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Deuterium isotope effects on the fluorescence of phenylpyridines

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Abstract

A comparison of the fluorescence behavior of 2-, 3- and 4-phenylpyridines in H_2O and D_2O confirms the excited state protonation of these molecules in the excited singlet state. In the case of 2-phenylpyridine, the ratio of the fluorescence yield in water to the value measured in D_2O is 2.73. Results indicate that two factors control the isotope effect on the fluorescence quantum yield: the faster mobility of the proton relative to the deuterium ion leading to a higher fluorescence yield, and an inverse effect associated with the slowing down of the deprotonation step in D_2O during intersystem crossing. The inverse effect observed with 4-phenylpyridine is attributed to a larger triplet yield and increased basicity relative to the 2- and 3-isomers. The absence of the excited state proton transfer and isotope effect with 2,6-diphenylpyridine is the result of inverted n,π and π,π states and a lower pK_a relative to the monosubstituted phenylpyridines. © 1997 Elsevier Science S.A.

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1. Introduction

In previous studies on the excited state behavior of phenylpyridines we have shown that these molecules require an excited state proton transfer (ESPT) in order to fluoresce [1,2]. Deuterium isotope effects have been demonstrated in the fluorescence behavior of molecules in which protonation is a rate determining step or in cases where C–H, O–H, or N–H relaxation processes are significant [3]. Deuterated acetone undergoes enhanced fluorescence and phosphorescence when compared to acetone by slowing down radiationless decay via C–D bonds relative to C–H bonds [4]. Since the excited state protonation should exhibit a deuterium isotope effect, we initiated a study of the fluorescence quantum yield of 2-, 3-, and 4-phenylpyridines and 2,6-diphenylpyridine in H_2O and D_2O.

2. Experimental

2.1. Materials

The phenylpyridines were obtained from Aldrich Chemical Co. and purified as follows: 2- and 3-phenylpyridines were vacuum distilled prior to use, and 4-phenylpyridine and 2,6-diphenylpyridine were recrystallized from hexane. Glass-distilled water was used after verifying that it had no fluorescence impurities, and deuterium oxide was used as received (from Aldrich Chemical Co.).

2.2. Apparatus and procedures

Fluorescence measurements were made at 300 nm with a Perkin-Elmer LS-50 fluorospectrophotometer, and UV absorption data were obtained with an HP-8452A diode array spectrophotometer. The fluorescence quantum yields in H_2O and D_2O were determined relative to the value $\Phi_F = 0.60$ for 2-aminopyridine in 0.1 N H_2SO_4 [5]. Phosphorescence yields for 2-phenylpyridine and 2,6-diphenylpyridine at 77 K were determined relative to $\Phi_P = 0.27$ for 4-phenylpyridine [1].

3. Results

The fluorescence results for 2- and 3-phenylpyridines clearly show enhanced fluorescence in H_2O relative to D_2O, and the effect is the largest for 2-phenylpyridine, which is shown in Fig. 1. The fluorescence envelope is the same for the two solvents; however, the fluorescence yield is 2.73 times larger in H_2O, clearly showing a significant isotope effect resulting from the faster excited singlet state protonation process in water. In the case of 3-phenylpyridine, the

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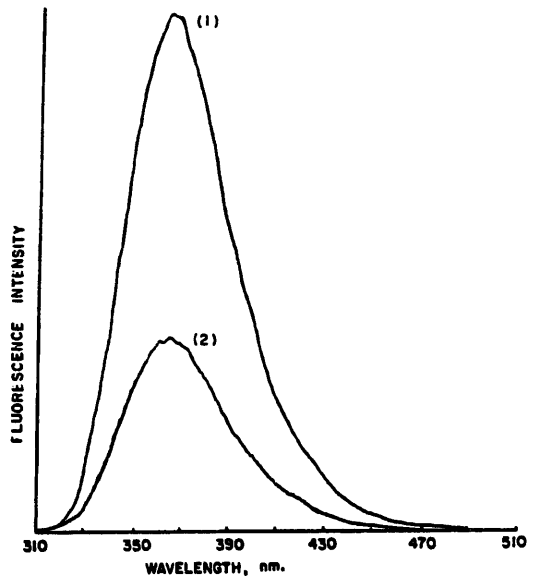


Fig. 1. Fluorescence spectrum of 2-phenylpyridine in (1) water and (2) D_2O (λ_{exc} = 300 nm).

ratio of the fluorescence yield in H_2O to the value in D_2O was determined to be 1.13. Noteworthy is the fact that with 4-phenylpyridine there is an inverse isotope effect with the quantum yield ratio dropping to 0.73.

