

Effect of High Pressure on Enol–Keto Tautomerization in Salicylic Acid: A Study by Steady-State Absorption and Fluorescence Measurements

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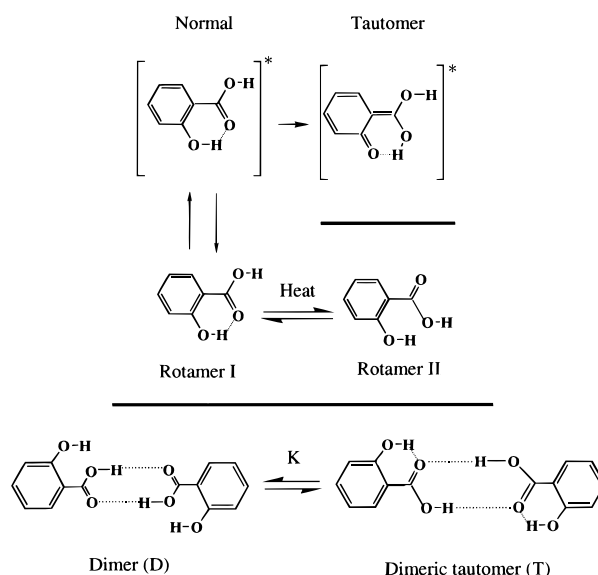
The effects of pressure (0.1–450 MPa) on enol–keto tautomerization reaction in salicylic acid (SA) have been investigated by steady-state absorption, fluorescence emission, and excitation spectroscopy. In dilute solutions, the emission intensity of the keto form of the monomer shows marked increase with pressure. In concentrated solutions, where only dimers are present, only a very small increase in the fraction of the keto form of the dimers is observed by applying high pressures. A possible reaction mechanism for such a behavior is discussed.

I. Introduction

Excited state intra- and intermolecular proton transfer (ESIPT) reactions are of great scientific and technological interest to people engaged in a wide range of fields of such as organic synthesis, oscillation of laser dyes, or design of functional materials.^{1–3} In order to deepen our experimental and theoretical understanding of the mechanism of ESIPT in complex biological systems and practical applications, it is desirable to study simpler systems such as salicylic acid (SA). ESIPT reactions in SA^{4–7} and its derivatives^{8–19} have been the subject of intense investigations. SA is unique because it provides an opportunity to study ESIPT in both monomer and dimer (Scheme 1). However, photophysical information on SA monomer, in particular, is scarce as compared to its derivatives,^{8–19} because the emission spectra of monomer and dimer overlap in condensed phase at moderate concentrations.

Monomeric SA molecule emits at ~450 nm whereas the concentrated solutions at 293 K show an overlapped UV (~370 nm) and blue (~450 nm) emission of the dimer in hydrocarbon solvents.⁴ As suggested by Weller and others,^{8–10} ESIPT from the vicinal hydroxyl group to the carbonyl group takes place in SA molecule (rotamer I). Rotamer II does not possess intramolecular hydrogen bond and can show UV emission but is absent in nonpolar solvents at room temperature. In the dimer, however, UV emission has been suggested to be due to the dimeric form, D, and the appropriate tautomeric form, T, which undergoes a fast ESIPT reaction, gives rise to a blue emission.⁴ From the studies on solid SA (dimer) at 10 K, emission from different sites has been observed upon red edge excitations.⁵ On the other hand, two rotamers of SA monomer and the dimer have been separated successfully in supersonic jet by using the fluorescence excitation and emission measurements.⁶ It has been found that upon excitation at the 0–0 band, the emission spectrum of rotamer I consists of a strong tautomer band and a very weak UV band. The latter gains intensity in a mode-specific manner upon excitation at higher vibrational bands of the absorption spectrum and becomes as strong as the former at ~850 cm⁻¹ excitation energy above the electronic origin. This is in contrast to a typical double-well potential, where with

