Study of Solvent Dependence and Kinetics of Proton Transfer Reaction of 9-Phenanthrol in the Excited Singlet State

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A study on the effect of solvents on absorption and fluorescence spectra has indicated that 9-phenanthrol acts as a hydrogen donor in both S_0 and S_1 states. Fluorimetric titration gives stretched sigmoid curves, giving pK_a 9.2 and pK_a* 1.8.

The effect of solvents and pH on the absorption and fluorescence spectra of naphthylamines [1-4] and naphthyl alcohols [5-8] has been studied extensively. These molecules have certain characteristic features. The fluorimetric titration curves of the former have indicated that there is a lack of correspondence between the removal of naphthylamines and the formation of naphthylammonium ions when the pH is decreased.[1,3] This phenomenon has been attributed to the proton-induced quenching of the amino-compounds [1] at moderate pH and the formation of naphthylammonium ions take place at lower pH (or in the Hammett acidity scale H_0). In the latter cases, one gets stretched sigmoid curves, giving two inflection points, one corresponding to the ground-state equilibrium and the second to the excited-state equilibrium. Recently it has been observed that the fluorescence of neutral naphthols is quenched diabatically by H^+ at a pH approximately between 0 and 1.[5] Depending upon the lifetimes of the acid–base species as well as the other rate constants, the intersection of the two curves corresponds to the excited-state equilibrium constant (pK_a*) for 1-naphthol [6] and ground-state equilibrium constant (pK_a) for 2-naphthol.[5]

Recently, similar behaviour, as observed for naphthylamines, has been noted for phenanthrylamines.[9,10] The present investigation was carried out to study the effect of pH on the fluorescence intensity of acid–base species of 9-phenanthrol (POH) and to see whether its behaviour is similar to those of naphthols. The effect of solvents on the absorption and fluorescence spectra has also been studied.

Experimental

9-Phenanthrol was obtained from Aldrich Chemical Company and was purified by repeated crystallisation. The purity was checked by getting similar fluorescence spectra, when excited with different wavelengths of radiation. Analytical grade NaOH, H_2SO_4, and spectral grade methanol (B.D.H.) were used as such. Hexane (B.D.H.) and acetonitrile (E. Merck) were purified as in the literature.[11] Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett scale [12] for H_2SO_4–H_2O was used for solutions below pH 1. The solutions for absorptiometric and fluorimetric titrations were prepared just before taking the measurements. The concentrations of the solutions were of the order 10^{-5}—10^{-4}M. In fluorimetric titrations, while measuring the relative fluorescence intensities at the analytical wavelengths as a function of H_0–pH, the isosbestic wavelength (316 ± 5 nm) was used for excitation.

Absorption spectra were recorded on a Cary 17D spectrophotometer. Fluorescence measurements were made on a scanning spectrofluorimeter made in our laboratory.[13] Excitation and emission monochromators were calibrated using a low-pressure mercury lamp. pH Measurements were made on a Toshniwal pH meter model CL-44A.

Table 1. Absorption maxima ($\tilde{\nu}_{abs}$/cm^{-1}) and $\varepsilon_{max.}$ (in parentheses) of 9-phenanthrol in different solvents

Hexane	Acetonitrile	Methanol	Water	Anion
28 288	28 169	28 011	28 248	26 266
(3.25)	(2.89)	(2.78)	(3.00)	(2.95)
29 761	29 673	29 411	29 673	31 060
(3.25)	(3.24)	(3.08)	(3.59)	(3.43)
32 840	32 460	32 679		
(3.75)	(3.54)	(3.52)		
33 990	33 670	33 500	33 898	37 880
(3.80)	(3.67)	(3.74)	(3.59)	(4.10)
36 769	36 697	36 429		
(4.11)	(4.08)	(4.01)		
39 840	39 682	39 525	39 840	39 680
(4.55)	(4.51)	(4.50)	(4.23)	(4.21)

Results and Discussion

Effect of Solvents on Absorption and Fluorescence Spectra.— The absorption spectra of POH was recorded in different solvents. $\tilde{\nu}_{max.}$(abs) values, along with $\varepsilon_{max.}$ in each solvent are listed in Table 1. When compared to the values in hexane, the absorption maxima in other solvents are red-shifted. But the red shift is not directly related either to the polarity or to the hydrogen-bonding ability of the solvents. The red shift in methanol is more than that in acetonitrile, showing that hydrogen-bonding interactions are more dominant than dispersive interactions. But in water, a blue shift is observed relative to the maxima in methanol.

