The Rate of Excited-state Proton Transfer to Solvent from Trifluoromethylphenols in Water

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The proton-transfer reactions to solvent from electronically excited *o*-, *m*-, and *p*-(trifluoromethyl)phenols (TFOHs) in water have been investigated by picosecond time-resolved fluorescence measurements. The rate constants for the proton dissociation of *o*-, *m*-, and *p*-TFOH are obtained to be 2.2×10^9, 8.6×10^8, and $2.5 \times 10^8\,s^{-1}$, respectively. On the basis of the rate constants, the effects of substituent and deuterium isotope effects on the proton-transfer reactions are revealed.

Hydroxyarenes such as 1- and 2-naphthols are well known to undergo excited-state proton-transfer (ESPT) to solvent in water because of drastic enhancement of the acidity in the first excited singlet (S_1) state.[1] The occurrence of ESPT is usually substantiated by appearance of dual fluorescence originating from the protonated and deprotonated species. In the case of phenol (PhOH) however, the extremely small fluorescence quantum yield ($\Phi_f = 8.0 \times 10^{-4}$ in water) and short lifetime ($\tau_f =$ 18 ps) of the phenolate anion render difficult the direct observation of the proton-transfer process in the excited state, and only a few papers can be found on ESPT reactions of phenols in the literature.[2–4] In the present study, we found that the introduction of an electron-withdrawing trifluoromethyl (CF_3) group into the aromatic ring of PhOH enhances significantly the fluorescence quantum yield and lifetime of the deprotonated forms, and the fluorescence spectrum exhibits dual fluorescence due to the protonated and deprotonated forms (Scheme 1). The acidity of PhOH is increased both in the ground and excited states by introducing a CF_3 group in the aromatic ring.

We report here the first direct measurement of the rate of proton-transfer to solvent from excited *o*-, *m*-, and *p*-TFOHs in water. Picosecond fluorescence lifetime measurements were made by using a femtosecond laser system which was based on a mode-locked Ti:sapphire laser pumped by a CW green laser (Spectra-Physics).[5] The third harmonic (266 nm, FWHM: ≈250 fs) was used as the excitation source. The instrument response function had a half-width of about 25 ps. The fluorescence time profiles were analyzed by deconvolution with the instrument response function.

Figure 1 illustrates the absorption and fluorescence spectra of PhOH and TFOHs in H_2O (pH 4.7) and D_2O (pD 4.7) at 293 K. It is noteworthy that the fluorescence spectra of *o*- and *m*-TFOH in H_2O exhibit dual fluorescence bands: normal and large Stokes-shifted fluorescence bands with maxima at around 310 and 345 nm, respectively. The fluorescence spectrum of *p*-TFOH in H_2O also shows a similar feature, although the intensity of the longer-wavelength band is much weaker than those of *o*- and *m*-TFOH, and both bands appear at shorter wavelengths. The shorter-wavelength bands of TFOHs resembled their fluorescence spectrum in acetonitrile (CH_3CN), and the longer-wavelength bands almost coincided with the fluorescence spectrum of the deprotonated forms (anions) in H_2O. The excitation spectrum of the longer- and shorter-wavelength bands agreed with the absorption spectrum. These indicate that both bands originate from the parent molecule and suggest the occurrence of ESPT to solvent. Another interesting feature of Figure 1 is remarkably large isotope effects on the fluorescence spectra; the longer-wavelength fluorescence bands of TFOD in D_2O almost disappear in all the isomers. This suggests significant decreases in the proton-transfer rate by deuterium substitution.

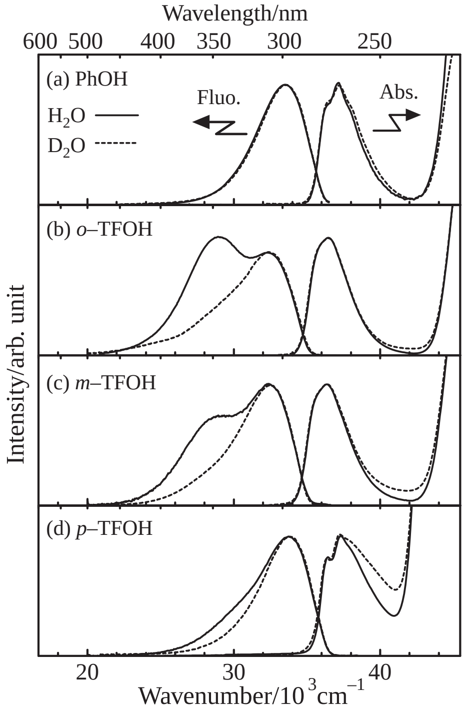
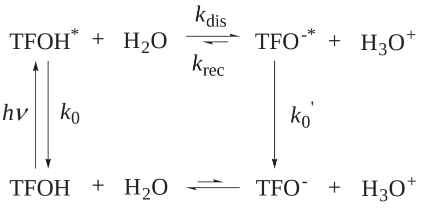


Figure 1. Absorption and fluorescence spectra of PhOH, *o*-TFOH, *m*-TFOH, and *p*-TFOH in H_2O (pH 4.7, solid line) and D_2O (pD 4.7, broken line).



Scheme 1.