SCHEME 1: Structures of Rotamer I, II, and Dimer of SA



increase in the excitation energy the fluorescence of the normal state decreases with collateral increase in the proton-transferred tautomer emission indicating a barrier in the excited state. The observation that the two emissions have the same fluorescence lifetime (9.6 ns) is an important information suggesting that the emission comes from the same species or the equilibrium between the two states is established within subnanosecond time scale. Therefore, it was suggested that the origin is due to a nonvertical excitation into the excited state minimum, which is displaced in the tautomer coordinate and the Franck–Condon maximum for SA monomer is located about 850 cm⁻¹ above the electronic origin under supersonic free jet conditions.⁶ This indicates that even in nonpolar solvents the observed weak emission band in the UV region may also have some contribution from the enol form of the monomer, besides that due to the dimers. This aspect of the presence of a weak UV emission in SA and its derivatives has been a subject of discussions in the past.^{12,13,20}

The application of high pressure to the solutions of SA is useful for the study of equilibrium associated with the monomer–dimer formation because the equilibrium is expected to shift toward the aggregates by increasing the pressure.^{21,22} Excited-

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state reactions governed by the diffusion such as excimer and exciplex formation are slowed down by increasing the pressure.²³ Despite the fact that the high pressure appears to favor the keto form,^{24,25} to the best of our knowledge, any study of the ESIPT reaction as a function of pressure has not been reported so far. In continuation of the studies of SA molecule, the aim of the present work is to investigate the effect of pressure on enol–keto tautomerization²⁶ in SA monomer which provides one of the simplest molecular systems for studying the ESIPT reaction.

II. Experimental Details

SA (Aldrich) was used as received. Methylcyclohexane (MCH) was of spectroscopic grade. The sample solutions were deaerated by bubbling with nitrogen for 20 min under nitrogen atmosphere unless otherwise specified. Absorption spectra were recorded by using a Shimadzu UV-260 spectrophotometer equipped with a high-pressure vessel. An optical cell with a variable optical path length was placed in the pressure vessel.²⁷ The absorption spectra were obtained by subtracting the baseline from the sample absorbance.

For the fluorescence emission and excitation measurements, a home-built spectrograph equipped with a high-pressure vessel was used. A cylindrical quartz cuvette with an inner diameter of 8 mm was used for such measurements and, hence, the measurements of the highly concentrated samples were carried out by front face geometry, thereby minimizing the self-absorption effects. The fluorescence excitation spectra were corrected for the variations in the lamp intensity or detector response with wavelength. Pressures were measured with a calibrated manganin wire. All experiments were carried out at room temperature.

III. Results and Discussion

1. Pressure Effect on Absorption Spectra. In dilute solutions of MCH (concentration range $\leq 10^{-5}$ M), SA monomer shows absorption maximum approximately at 310 nm. Upon increasing the concentration, dimer formation takes place with an equilibrium constant of ~ 5200 M⁻¹, and the absorption maximum shifts to longer wavelength.⁴ When the dimerization is achieved thoroughly in the ground state, the absorption band has a maximum at ~ 315 nm.⁴ Figure 1 shows the absorption spectra of SA (2×10^{-4} M) in MCH as a function of hydrostatic pressure. At this concentration, both SA monomer (57%) and dimer (43%) exist at 0.1 MPa. Upon application of pressure, the absorption spectrum does not change appreciably except a small increase in the optical density accompanied by a very small continuous shift of the maximum absorption toward the longer wavelength. Such increments in the optical density and continuous red shifts (pressure-induced spectral shift) in the absorption, fluorescence emission, and excitation spectra are observed generally with increasing pressure.²⁸ While these red shifts occur due to the pressure-induced change in the refractive index and the dielectric constant of the solvent, the observed increase in the optical density is due to the decrease in the volume of the solvent thereby increasing the concentration of the solute. In fact, the observed changes in the optical density with pressure are consistent with the increase in the density of MCH (0.798 g/cm³ at 0.1 MPa to 0.910 g/cm³ at 400 MPa) which corresponds to an increase in the optical density of SA by a factor of 1.14. Application of high pressures also results in an increase in the extinction coefficient, but it is usually very small (within a few percent) unless any significant structural change in the molecule under study is brought about by pressure. The molar extinction coefficients of monomer and dimer are