The fluorescence spectra of POH in different solvents are shown in Figure 1 and the $\tilde{\nu}_{max.}$(flu) are listed in Table 2. The fluorescence spectrum of POH in water at neutral pH indicated two fluorescence bands, one at 2.6 × 10^4 cm^{-1} and the other at 2.08 × 10^4 cm^{-1}, whereas in aqueous solutions at pH < 1 only one band at 2.6 × 10^4 cm^{-1} and at pH > 12.0 at 2.08 × 10^4 cm^{-1} is observed. This indicates that the former band is due to POH (neutral phenanthrol molecule) and the latter is due to PO^- (phenanthrolate ion). In hexane, the fluorescence spectrum is nicely structured whereas the structure is lost as the polarity or hydrogen-bonding capacity of the solvent increases. This is quite expected because of the increase in the interaction of the solvent with the solute molecule in S_1. The fluorescence spectra is red-shifted with the increase in the hydrogen-bond tendency of the solvents and deprotonation results in a further red shift.

Like the amino-group, the hydroxy-group can also act like a bifunctional system, *i.e.* it can interact with hydrogen-donating solvents through its lone pair or with hydrogen-accepting solvents through the hydrogen atom of the hydroxy-group. Thus, with the increase in the hydrogen-bonding capacity of the solvents, a blue shift in the former case and a red shift in the latter case should be observed. In POH, the

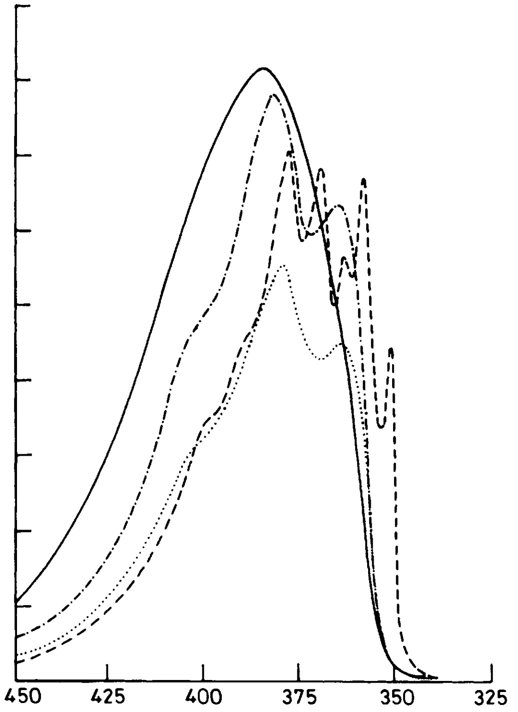


Figure 1. Fluorescence spectra of 9-phenanthrol (10^{-5}M) in different solvents: — — — —, hexane; · · ·, acetonitrile; — · — ·, methanol; ——, acid solution (H_0 −0.5)

Table 2. Fluorescence maxima ($\tilde{\nu}_{flu}$/cm^{-1}) of 9-phenanthrol in different solvents

Hexane	Acetonitrile	Methanol	Water [a]	Anion
28 450				
27 855				
27 427	27 397	27 359	25 974	20 830
27 063				
26 455	26 280	26 110		
25 000				

[a] At H_0 −0.5.

charge-transfer interaction of the lone pair of the hydroxy-group with the phenanthrene ring is less, as is clear from the structured absorption spectrum in all the solvents and structured fluorescence spectrum in less polar solvents, in comparison to that of the lone pair of the amino-group of 9-phenanthrylamine.[10] Moreover owing to the high polarity of the O–H bond, the solute molecule will be acting preferentially as a hydrogen-atom donor rather than a hydrogen-accepting one. This would explain the red shift observed in the absorption spectra in acetonitrile and methanol. When compared to methanol, a blue shift is observed in water, indicating a hydrogen-donor interaction due to its greater hydrogen-donating capability than that in methanol. But in the first excited singlet state, the polarity of the O–H bond is further increased due to the increased charge-transfer interaction from the hydroxy-group to the aromatic ring and thus a continuous red shift is observed from hexane to water. Except for water, the site of interaction is found to be the same in the excited as well as in the ground state.

