# Hydroxystilbene Isomer-Specific Photoisomerization versus Proton Transfer

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Electronic excitation can result in a marked increase in the acidity of hydroxyaromatic molecules ($pK_a > pK_a^*$).[1−3] For example, 1- and 2-naphthol (1N and 2N) have pK_a^* values of 0.4 and 2.8, respectively, and ground-state pK_a values of 9.2 and 9.5, respectively (Table 1).[3,4] The rate constants for excited-state proton transfer (ESPT) from 1N and 2N to water are 2.5×10^{10} and $\sim10^8$ s^{-1},[4] sufficiently large for proton transfer to compete effectively with other singlet-state decay processes. The failure of some hydroxyaromatic molecules to undergo ESPT may reflect either slow proton transfer or rapid competing decay processes. We report here the isomer-specific photochemical behavior of 3- and 4-hydroxystilbene (3SOH and 4SOH). 3SOH behaves as a photoacid in aqueous solution, whereas 4SOH does not. This isomer-specific behavior is attributed to a difference in the barriers for C=C torsion, 4SOH having a small barrier and short singlet lifetime and 3SOH having a larger barrier and a relatively long singlet lifetime in polar aprotic solvents.
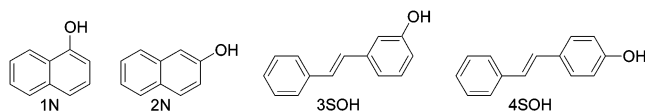
The absorption and fluorescence emission spectra of 4SOH and 3SOH in tetrahydrofuran (THF), water, and water containing 0.1 M KOH are shown in Figure 1. Spectral data for these solvents and cyclohexane (C_6H_{12}) are reported in Table 2. The absorption spectra of both hydroxystilbenes display only small red shifts with increasing solvent polarity (C_6H_{12}, THF, and water). The fluorescence spectra of both hydroxystilbenes display larger solvatochromic shifts than do their absorption spectra. This behavior is analogous to that of the 3- and 4-aminostilbenes[5] and is indicative of an increase in dipole moment upon excitation. A second, long-wavelength fluorescence band is observed for 3SOH, but not for 4SOH in water.

Spectrophotometric determination of the ground-state pK_a[6] of 3SOH and 4SOH in aqueous solutions provides values of 10.1 and 9.3, respectively (Table 1). The greater acidity of 4SOH is consistent with more effective resonance delocalization of the conjugate base of a phenol by a 4- versus 3-styryl substituent. In water−KOH, both hydroxystilbenes are completely in the form of their conjugate bases, 3SO$^-$ and 4SO$^-$. The absorption spectra of 3SO$^-$ and 4SO$^-$ are similar to those of 3- and 4-aminostilbene.[5]

Both 4SO$^-$ and 4-aminostilbene have a single, allowed long-wavelength transition, whereas 3SO$^-$ and 3-aminostilbene have two long-wavelength bands as a consequence of lowered molecular symmetry.[5] The fluorescence spectra of both 3SO$^-$ and 4SO$^-$ are red-shifted in comparison to their conjugate acids in aqueous solution, the larger Stokes shift being observed for 3SO$^-$. A larger Stokes shift is also observed for 3- versus 4-aminostilbene and is attributed to a larger excited-state dipole moment for the 3-isomer.[5] Comparison of the fluorescence spectra of 3SOH and 4SOH in

Table 1. Ground- and Excited-State pK_a Data for the Naphthols and Hydroxystilbenes in Water

	1N	2N	3SOH	4SOH
titrametric pK_a	9.2[a]	9.5[a]	10.1	9.3
SVD-SM pK_a		9.0	9.4	9.2
Förster pK_a^*	0.7−2.0[a]	2.5−3.4[a]	0.1	2.0
kinetic pK_a^*	0.4[b]	2.8[b], 3.0[c]	2.3[c]	