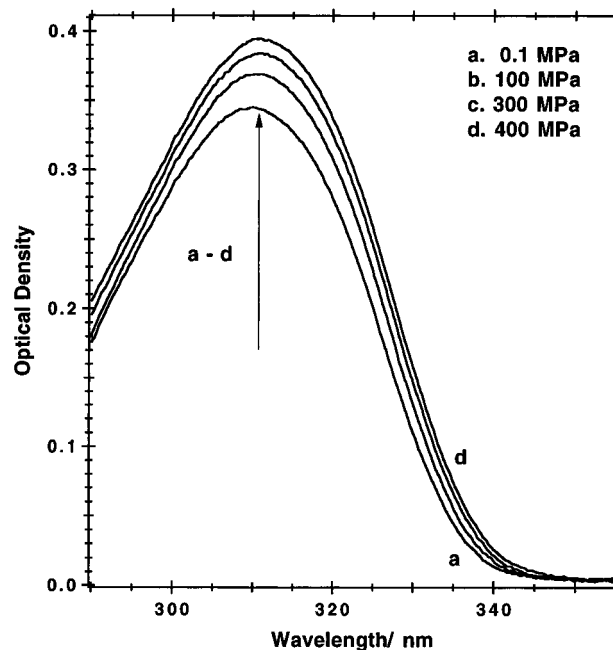


Figure 1. Absorption spectra of SA (2×10^{-4} M) in MCH measured at different indicated pressures in a cuvette of pathlength of 6 mm.

3400 and 4600 M⁻¹ cm⁻¹ at the absorption maxima, respectively.⁴ Therefore, small changes in the monomer–dimer equilibrium as a function of pressure may also contribute to the increase in the apparent optical density. At a higher SA concentration (10^{-3} M), where the dimers dominate, the increase in the value of the optical density (1.26 times) is more than that expected from the change in the density of MCH and the absorption spectra at higher pressures also show a small red shift, indicating a possibility of the formation of higher order aggregates.

2. Pressure Effect on Fluorescence Spectra. Figure 2 shows the fluorescence emission spectra of a dilute solution of SA (2×10^{-5} M in MCH) as a function of pressure. The emission spectrum of SA monomer at 0.1 MPa exhibits a largely Stokes-shifted (~ 9600 cm⁻¹) broad emission band with a maximum located approximately at 450 nm which can be ascribed to the keto form.⁴ Upon increasing the pressure, the emission band gains intensity without any change in its shape and full width at half-maximum (fwhm = 4900 cm⁻¹). The intensity of the emission due to the keto form increases by a factor of ~ 2 at 450 MPa as compared to that at 0.1 MPa.

A very weak emission band exists around 350–380 nm which may have contribution from dimers.⁴ At still lower concentrations of SA, a very small emission intensity along with an intense contribution of the Raman bands of the solvent at this wavelength region is observed, which prevents us from making a clear assignment to this weak band. The difference of the fluorescence emission spectra at 450 and 0.1 MPa shows only one emission band with a maximum located at ~ 450 nm as is shown in panel B.

At higher concentrations of SA, the emission spectra are dominated by the dimers and more than 75% of SA exists in the form of the dimers at a concentration of 10^{-3} M.⁴ The emission spectrum of the dimer consists of the two emission bands (~ 370 nm (UV band) and ~ 450 nm (blue band)). Figure 3 (panel A) shows the emission spectra of SA (10^{-3} M) in MCH as a function of pressure. Apart from a small red shift of the spectrum, an increase in the emission intensity of the blue band is observed. Panel B shows the differences of the emission spectra between the one at 0.1 MPa and those observed at the

