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Luminescence of Pyridinols and Related Molecules

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Synopsis. Quantum yields of fluorescence and phosphorescence together with lifetimes at 77 K suggest that 2-pyridinol exists in the keto form in the excited states as well as in the ground state, and the lowest excited singlet and triplet states for 2-, 3-pyridinol, 2-methoxypyridine, and *N*-methyl-2-pyridone are ($\pi\pi^*$) states. The lowest triplet state for 4-pyridinol takes the keto form, and is assigned to ($\pi\pi^*$).

Studies on tautomerism of pyridinols in the ground state carried out by Mason and others[1)] show that 2- and 4-pyridinol exist as the tautomeric pyridones in aqueous solutions, whereas 3-pyridinol exists as an equilibrium mixture of the enol and keto form in the same solvent. Closely related compounds such as 2-methoxypyridine and *N*-methyl-2-pyridone correspond to the enol and keto forms of 2-pyridinol, respectively. Quantum yields of fluorescence Φ_f and phosphorescence Φ_p for these compounds in an alcohol (ethanol containing 10% methanol) mixture (A), an acidic (1 N sulfuric acid) alcohol mixture (H+), and an alcohol mixture containing 0.1 N sodium hydroxide (B) at 77 K and at 300 K are given in Table 1, together with lifetimes of fluorescence τ_f and phosphorescence τ_p. Temperature dependence and/or protonation effect of Φ_f's, which are characteristic of some nitrogen heterocyclics, clearly show the contribution of the close $^1(n\pi^*)$ or $^3(n\pi^*)$ state in energy[2)] to radiative and/or radiationless transitions from the lowest excited singlet state. The lowest excited singlet and triplet states for 2-pyridinol and its derivatives in protic solvents are assigned to ($\pi\pi^*$) from ϕ_f's and τ_p's. Fluorescence spectra of 2-pyridinol do not resemble those of 2-methoxypyridine. From a comparison of these spectra and quantum yields it is evident that 2-pyridinol takes the keto form (pyridone) even in the excited state just as in the ground state.

The temperature dependence and protonation effect of Φ_f's and Φ_p's for 3-pyridinol closely resemble those for 2-methoxypyridine. In solvent (B), the formation of the 3-pyridinolate anion[3)] may partly be responsible for the temperature independence of Φ_f's. These observations together with τ_p's suggest that 3-pyridinol takes the enol form in the excited state in the solvents

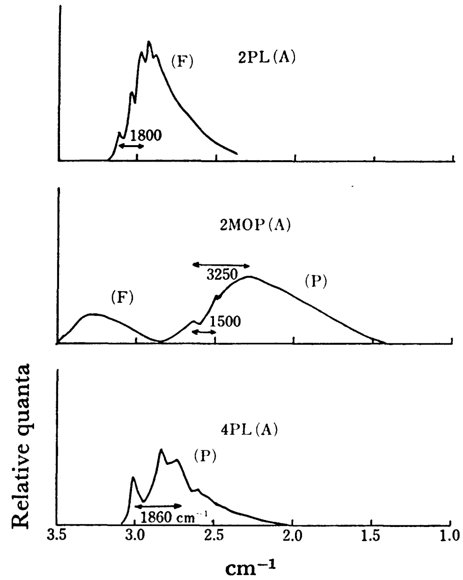

Fig. 1. Fluorescence (F) and phosphorescence (P) spectra at 77 K.