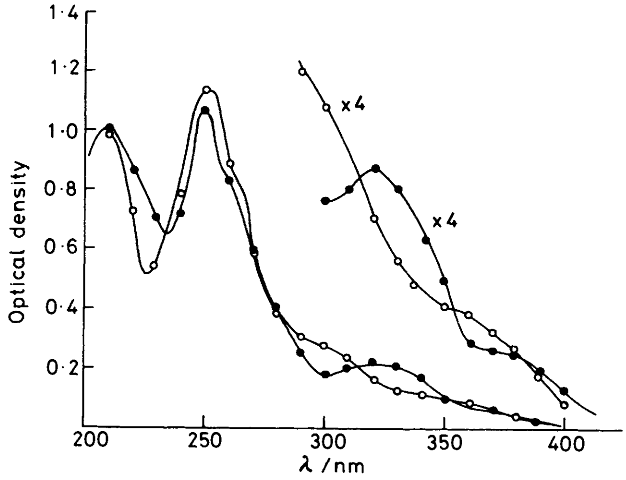


Figure 2. Absorption spectra of 9-phenanthrol at pH 6.8 and 12.0

Effects of pH.—The absorption spectra of POH in water as a function of pH are shown in Figure 2. With an increase in pH, the absorption peaks move to longer wavelength, due to the shift in the ground-state equilibrium (1) for POH. The

$$\mathrm{POH} + \mathrm{OH}^- \rightleftharpoons \mathrm{PO}^- + \mathrm{H_2O} \qquad (1)$$

longest wavelength absorption maxima found in water were at 2.83×10^4 and 2.63×10^4 cm^{-1} for the acidic and basic forms respectively. The ground-state pK_a value for equilibrium (1) was calculated using the Henderson–Hasselbach equation and relevant absorption data. The pK_a for POH in water was found to be 9.1 ± 0.1.

The fluorescence spectra of POH have been studied from H_0 −1 to pH 13 and fluorescence spectra of only two species were observed. $\tilde{\nu}_{max.}$(flu) at 2.6×10^4 cm^{-1} at H_0 −0.05 is attributed to the neutral POH molecule and $\tilde{\nu}_{max.}$(flu) at 2.08×10^4 cm^{-1} at pH > 12 is due to PO$^-$ anion. The pK_a* (1) value was calculated using the Förster cycle method [14] and the absorption, fluorescence, and average of absorption and fluorescence data of the acid–base pair. The values obtained by each method are 4.9, −1.75, and 1.65, respectively, indicating clearly that the molecule is a stronger acid in S_1 than in S_0.

The relative fluorescence intensities for the acidic (φ/φ_0) and basic (φ'/φ_0') forms were determined experimentally from the fluorescence measurements, using the method of Weller,[15] which corrects the overlap of fluorescence (*i.e.* the contribution of pure acid form to basic fluorescence and *vice versa*) as well as quenching in the strongly acid solution. In the present case, virtually no proton-induced fluorescence quenching of POH is observed at low pH. The values of the relative fluorescence intensities φ/φ_0 and φ'/φ_0' are plotted in Figure 3, as a function of pH. Examination of the fluorimetric titration curves indicates that these are stretched sigmoid curves with two inflection points, one of which corresponds to pK_a (9.2) and the other to pK_a* (1.9). Even though the point with $\varphi/\varphi_0 = \varphi'/\varphi_0' \sim 0.5$ occurs at pK_a* 1.9, the extension of the curves up to pH 13 shows that the equilibrium in the excited state is not complete. This type of behaviour indicates that the rate of proton transfer in S_1 is comparable to the rate of fluorescence. The shapes of the fluorimetric titration curves obtained can be explained on the basis of the kinetics of excited-state proton transfer.

