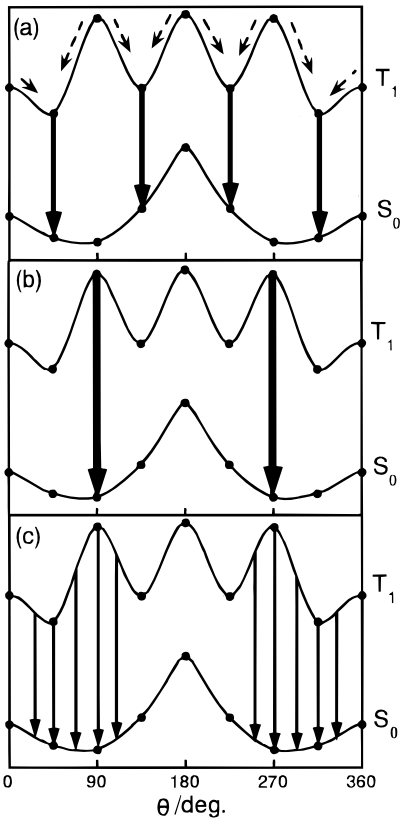

Figure 8. Transitions from T_1 to S_0 for vanillin in ethanol at $T = 115$ K (a), 77 K (b), and 120 K (c). The transition probability is represented by the line width of the vertical arrows. The dotted lines in (a) denote conformational changes.

to emit 460 nm light, to more stable conformations. At 77 K, where the solvent is completely frozen and the movement of the methoxyl group is suppressed, both decays for 460 and 520 nm emission are almost identical.

With heating from 77 K, the spectral changes are reversed as with cooling; at about 115 K, the solvent cages have relaxed, and thermal movements of vanillin have restored. As *T* is raised above 115 K, i.e., to the "hysteresis" temperature region, ethanol begins to crystallize, trapping vanillin in its crystal structure. The trapped vanillin undergoes compression from surrounding ethanol, and its molecular movements are substantially restricted. This situation has a parallel in that at 77 K; in fact, the phosphorescence decay curve approaches a single exponential again. Thus, the conformations in S_0 are preserved in T_1. It is considered, however, that at the "hysteresis" temperatures vanillin in S_0 has conformations energetically higher than those at 77 K. Therefore, the transition from T_1 occurs as shown in Figure 8c, and phosphorescence appears in a wavelength region that is intermediate between the phosphorescence wavelengths at 77 amd 115 K.

On the other hand, the energies between S_0 and S_1 are almost independent of θ. This explains that, in contrast to phosphorescence, fluorescence of vanillin shows no spectral shifts.

4.3. Conformations of Vanillin Causing RTP. A comparison of the RTP spectra of vanillin (Figure 6) to its low-temperature spectra in ethanol (Figure 1) reveals that the RTP spectra for filter paper and PVA substrates resemble the spectra in ethanol at an "onset" temperature of 115 K and at the "hysteresis" temperatures, respectively. The spectral resemblance of vanillin in such different conditions indicates that vanillin molecules are situated in a similar environment. Then we can deduce the conformation of vanillin supported by filter paper and PVA causing RTP on the basis of the spectral resemblance, because we have investigated its conformations in ethanol.

From the similarity of the phosphorescence spectra, it is deduced that vanillin adsorbed on filter paper is enclosed within certain cages and is considerably free to rearrange in both ground and excited states, as in ethanol at 115 K (section 4.2). In fact, McAleese and Dunlap reported that phosphorescent molecule adsorbed on filter paper are trapped in submicroscopic pores made by cellulose chains of the paper.[10] Moreover, such pores are considered to be fairly large because hydrogen bonding generally provides an open structure.[11] This is consistent with that the RTP spectra appear at longer wavelengths. Namely, on irradiation vanillin rearranges in pores and reaches the most favorable conformation in T_1, from which phosphorescence transitions occur as shown in Figure 8a.

On the other hand, vanillin in PVA films phosphoresces in the "intermediate" wavelength region, as dose vanillin in ethanol at the "hysteresis" temperatures. This is because in both cases vanillin is embedded within a stiff matrix of aggregated molecules; at the "hysteresis" temperatures, vanillin is trapped in an ethanollic crystal (section 4.2). Therefore, also in PVA films, the conformations of vanillin in S_0 are conserved during the photophysical processes due to the matrix stiffness; as a result, the transition occurs as illustrated in Figure 8c. It is noted that thermal energy for a PVA substrate at room temperature is considerably larger compared to that for ethanol at the "hysteresis" temperatures (say 120 K) so that vanillin in PVA can have conformations of much higher energies in S_0. In fact, this thermal energy difference is found to affect the phosphorescence spectra slightly; the spectrum for a PVA substrate is red-shifted by about 6 nm compared to that in ethanol at 120 K.

5. Conclusions

4-Hydroxy-3-methoxybenzaldehyde (vanillin) and 4-hydroxybenzaldehyde in ethanol show hysteresis in the temperature dependence of their phosphorescence spectra; namely, the "threshold" temperature for phosphorescence with cooling differs from that with heating. Such hysteresis arises from the supercooling of ethanol, and it is a rather general phenomenon in ethanol solution; compared to fluorescence, phosphorescence markedly undergoes the hysteresis because the latter occurs around the supercooling temperatures of ethanol. Vanillin also exhibited a peculiar change in the shape and position of the phosphorescence spectra in the *T* range of 77−155 K. Semiempirical molecular orbital calculations revealed that the spectral changes are attributed to conformational changes of vanillin due to interaction between the methoxyl and hydroxyl groups. Furthermore, comparison of the RTP spectra of vanillin to its low-temperature spectra in ethanol showed that "oblique" and "perpendicular" conformations lead to RTP for a filter paper and PVA substrate, respectively.

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