[a] Data from ref 3. [b] Data from ref 4. [c] Data from SVD-SM analysis of fluorescence titration data.
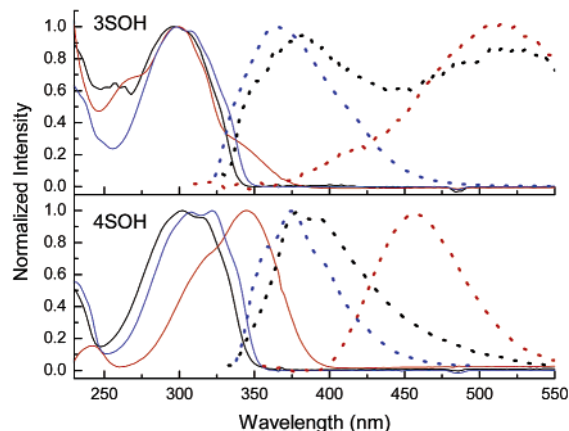

Figure 1. Absorption (solid lines) and fluorescence emission (dotted lines) of 3SOH and 4SOH in THF (blue), water (black), and 0.1 M KOH (red).

Table 2. Absorption and Fluorescence Data for the Hydroxystilbenes

stilbene	solvent	λ_{abs}, nm [a]	λ_{fl}, nm[b]	Φ_{iso}[c]	Φ_{fl}[d]	τ_s, ns[e]
3SOH	C_6H_{12}	296	354	0.32	0.16	
	THF	298	365	0.04	0.92	2.0 (2.8)
	water	298	386 (522)		0.008	0.2, 1.3[g]
					(0.008)[f]	
	aq KOH	300, 340*	513	0.10	0.003	0.5, 2.7[h]
4SOH	C_6H_{12}	302, (318)	359	0.42	0.025	
	THF	(308), 322	375		0.05	0.03 (1.4)
	water	302, (314)	387		0.01	
	aq KOH	342	455	0.27	0.007	0.05

[a] Absorption maxima, shoulders designated by *, second band in parentheses. [b] Fluorescence maxima, second band in parentheses. [c] Quantum yield of photoisomerization determined from change in absorbance on irradiation at low conversion. [d] Quantum yield of fluorescence determined using triphenylene ($\Phi_{fl} = 0.08$ in cyclohexane[10]) as a secondary standard. [e] Singlet decay times at room temperature or 77 K (values in parentheses). Nanosecond decays were determined as described in ref 5. Picosecond decays were determined as described in ref 11. Dual exponential decay for 3SOH in H_2O and in aqueous KOH is ca. 70% and 30% short component, respectively. Determined at λ_{fl}, except as noted. [f] Value in parentheses is Φ_{fl} of 3SO$^-$. [g] $\lambda_{em} = 510$ nm. [h] $\lambda_{em} = 490$ or 540 nm.

water with those in water−KOH indicates that on excitation 3SOH is partially dissociated in water, but that 4SOH is not.

Further information about the behavior of the excited states of 4SOH and 3SOH and their conjugate bases is provided by the

quantum yields for isomerization (Φ_{iso}) and fluorescence (Φ_{fl}) and the fluorescence lifetimes (τ_s), reported in Table 2. In the organic solvents C_6H_{12} and THF, the parameters for 4SOH are similar to those for stilbene[7] or 4-aminostilbene[5,8] and are indicative of a low barrier for singlet-state C=C torsion. The large increase in τ_s for 4SOH at 77 K in MTHF provides further support for singlet decay via a thermally activated process at room temperature. In contrast, the parameters for 3SOH in THF, particularly the large value of Φ_{fl} and the modest increase in τ_s at 77 K, are indicative of a large barrier for singlet-state torsion, as previously observed for 3-aminostilbene.[5] The larger value of Φ_{fl} and smaller value of Φ_{iso} for 3SOH in THF versus C_6H_{12} may reflect stabilization of the planar singlet state, but not the twisted singlet state by THF, which can serve as a hydrogen bond acceptor.[9] Both $4SO^-$ and $3SO^-$ are very weakly fluorescent. The fluorescence decay of $4SO^-$ is dominated by a short-lived component. Its short lifetime and moderately large isomerization quantum yield suggest that it decays predominantly by singlet C=C torsion, as is the case for its conjugate acid. The decay of $3SO^-$ both in water and in aqueous KOH is best fit to a dual exponential, tentatively assigned to two conformers which differ in the orientation of the styryl group. The decay times for both components are shorter in water versus aqueous KOH, plausibly reflecting the occurrence of reprotonation in water. The low values of Φ_f and Φ_{iso} for $3SO^-$ in aqueous solution suggest the presence of a competing decay pathway. There was no indication of either C−H/D exchange[4] or hydration of the C=C bond[12] upon irradiation in D_2O with analysis by ^{1}H NMR. Donor−acceptor stilbenes with values of $\lambda_{fl} > 500$ nm decay predominantly via internal conversion as a consequence of the small S_1−S_0 energy gap.[13]