The fluorescence yield of 2,6-diphenylpyridine does not exhibit any isotope effect when changing from H_2O to D_2O as was observed with the 2-, 3- and 4-derivatives. In this case, an excited state protonation does not occur and in fact fluorescence can be seen in cyclohexane as well as in dioxane, acetonitrile, alcohol and water. A comparison of the fluorescence spectra for the neutral molecule in dioxane and water and for the pyridinium ion in acidic solutions is presented in Fig. 2. From the pH dependence of its absorption spectrum, we estimated the pK_a for the pyridinium ion to be 3.6, which

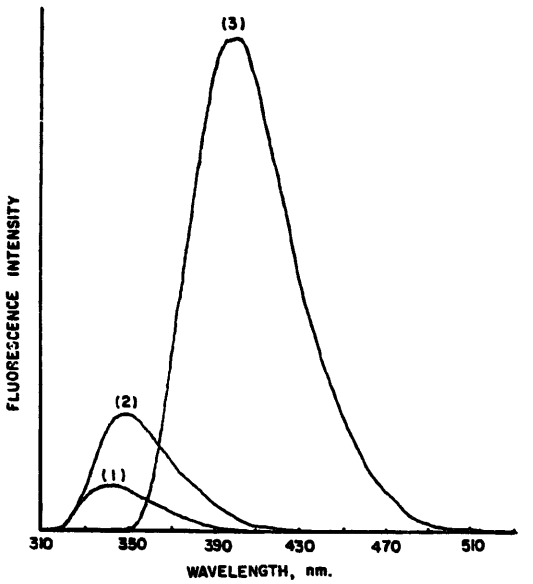


Fig. 2. Fluorescence spectrum of neutral 2,6-diphenylpyridine in (1) dioxane and (2) water, and (3) as the pyridinium ion in 0.1 N H_2SO_4 (λ_{exc} = 300 nm).

is anomalously low when compared to the other phenylpyridines.

It appears that steric hindrance induced by the second phenyl group is partially responsible for the small pK_a. In 2-, 3-, and 4-phenylpyridines, the lowest excited singlet, S1, is n,π^* and is more basic than S1 in 2,6-diphenylpyridine, which is of π,π^* character. The pK_a^* for the pyridinium ion is 9.0 ± 0.5 [2], which together with the lifetime of the singlet state determines whether or not ESPT occurs.

A summary of the fluorescence quantum yields in H_2O and D_2O for the four molecules investigated is given in Table 1, which shows a decreasing ratio of quantum yields from 2.73 in 2-phenylpyridine to 0.73 for 4-phenylpyridine, while the pK_a for the pyridinium ion increased from 4.5 to 5.3 and the phosphorescence yield, measured at 77 K, increased from 0.017 to 0.27. 2,6-Diphenylpyridine does not show any isotope effect since its pK_a is too small to undergo excited singlet state protonation.

4. Disussion

It is evident from our results that the excited state protonation observed for 2- and 3-phenylpyridines is a significant process, leading to a larger fluorescence quantum yield in water relative to D_2O. The magnitude of the isotope effect decreases with increasing basicity of the molecule and shows an inverse effect in 4-phenylpyridine due to a slower deprotonation during intersystem crosssing. With 2,6-diphenylpyridine, fluorescence can be observed in a hydrocarbon, and polar and hydrogen-bonding solvents, and is attributed to an inversion from an n,π to a π,π excited singlet state. The anomalously low pK_a value of 3.6 for this molecule accounts for the absence of excited state protonation in its fluorescence, as is seen with 2-, 3- and 4-phenylpyridines. A lower than expected basicity in 2,6-disubstituted pyridines has been reported by Hopkins et al. [6].

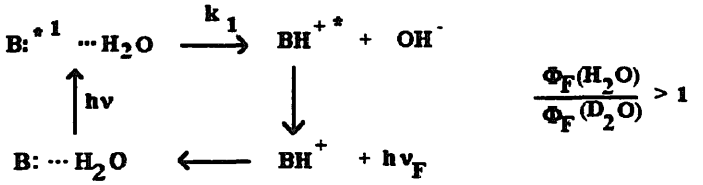
The result that we consider interesting and unexpected is the inverse isotope effect observed with 4-phenylpyridine. This molecule, when dissolved in water, undergoes an excited singlet state protonation leading to a fluorescence yield and spectrum that is indistinguishable from the case when all the molecules are protonated in the ground state. To account for the isotopic fluorescence yield ratio of 0.73 given in Table 1, we need to consider an additional radiationless contribution involving the excited singlet state. Since intersystem crossing is also important in these molecules, and the protonated excited singlet state deprotonates in converting to the triplet state, there are two opposing isotopically sensitive processes that involve the protonated singlet state, indicated as Schemes 1 and 2.