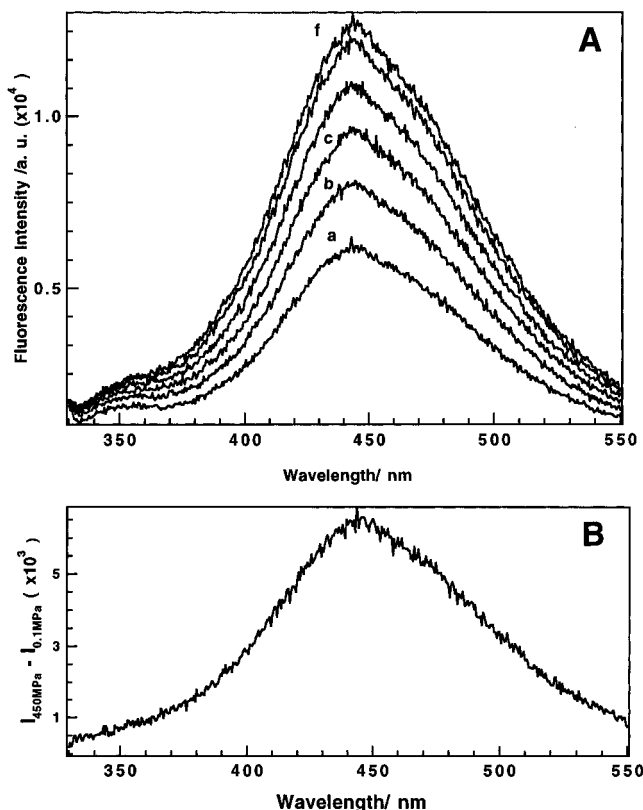


Figure 2. Emission spectra of SA (2×10^{-5} M) in degassed MCH at 293 K with varying values of pressure as 0.1, 100, 200, 300, 400, and 450 MPa, for the curves a to f, respectively (panel A, $\lambda_{\text{exc}} = 315$ nm). Panel B shows the difference of the intensities of the emission spectra observed at 450 and 0.1 MPa.

other pressures. Up to 300 MPa total emission intensity of the dimers increases. This is probably due to an increase in the concentration of the dimers due to the equilibrium shift induced by pressure. At higher pressures, the blue emission of the dimer increases with respect to its UV band. The emission spectra as a function of pressure do not show a large change in the intensity as compared to the dilute solution. The difference spectra also show a negative spectrum with a minimum in the range 340–350 nm (panel B). The intensity of the negative spectrum increases and its peak shows a red shift with increasing the pressure. Increased self-absorption effects caused by increase in the optical density at higher pressures and the pressure-induced red shift of the absorption probably account for this.

Figure 4 shows the plots of the ratio of the emission intensities at 370 and 450 nm, $I_{\text{blue}}/I_{\text{UV}}$, against the pressure at different concentrations of SA. The middle plots (b and c) contain contribution from both the monomer and dimer, whereas the plots a and d represent the cases dominated by the monomer and the dimer, respectively. The large slope of the ratio (plot a) shows that there is a relative enhancement of the intensity of the blue emission with pressure at a dilute concentration.

By increasing pressure the equilibrium constant of aggregation is also changed. However, the fluorescence intensity changes observed are not due to dimers as the fwhm of the difference of the emission spectra as a function of pressure does not change (c.f. Figure 2). This is probably due to the fact that the concentration of the dimers resulting from the change of the equilibrium at low concentrations of SA may not be enough to cause the changes in the total fluorescence. The absorption spectra of monomer and dimer are broad in shape and have a strong overlap. The extinction coefficients also are of the same order. The ratios given in Figure 4 are not corrected for the

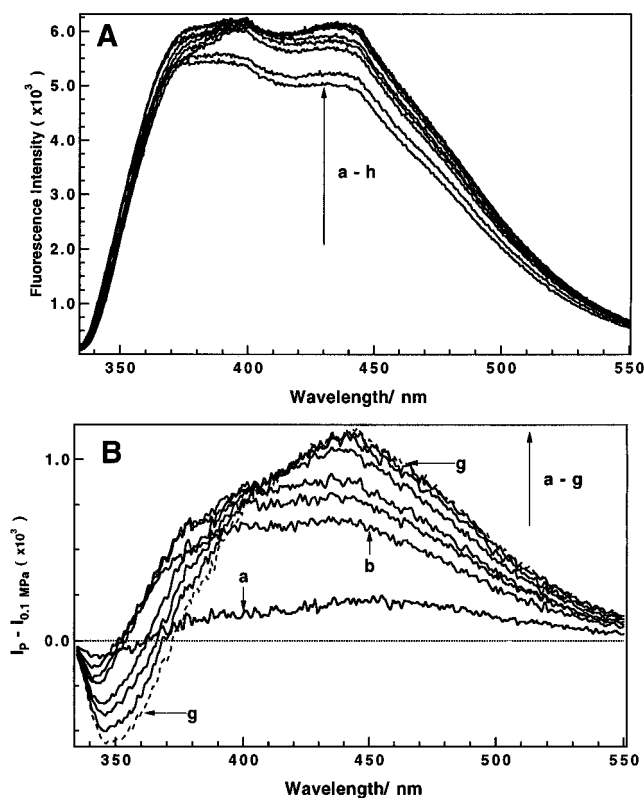


Figure 3. Emission spectra of SA (10^{-3} M) in degassed MCH at 293 K with varying values of pressure as 0.1, 50, 150, 200, 300, 350, 400, and 450 MPa, for the curves a to h, respectively (panel A, $\lambda_{\text{exc}} = 315$ nm). Panel B shows the difference of the emission spectra observed at different pressures (I_P) and that at 0.1 MPa ($I_{0.1 \text{ MPa}}$) with varying values of P as 50, 150, 200, 300, 350, 400, and 450 MPa, for the curves a to g, respectively.