An approximate value for the excited-state acidity, pK_a^*, can be obtained from the Förster equation,[1,14] eq 1

$$pK_a^* = pK_a - (h\nu_1 - h\nu_2)/2.3RT \qquad (1)$$

where $h\nu_1$ and $h\nu_2$ are the zero−zero transitions for the acid and its conjugate base, and pK_a is the ground-state acidity. The Förster acidities of 3SOH and 4SOH are 0.1 ± 0.8 and 2.0 ± 0.4, respectively (Table 1). The large uncertainty for 3SOH is a consequence of its very broad, weak fluorescence. Its weak fluorescence also frustrated attempts to determine a pK_a^* value by conventional fluorescence titration analysis.[14] However, the noisy fluorescence titration data can be analyzed by singular value decomposition with self-modeling (SVD-SM)[15] to provide the fluorescence titration curves shown in Figure 2. As a control, this method was also applied to 2N and found to provide results in good agreement with literature data (Table 1). In the case of 4SOH (Figure 2b), the single transition provides a value of $pK_a = 9.2$, in good agreement with the spectrophotometric value. Two transitions are observed for 3SOH, one providing a pK_a somewhat smaller than the spectrophotometric value and the other providing a pK_a^* larger (more positive) than the Förster pK_a^*.

In conclusion, the photoacidity of the hydroxystilbenes is dependent upon the location of the hydroxyl substituents. The failure of singlet 4SOH to behave as a photoacid is consistent with a previous study of a 4-hydroxystilbene derivative by El-Sayed and co-workers.[16] Because the Förster acidity of 4SOH is similar to that of 2N, it seems unlikely that its failure to undergo ESPT is a consequence of low inherent photoacidity. This failure can,
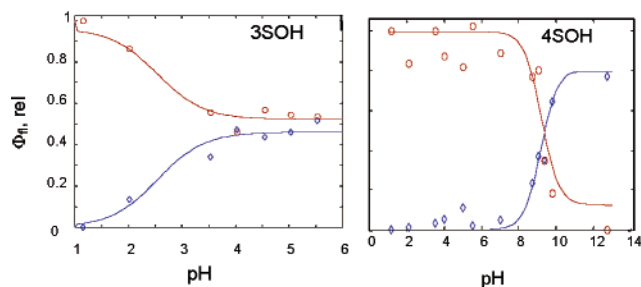

Figure 2. Relative fluorescence quantum yields (dots) and kinetic fits to data (solid lines) of the acid (red) and base (blue) forms of 3SOH (a) and 4SOH (b) as a function of pH, obtained by SVD-SM. Only the low pH (pK_a^*) transition is shown for 3SOH.

however, be attributed to a short singlet lifetime. For example, a proton-transfer rate constant of 10^9 s^{-1} would be too slow to compete with the rapid singlet decay of 4SOH, but would be comparable to the decay of 3SOH in nonaqueous solution. Thus, it is the difference in C=C torsional barriers, which determine the singlet lifetimes, that is ultimately responsible for the isomer-specific photoacidity of the stilbenols. The distinctive behavior of 3SOH is in some respects analogous to that of the 3-aminostilbenes, thus providing another example of the "meta effect" for substituted stilbenes.[5,13,17]

Supporting Information Available: Experimental methods for determination of isomerization quantum yields and pK_a^* values (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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