Since the decay time constant of the deprotonated anion TFO^{-*} is relatively short (260, 450, and 290 ps for *o*-, *m*-, and *p*-TFO^-, respectively), the excited-state protonation reaction ($k_{rec}[H_3O^+]$ in Scheme 1) can be neglected under moderately acidic conditions ($[H_3O^+] < 10^{-4}$ M).[6] The fluorescence

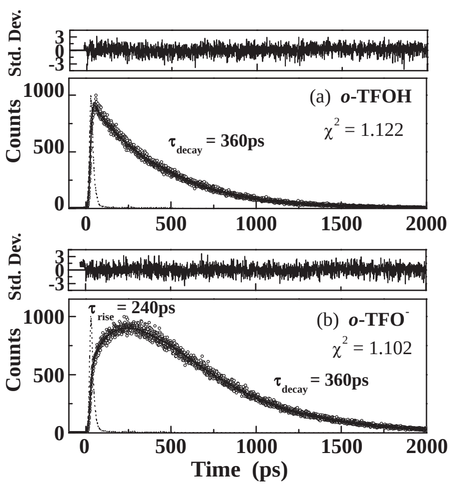


Figure 2. Fluorescence time profiles of *o*-TFOH monitored at (a) 300 and (b) 360 nm in H_2O at 293 K.

kinetics of ^{1}TFOH* and ^{1}TFO^{-*} on excitation by a δ-pulse follows the monoexponential and biexponential laws, respectively:

$$I_f^{TFOH}(t) = A_0 e^{-(k_0+k_{dis})t} \qquad (1)$$

$$I_f^{TFO^-}(t) = A_0'[e^{-(k_0+k_{dis})t} - e^{-k_0' t}] \qquad (2)$$

In order to determine the proton dissociation rate constant (k_{dis}) of ^{1}TFOHs*, the fluorescence time profiles of TFOHs in H_2O and D_2O were taken as shown in Figure 2.

The fluorescence time profiles of the shorter-wavelength band (monitored at 300 nm) and the longer-wavelength band (monitored at 360 nm) of *o*-TFOH are displayed along with the least-square fitting curves based on eqs 1 and 2. The solid lines represent the deconvoluted best fit of (a) a single-exponential function ($\tau_{decay} = 360$ ps) and (b) a two-exponential function ($\tau_{rise} = 240$ ps and $\tau_{decay} = 360$ ps) superimposed on the experimental data points. The rise time (240 ps) of the time profile in Figure 2b is in fair agreement with the lifetime of the deprotonated anion (260 ps). This demonstrates that the reaction sequence from TFOH* to TFO$^-$ (see Scheme 1) follows a consecutive reaction with the rate constants k_{dis} and k_0' ($k_{dis} < k_0'$). Since the decay rate (τ_{decay}) of ^{1}TFOHs* corresponds to ($k_0 + k_{dis}$), the magnitude of k_{dis} can be estimated from ($\tau_{decay}{}^{-1} - \tau_0{}^{-1}$). We assumed that τ_0 ($=1/k_0$) is equal to the fluorescence lifetime of TFOHs in CH_3CN where no dissociation occurs.[7] From the above kinetic analyses the rate constants for the proton-dissociation reaction of *o*-, *m*-, and *p*-TFOH were obtained to be 2.2×10^9 s^{-1}, 8.6×10^8 s^{-1}, and 2.5×10^8 s^{-1}, respectively, at 293 K. The k_{dis} values of *o*- and *m*-TFOHs are much larger than that of PhOH which can be evaluated to be less than 2.0×10^8 s^{-1} from the fluorescence lifetime in H_2O (3.1 ns) and CH_3CN (6.4 ns). The enhancement of the ESPT rate in TFOHs can be attributed to the electron-withdrawing effect of the TF group. The electronic effects of substituents are composed of two main parts: a field/inductive component and a resonance component.[8] In the ESPT of TFOHs, the CF_3 group is anticipated to accelerate the proton-dissociation rate by the inductive effect acting through the intervening σ bonds. According to Hynes et al.,[9] the differences in ground-state acidity among several substituted phenols are due mainly to effects in the phenolate anions, the effects in the corresponding phenols being of minor importance. Our results reveal that a similar effect of the CF_3 group is also applicable for the excited-state acidity of TFOHs.

Table 1. Proton-dissociation rate (k_{dis}) and ($k_{dis}{}^H/k_{dis}{}^D$) at 293 K, activation energy (E_a), and frequency factor (A) for excited-state proton-transfer reactions of TFOHs in H_2O (pH 4.7) and D_2O (pD 4.7)

Compound	Solvent	k_{dis} /10^8 s^{-1}	E_a /kJ mol^{-1}	A /10^{11} s^{-1}	$k_{dis}{}^H/k_{dis}{}^D$
o-TFOH	H_2O	22	9.8	1.2	3.3
	D_2O	6.6	13	1.4	
m-TFOH	H_2O	8.6	12	1.1	3.9
	D_2O	2.2	15	1.2	
p-TFOH	H_2O	2.5	14	0.87	5.7
	D_2O	0.44	21	2.9	

The Arrhenius plot of the k_{dis} values of TFOHs in H_2O and D_2O gave straight lines in the temperature range between 278 and 323 K, and the activation energy and the frequency factor were obtained as shown in Table 1. Although the magnitude of the frequency factor is nearly constant among TFOHs, the activation energy of *o*-, *m*-, and *p*-TFOH increases in that order, and all TFOHs shows larger E_a values in D_2O than in H_2O. The ESPT rates ($\approx 10^8$–10^9 s^{-1}) of TFOHs at the temperature range between 275 and 323 K are significantly slower than that ($\approx 10^{11}$ s^{-1}) of the solvent relaxation rate of water.[10] These indicate that at the above temperature range, the solvent relaxation is sufficiently fast and the rate-determining step in the ESPT reaction is the actual proton-transfer step. The activation energy and the deuterium isotope effect ($k_{dis}{}^H/k_{dis}{}^D = 3.0$–$6.0$) are ascribed to the proton motion along the proton-transfer coordinate.

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