Scheme 1 illustrates the process leading to a lower fluorescence yield in D_2O and the ratio $\Phi_F(H_2O)/\Phi_F(D_2O) > 1$, while Scheme 2 illustrates that the deprotonation step occurring during intersystem crossing to the triplet which should slow down in D_2O, allows the excited singlet to live longer,

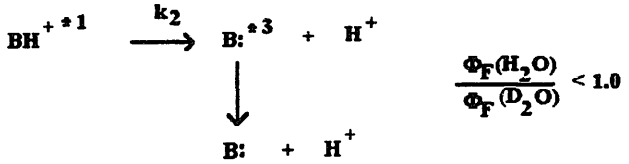
Table 1
Summary of fluorescence data for the phenylpyridines in H_2O and D_2O[a]

Molecule	pK_a	$\Phi_F^{298}(H_2O)$	$\Phi_F(H_3O^+)/\Phi_F(H_2O)$	$\Phi_F(H_2O)/\Phi_F(D_2O)$	Φ_P^{77}(EPA)
2-Phenylpyridine	4.5[b]	0.12	5.92	2.73	0.017
3-Phenylpyridine	4.8[b]	0.08	1.63	1.3	0.09[e]
4-Phenylpyridine	5.3[c]	0.19	1.00	0.73	0.27[f]
2,6-Diphenylpyridine	3.6[c]	0.16[d]	4.00	1.0	0.021

[a] $\lambda_{exc} = 300$ nm.
[b] [7].
[c] pK_a value for the pyridinium ion determined from the pH dependence of the absorption spectra.
[d] The neutral molecule fluorescence maximum appears at 350 nm in water; protonated molecular fluorescence has a wavelength maximum at 396 nm. The fluorescence envelope remains the same in neutral aqueous and acidic solutions of 2-, 3- and 4-phenylpyridines since the neutral molecule of these isomers do not fluoresce.
[e] [2].
[f] [1].



Scheme 1.



Scheme 2.

and leads to $\Phi_F(H_2O)/\Phi_F(D_2O) < 1$. These opposing effects are important with 4-phenylpyridine, which is the most basic. The pK_a^* of the triplet state is usually similar to that of the ground state, and with 4-phenylpyridine the pK_a^* of the excited singlet state is more basic than the ground state by 4 pK units. The deprotonation step during intersystem crossing is slower for the most basic molecule and extends the lifetime of the protonated excited singlet state to yield more fluorescence. From the two processes indicated in Schemes 1 and 2, the former is dominant in the case of 2-phenylpyridine, which has the smallest phosphorescence yield and the largest isotope effect. In the case of 3-phenylpyridine, the phosphorescence yield is larger, thereby diminishing the isotopically sensitive quantum yield ratio from 2.73 to 1.13. The inverse isotope effect observed with 4-phenylpyridine is due to the higher triplet and phosphorescence yield. This molecule is the most basic and tightly H-bonded system. It is seen in Table 1 that for 2-, 3- and 4-phenylpyridines, the isotope effect decreases as the phosphorescence yield increases.

With 2,6-diphenylpyridine it appears that there are two factors that negate a deuterium isotope effect: (1) inversion of the n,π^* and π,π^* singlet states, since it fluoresces in a hydrocarbon as well as a polar and hydrogen-bonding solvent; and (2) the determined pK_a value 3.6 is too small to contribute any ESPT fluorescence, as is seen with the 2-, 3- and 4-phenylpyridines.

In summary, our results indicate that the ESPT fluorescence in the phenylpyridines leads to a higher quantum yield in H_2O than in D_2O; however, if there is a significant population of the triplet state, which is accompanied by deprotonation, then an inverse effect is possible due to the slowing down of this process in D_2O.

References

[1] S. Hotchandani and A.C. Testa, *J. Photochem. Photobiol. A: Chem.*, *55* (1991) 323.
[2] J. Kubin and A.C. Testa, *J. Photochem. Photobiol. A: Chem*, *83* (1994) 91.
[3] L. Stryer, *J. Am. Chem. Soc.*, *88* (1966) 5708.
[4] (a) M. O'Sullivan and A.C. Testa, *J. Am. Chem. Soc.*, *92* (1970) 258 (1970); (b) 92 (1970) 5842.
[5] R. Rusakowicz and A.C. Testa, *J. Phys. Chem.*, *72* (1968) 2680.
[6] H.P. Hopkins, Jr., D.V. Jahagirdar, P.S. Moulik, D.H. Aue, H.M. Web, W.R. Davidson and M.D. Pedley, *J. Am. Chem. Soc.*, *106* (1984) 4341.
[7] A.R. Katritzky and P. Simons, *J. Chem. Soc.*, (1960) 1511.