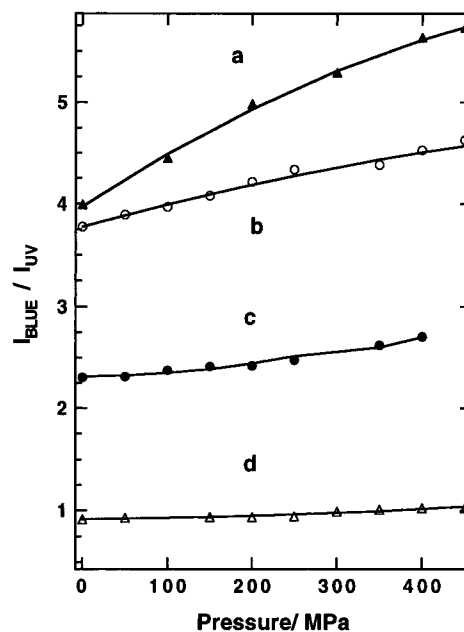


Figure 4. Plot of the ratio $I_{\text{blue}}/I_{\text{UV}}$ vs pressure with a variation in the SA concentrations as (a) 2×10^{-5} M, (b) 4×10^{-5} M, (c) 2×10^{-4} M, and (d) 10^{-3} M.

change in the concentrations of monomers and dimers in the ground state with pressure. A decrease in the quenching of the fluorescence by the dissolved oxygen at higher pressures due to the increased viscosity of MCH is also ruled out since exactly similar intensity enhancements were reproduced irrespective of deaerating conditions of the samples with nitrogen.

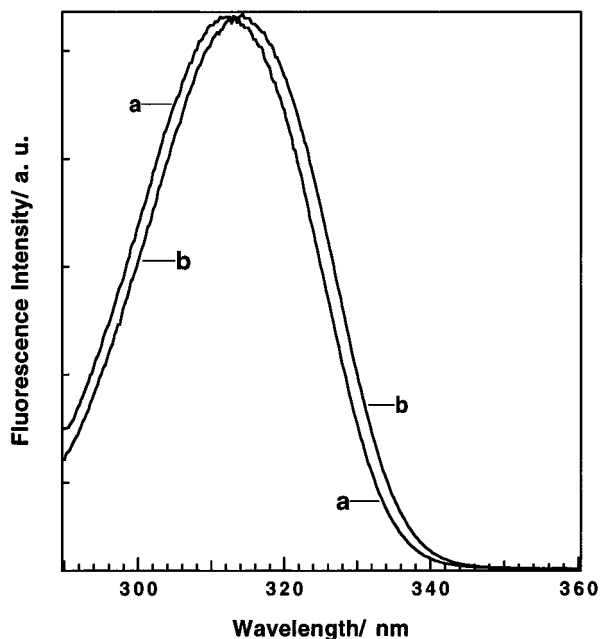


Figure 5. Excitation spectra of SA (2×10^{-5} M) in degassed MCH at 293 K ($\lambda_{\text{em}} = 450$ nm). The pressures are (a) 0.1 MPa and (b) 400 MPa. The intensities are normalized at the peak.

In a solution where dimeric SA is the dominant species, the blue intensity increases only by a factor of ~ 1.15 . As can be seen from Figure 4, the observed pressure effect on the intensity of the blue emission is largest for the lowest SA concentration and the effect decreases with increasing the SA concentration. At the highest concentration, most of the increase is accounted for by the density change of MCH with pressure, but still, the ratio of the intensity of the blue emission to that of the UV emission appears to increase, though slightly, above 250 MPa (curve d). A possibility of formation of higher aggregates at higher pressures exists at higher concentrations. Existence of monomer, though little, can also result in the small intensity enhancement. These factors make the situation more complicated. Therefore, we will now focus mainly on the behavior of the monomers.