At pH *ca.* 0.0, in strong acid, the φ/φ_0 curve starts descending gradually with increase in pH, until a plateau value of

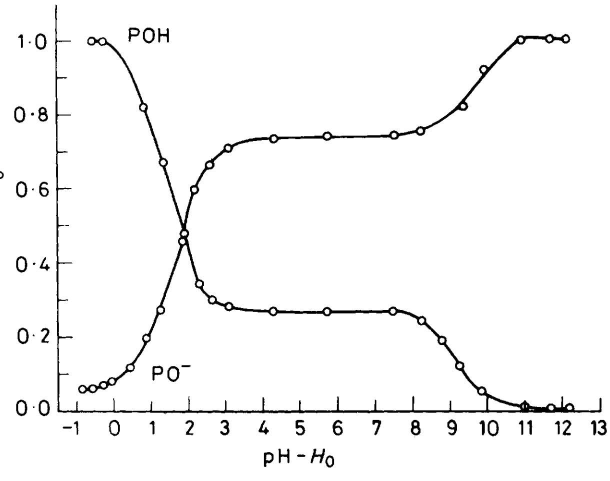


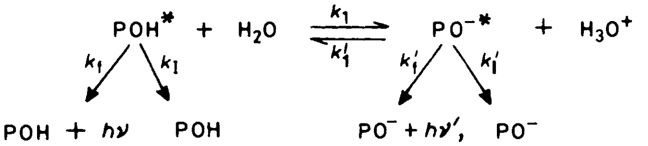
Figure 3. Plot of relative fluorescence intensities of 9-phenanthrol and its anion *versus* pH–H_0

0.265 is obtained at pH *ca.* 3. For this pH range, the φ'/φ_0' curve, starting at *ca.* 0 in the strong acid, starts increasing with the increase of pH until a plateau value of 0.75 is obtained at pH *ca.* 3 and also intersecting with φ/φ_0 curve at pH 1.9, giving pK_a^* for deprotonation of POH in the S_1 state. The plateau regions for φ/φ_0 and φ'/φ_0' continued for both curves up to pH 8. At pH *ca.* 8, there is a further sharp decrease in the φ/φ_0 curve and an increase in φ'/φ_0', until the quenching of the former and the formation of the latter is complete by pH 12. The two curves do not cross each other again but there is an inflection point at pH 9.2, which is the ground-state pK_a of reaction (1).

The shapes of the early part of the curves (at low pH) may be understood on the basis of reaction (2) occurring in the S_1

$$\mathrm{POH^* + H_2O \rightleftharpoons PO^{-*} + H_3O^+} \tag{2}$$

state. In the plateau region (pH 3—7), fluorescence is emitted from the excited POH and PO^- ions. The presence of appreciable amounts of excited phenanthrolate ions at pH 3—8 clearly indicates that these ions must have been formed from some excited-state reaction as PO^- is nearly nonexistent in the ground state at more than 2—3 pH units to the low side of the pK_a of 9.1. Further, water molecules are the only species which can accept protons in this pH range. It cannot be OH^- ions as the concentration of OH^- is very small in this range of pH and the rate does not depend upon $[OH^-]$. Also in the plateau region, the rate of the back reaction must be very small as no pH dependence of this rate is observed. The behaviour of the latter part of the curves (pH > 8) is due to the ground-state equilibrium reaction (1) being shifted appreciably to the right in the region of the pK_a of POH. Owing to this, there will be a decrease in POH, which in turn leads to POH* and subsequently increase in PO^- leads to increase in PO^{-*}. A similar kind of behaviour has been observed for 1-naphthol[6] and 2-naphthol.[5] The Scheme explains the above behaviour where k_1 is the pseudo-first-order rate constant for proton transfer from the excited POH molecule and k_f and k_i are the rate constants for light emission and radiationless deactivation of the excited phenanthrol molecule. The primed values are the analogous terms for the excited phenanthrolate ion. If the equations derived by Weller[16-18] using simple steady-state kinetics are applied, then the relative quantum yields of POH (φ/φ_0) and PO^- (φ'/φ_0') are given by equations (3) and (4) where τ_0 and τ_0' are the lifetimes of the POH and PO^-, respectively. If the rate of the reaction with solvent molecules in equation (2) is comparable to or greater than the rate of fluorescence of POH and the rate of the second-order protonation of PO^- is much less than the rate of fluorescence (which is true as explained earlier) equations (3) and (4) become (5) and (6). Equations (5) and (6) indicate that



Scheme.