Table 1. Quantum yields and lifetimes of fluorescence and phosphorescence for pyridinols and related molecules

	300 K		77 K							
	$\lambda_{f\,max}$ (nm)	Φ_f	$\lambda_{f\,max}$ (nm)	Φ_f	τ_f (ns)	$\lambda_{p\,max}$ (nm)	Φ_p	τ_p (s)	$k_f \times 10^{-7}$ (s^{-1})	$k_{nr} \times 10^{-7}$ (s^{-1})
2PL(H+)	364	0.014	337	0.33	5.6	449	0.05	1.29	5.9	12
(A)	365	0.009	344	0.54	8.5	476	<0.005	0.39	6.4	5.4
(B)	351	0.10	328	0.16	4.9	444	0.26	0.91	3.3	17
2MOP(H+)	317	0.008	309	0.14	1.3*	417	0.19	2.65		
(A)	303	0.014	295	0.06	0.9*	430	0.17	1.34		
NM2P(H+)	357	0.009	335	0.31	8.4	444	0.08	1.44	3.7	8.2
(A)	364	0.006	342	0.53	10.6	476	<0.005	0.6	5.0	4.4
3PL(H+)			317	0.18	9.1	476	0.04	0.84	2.0	9.0
(A)	306	0.009	306	0.06	1.1*	417	0.22	1.68		
(B)	357	0.06	326	0.06	1.2*	449	0.34	0.92		

2PL, 2MOP, NM2P, and 3PL are abbreviations for 2-pyridinol, 2-methoxypyridine, *N*-methyl-2-pyridone, and 3-pyridinol, respectively. The symbol * means the calculated lifetimes obtained from integrations of absorption and fluorescence spectra together with the observed Φ_f's.[8)]

The character k_f and k_{nr} are transition rates of fluorescence and radiationless processes from the lowest excited singlet state, respectively.

used in this work, and that the lowest excited singlet and triplet states are assigned to $(\pi\pi^*)$.

Φ_f's and Φ_p's for 4-pyridinol at 77 K are smaller than 0.01 irrespective of solvents, except Φ_p in solvent (A), in which Φ_p is 0.15. τ_p's for 4-pyridinol at 77 K vary from 0.3 to 1 s, depending on solvents. The phosphorescence spectra for 4-pyridinol in solvent (A) show the well defined vibrational structure, in which a characteristic vibration indicative of the keto form may be found,[4] as in the fluorescence spectra for 2-pyridinol in the same solvent. These observations lead to the conclusion that 4-pyridinol takes the keto form in the lowest triplet state which is assigned to $(\pi\pi^*)$. Calculations[2] suggest the $(n\pi^*)$ assignment for the lowest excited singlet state of 4-pyridinol in the keto and enol forms, but it is difficult to make conclusive assignment from observation of the small Φ_f values only.

Experimental

2-, 3-, and 4-pyridinol were recrystallized five times from ethanol and/or acetone, then purified by zone melting, and finally sublimed *in vacuo*. 2-methoxypyridine and *N*-methyl-2-pyridone were distilled through a spinning band column at reduced pressure, then purified through a basic alumina column, and finally distilled *in vacuo*. Ethanol (Wako pure chemicals, analytical grade) was refluxed over silver nitrate and potassium hydroxide, and then distilled through a glass packed column. Methanol (Wako pure chemicals, analytical grade) was distilled through a glass packed column. Sulfuric acid and sodium hydroxide were of analytical grade (Wako pure chemicals and Yashima chemicals, respectively).

Φ_f's and/or Φ_p's for luminescence were determined by comparison with those of quinine hydrogensulfate (5×10^{-3} M, $\Phi_f=0.51$ at 300 K),[5] and not corrected for change in refractive indices of solvents. The optical arrangement used in measurements of Φ_f's and Φ_p's was of surface type, which allows for the exciting light to be absorbed completely through the first 1—2 mm optical path (concentration 10^{-2}—5×10^{-4} M). The concentration quenching was negligibly small for these molecules, as is estimated by Stern-Volmer's plot (not given). The sensitivity correction of the combination of monochromator with photomultiplier was made with the use of a standard lamp.[6] The lifetime measurements for fluorescence were carried out by the stroboscopic technique,[7] and those for phosphorescence with a Tektronix 454A oscilloscope with manually operated shutter. Concentrations used in lifetime measurements were 10^{-4}—10^{-5} M. All the samples were evacuated by repeated cycles of freezing, pumping, and thawing. The sample cells were then sealed off from the evacuation system.

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