Fluorescence excitation spectra were taken at a dilute concentration to identify the species responsible for the observed emission enhancement. Figure 5 gives the fluorescence excitation spectra of 2×10^{-5} M SA in MCH at two different pressures by monitoring the keto emission. The excitation spectra exhibit a small pressure-induced red shift but show no difference when monitoring the emission at two different wavelengths at a given pressure. This indicates that the observed emission intensity changes are due to the same emitting species at all pressures under dilute conditions. The excitation spectra were also recorded at a higher concentration (10^{-3} M SA) as a function of pressure. Although the spectra corresponding to the dimer showed a larger red shift with increasing pressure, a contribution from the self-absorption effect could not be removed to give a clear picture of formation of the higher aggregates at higher pressures.

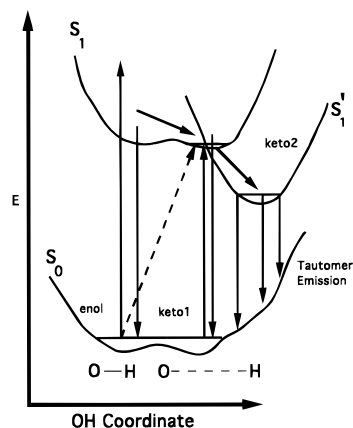
3. Stabilization of Keto Form. Rotamer I of SA monomer is thermodynamically more stable than rotamer II due to intramolecular hydrogen bonding. In the case of methyl salicylate (MS) two emission bands corresponding to two rotamers have been observed in alcohols.²⁰ SA, however, exhibits only one emission band even in alcoholic solutions, which arises not from the excited enol or keto forms but from the excited ionized species.²⁹ However, in nonpolar hydrocarbon solvents ionized species is not present. In supersonic jet

study of SA, emission of the keto form was observed even upon excitation at the weak origin of the electronic absorption band. The observed weakness of the origin was expressed to be due to a nonvertical transition between the ground “enol” to the excited state “keto” minimum.⁶ In other words, we can assume that in the ground state we have two isoenergetic forms (enol and ketol), with a difference in the tautomerization in OH coordinate and also a vertical excitation. Upon excitation at the higher vibrational bands, a strong emission from the enol form was also seen, which was explained on the basis of location of the Frank–Condon maximum toward the higher energy. However, a direct comparison of the supercooled isolated molecules and that in the solution phase does not have much relevance since the energy associated with the vibrations may lead to intramolecular vibrational relaxation (IVR) at higher excitation energies, giving rise to the broad emission spectra. Nevertheless, the strong enol emission with characteristic progression of frequency of 240 cm^{-1} observed by excess excitation energies of $\sim 400\text{ cm}^{-1}$ above the origin suggests that the enol emission can be seen in SA. The onset of the IVR appeared at about 1054 cm^{-1} above the origin, when the progression of 240 cm^{-1} disappeared from the emission spectra. Although it seems that there is no barrier for the proton transfer even at the electronic origin, the strong intensity of both UV and blue emissions at the vibrations of $364\text{--}900\text{ cm}^{-1}$ energies above the origin indicate that besides the shift of the Franck–Condon maximum toward the higher energy, SA also shows UV emission that arises from enol form. The potential well also shows strong displacements in the OH coordinates in the ground and excited state. Generally, the intensity of the fluorescence of an excited molecule remains constant or can increase a little with pressure according to the changes in the density of the solvent system. However, in the present case, a marked increase (by 2.2 times) in the emission intensity of the keto form of SA is observed at 450 MPa as compared to that at 0.1 MPa. The change in the partial molar volume (ΔV) for total enol–keto tautomerization as calculated from the observed changes in the intensity comes out to be $-4.3\text{ cm}^3/\text{mol}$. This value is close to that calculated from infrared spectroscopy.²⁴ Therefore, we attribute the observed enhancement of the ratio of emission intensity for the keto emission of monomer to the stabilization of the keto form in the ground and excited state at higher pressures.