$$\varphi/\varphi_0 = \frac{1 + k_1'\tau_0'\,[\mathrm{H_3O^+}]}{1 + k_1\tau_0 + k_1'\tau_0'[\mathrm{H_3O^+}]} \tag{3}$$

$$\varphi'/\varphi_0' = \frac{k_1\tau_0}{1 + k_1\tau_0 + k_1'\tau_0'[\mathrm{H_3O^+}]} \tag{4}$$

$$\frac{\varphi}{\varphi_0} = \frac{1}{1 + k_1\tau_0} \tag{5}$$

$$\frac{\varphi'}{\varphi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0} \tag{6}$$

φ/φ_0 and φ'/φ_0' are independent of $[H^+]$ or $[OH^-]$. Thus the plot of φ/φ_0 or φ'/φ_0' *versus* $[H^+]$ or $[OH^-]$ should give a flat horizontal line for each species and this is observed for both the acid and the base forms of POH in the pH range 3.2—7.7. The independence of φ/φ_0 and φ'/φ_0' from pH may be due to small values of k_1' relative to $1/\tau_0'$ or due to the low concentration of H^+ ions, since at low pH ($[H^+]$ *ca.* 0.1M) the excited PO^- ions formed from POH* are protonated quickly. The latter seems to be the favoured reason. At 298 K, the values of φ/φ_0 and φ'/φ_0', obtained from the flat regions of the curves, are 0.265 and 0.75, respectively. Thus, using equations (5) and (6), the calculated values of $k_1\tau_0$ are 2.77 and 3.0, respectively, giving the mean as 2.88.

Equations (3) and (4) also leads to expression (7) for the ratio of the relative quantum yields. The plot of the ratio of

$$\frac{\varphi\varphi_0'}{\varphi_0\varphi'} = \frac{1}{k_1\tau_0} + \frac{k_1'\tau_0'}{k_1\tau_0}\,[\mathrm{H_3O^+}] \tag{7}$$

the experimentally determined quantum yield *versus* $[H_3O^+]$ should be a straight line, with slope $k_1'\tau_0'/k_1\tau_0$ and intercept $1/k_1\tau_0$. Figure 4 shows that this plot is linear in the $[H^+]$ range from pH 3 to 2. A deviation from linearity at higher concentrations for POH was observed. This could be due to the variation in ionic strength at high proton concentration and non-ideal behaviour of the solution and thus, equation (7) should be modified by including the activity coefficients to take account of non-ideal behaviour of the solution. The values of $k_1\tau_0$ and $k_1'\tau_0'$ obtained from the linear portion are 2.94 and 112.7 l mol^{-1} respectively. The value of $k_1\tau_0$ calculated from this plot agrees nicely with that obtained from the plateau. Knowing the lifetimes τ_0 and τ_0' one can calculate the respective rate constants k_1 and k_1' and thereby the pK_a^* value.

The values of pK_a^* calculated by the Förster cycle method and from absorption and fluorescence data disagree with each other. The difference between the two could be due to (i) location of the 0–0 band (especially in the absorption spectrum of POH) and (ii) different solvent relaxation of POH and

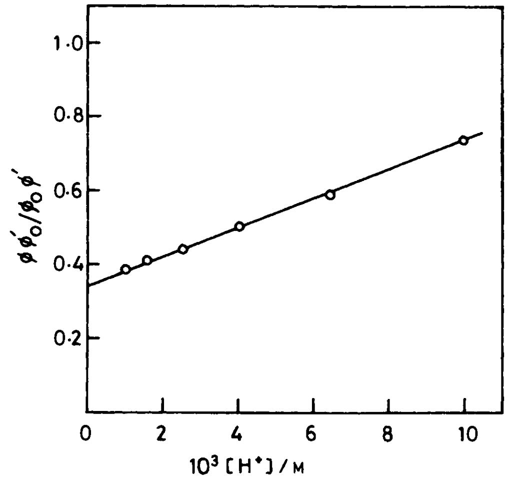


Figure 4. Plot of $\varphi\varphi_0'/\varphi_0\varphi'$ *versus* [H$^+$]

PO$^-$ in the ground and excited states. The agreement between the pK_a* calculated from the average of fluorescence and absorption maxima and that with the help of the fluorimetric titration method is quite good. This only indicates that the above effects are acting in opposite directions for the acid–base pair in the two electronic states. Of course the best value can only be calculated provided the lifetimes of the acidic and basic species are known.

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