On the basis of the discussion above, the schematic potential energy diagram for SA monomer can be described in Scheme 2. In the ground state there is an equilibrium between isoenergetic tautomers of rotamer I (enol and ketol). The difference between the two is the extent of the tautomerization in the OH coordinate. The absorption of a photon can produce the enol as well as ketol form as depicted in the diagram. Since there is no barrier to ESIPT reaction and the relaxation to S_1' (new tautomer state, keto2) proceeds rapidly,³⁰ the emissions occur from the excited enol, the excited ketol, and the keto2. The last one decays to the repulsive potential of the ketol form in the ground state. Hence, the observed emission is broad and largely Stokes-shifted. The fluorescence lifetime of the rotamer I is short (~ 350 ps at room temperature),⁷ but is still too long to compete with the fast ESIPT reaction and the nonradiative pathways. This results in a weak UV emission.

The absorption spectrum of SA is broad, and it is not possible to make any estimate for the ground state populations of enol and ketol forms from the absorption spectra. With increasing the pressure the population of the ketol form in the ground and excited state is increased, resulting in the increased emission yield of the blue emission. The emission intensity of the keto2

SCHEME 2: Schematic Potential Energy Diagram To Understand the Observed Photophysical Behavior of the SA Monomer with Pressure^a



^a Possible transitions are enol to enol, enol to ketol (nonvertical), or ketol to ketol (vertical). There is no barrier for the proton transfer and the emission maximum is observed due to a transition from the keto2 state to the repulsive state of the ketol in the ground state.

form will be a function of both ESIPT and excitation of the increased population of the ketol form in the ground state. The ketol state in the excited state is different from the keto2 tautomer state but classically closer to the tautomer form (due to displacement in O—H coordinate, as is shown schematically) with a virtual curve crossing with the tautomer state, or it may correspond to a state in which the changes in the configuration of the benzene moiety take place, which is a prerequisite for tautomerization.³¹

The present study shows that for SA in MCH the equilibrium for the dimerization and aggregation is not affected drastically upon applying the hydrostatic pressure. Although the enol and keto forms appear to be indistinguishable from the absorption and excitation spectra, the emission spectra at the lowest concentration suggest that the keto form is favored at higher pressures. The dimerization does not seem to be the cause for the observed intensity changes at low concentration as the dimer emission spectrum has two bands, while the difference spectrum in Figure 2 shows only one emission corresponding to the monomer. This is further confirmed by the plots of Figure 4 where the intensity enhancement for the keto form is large only under dilute concentrations. In the case of dimer, the intensity of the blue emission seems to be less sensitive to the pressure. This indicates that the equilibrium between D and T forms (Scheme 1) is not affected by pressure. On the other hand, increase in the self-absorption effects in emission spectra of concentrated solution with pressure may indicate a possibility of formation of higher aggregates having red-shifted absorption spectra.

A determining factor in the efficiency of the fluorescence of the tautomer produced by ESIPT excitation is the role played by the lowest triplet state between the normal and the tautomer species.³² Nevertheless, little direct evidence for the involvement of the lowest triplet state exists.³³ It is important to point out that there is a drastic increase in the fluorescence lifetime of SA from ~350 ps (room temperature) to 9.6 ns (in supersonic jet for both UV and blue emission of monomer).⁶ Those changes in the lifetime indicate that there exists a rapid radiationless decay for the excited state which is prohibited at low temperatures. The radiationless decay rate as calculated in case of MS is about $2.8 \times 10^9 \text{ s}^{-1}$ at room temperature.²⁰ The observed intensity changes, therefore, can also be understood if there exists a close low-lying triplet state in case of

monomer, for which a level inversion takes place at higher pressures similar as in case of anthracene derivatives with temperature³⁴ or pressure.³⁵ However, we were unable to detect a signal corresponding to the triplet state for very dilute solutions of the SA monomer. For a concentrated solution, an extremely weak triplet-triplet absorption was observed at 0.1 MPa in the wavelength range 440–520 nm. The optical density of the solutions at 337 nm was not enough to observe the triplet state clearly, and the very weak triplet absorption was not sufficient to study the effect of pressure on intersystem crossing directly.

IV. Summary

Pressure effects on the enol-keto tautomerization reaction in salicylic acid (SA) monomer and dimer have been investigated by steady-state absorption, fluorescence emission, and excitation spectroscopy. In dilute solutions, emission intensity of the keto form of the SA monomer increases substantially with pressure. In concentrated solutions, where only dimers are present, a very small increase in the intensity of the keto form of the dimer is observed. On the basis of the available information on the SA molecule, the stabilization of the keto form in the ground and excited state at higher pressures has been accounted as a possible explanation for the observed behavior.

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