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# Effects of long-chain alkyl substituents on the protolytic reactions of naphthols

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## Abstract

Kinetics and mechanism of excited-state proton-transfer reactions of 1-naphthol (1N) and 2-octadecyl-1-naphthol (2O1N) were studied in aqueous acetonitrile and absolute ethanol. Dissociation of 1N and 2O1N in the singlet excited state was characterized by similar rate and equilibrium constants ($k_1 \sim 0.5\,\mathrm{ns}^{-1}$, p$K \sim 1$) in contrast to the ground state, where 2O1N is a weaker acid than 1N ($\Delta$p$K = 0.6$ in an acetonitrile–water mixture 2:1, v/v). Main features of the ground and excited-state p$K$ and p$K$* and excited-state protolytic dissociation rate constants $k_1$ and $k_R$ were rationalized in terms of solvent effects on the energetics of equilibrium between hydrogen bonded complex and ion pair and in terms of electron donating effects of alkoxy group in the ground state and aromatic system in the excited singlet state.

An efficient deactivation process competing with the excited-state proton transfer (ESPT) was observed both for 1N and 2O1N. This needs more complicated kinetic analysis, yet provided a deeper insight into mechanisms of the excited-state proton-transfer reactions. A simple kinetic scheme including transient formation of excited hydrogen-bonded complex and geminate ion-pair and fast deactivation of both transients provided a good description of the protolytic photodissociation for the compounds studied. The rate constants for proton transfer and induced deactivation were determined for photodissociation of excited 1N and 2O1N in aqueous acetonitrile and their reactions with acetate anion in absolute ethanol. A remarkable decrease of ESPT rate constant and a substantial increase of the radiationless decay rate constant was observed in aqueous acetonitrile as compared to water. The origin of dissimilar solvent effects on these rate constants was discussed.

*Keywords:* Excited-state proton transfer; Kinetics; Naphthol; Diffusion-controlled reaction

## 1. Introduction

Proton transfer is an important elementary step in many chemical and biological processes [1–3]. Kinetics of the protolytic dissociation, i.e. proton transfer from an acid to solvent molecules, provides valuable information on solvation and reaction dynamics. It is known that the acidity of hydroxyaromatic compounds (ArOH) and protonated aromatic amines ($ArNH_3^+$) substantially increase upon electronic excitation [4]. For more than 50 years, photoinduced proton transfer to solvent was being studied in various systems ranging from gas-phase clusters in molecular beams [5] to simple liquids, and to surfactant ensembles [4e,f,i,6,7], inclusion complexes [8], and proteins [4f,9]. Steady-state and time-resolved fluorescence measurements of the protolytic photodissociation rates have been utilized to probe solvent structure and proton acceptor entity in various microheterogeneous systems. Recently we introduced several long-chain alkyl derivatives of naphthols [10] as promising fluorescent probes undergoing excited-state proton transfer in surfactant assemblies. Excited-state kinetics of their reactions in micelles was rationalized within the framework of a pseudophase model, which included micellar effects on the proton transfer equilibrium and interfacial diffusion of hydronium ions [11].

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It is generally recognized that kinetic analysis of proton transfer reactions in solution has to include a description of transport phenomena (approach and separation of reactants and products) in addition to protonation-recombination within a contact ion pair. Several approaches to analysis of kinetic data have been used to gain a better understanding of mechanisms of proton transfer reactions: analysis of relationships between reaction kinetics and thermodynamics (correlation between $\log k_1$ or $\log k_{-1}$ and p$K$, where $k_1$ and $k_{-1}$ are overall rate constants of excited-state deprotonation and recombination, and $K$ is the excited-state acidity constant [4c,e–g]), detailed investigation of systems with competing processes such as proton-induced deactivation, and in-depth analysis of the diffusion-controlled reaction kinetics [4j,11–15].

Proton transfer reactions are of the association–dissociation type, $A + B = C$, which has been intensively studied in the last decade [12]. Different theoretical approaches have been accompanied by advanced numerical simulations [13]. These studies revealed the existence of three kinetic regimes which are the characteristic for the diffusion-assistant reactions:

1. In accordance with the Smoluchowski theory [14], a short initial period (not more than several nanoseconds [15]) is determined by a diffusional equilibration, and the observed relaxation rates of concentrations correspond to the intrinsic rates of proton transfer within contact ion pair. They are larger than those in the following steady-state regime.
2. In this regime the established diffusion produces a constant flow of reactants through the potential barrier. For fast enough relative diffusion of reactants, this is the most noticeable process because of its long lasting period. The ordinary kinetic scheme with the steady-state rate constants, $k_1$ and $k_{-1}$, describes the reaction kinetics very well.
3. The last regime relates to the relaxation of density fluctuations which gives the power-law (rather than exponential) decay for the time-dependent concentration profiles. This non-exponential behaviour is observed at the times $t \gg \frac{2}{3k_1} \ln \frac{D^{3/2}}{k_{-1}\sqrt{k_1}}$ [16], where $D$ is the mutual diffusion coefficient of the reactants.

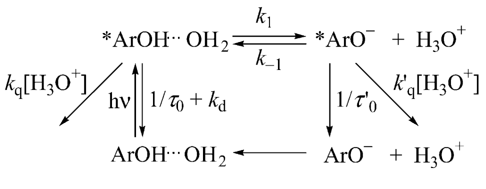
It was shown in Ref. [17] that the Smoluchowski-type kinetics, which covers regimes (1) and (2), is the leading term even in the geminate case when isolated A–B pairs are considered. It helps to understand why the deviation from exponential decays is observed only in a very limited range of experimental systems. In relation to ESPT reactions the prerequisites for deviation of the kinetics from exponential are: fast deprotonation coupled with very effective geminate recombination, such as protolytic photodissociation of "super" photoacids in the solvents of low polarity [4j].

Ultrafast spectroscopies have been utilized to provide a more penetrating insight into proton-transfer mechanisms. Of special interest are recent experimental studies of Huppert [18,19] and Pines groups and the results reported by Tran-Thi, Hynes and coworkers [20]. Huppert et al. performed systematic studies of various hydroxyaromatic compounds in water and alcohols in the extended temperature (150–413 K) [18] and pressure (0.1–2.5 GPa) [19] regimes. To explain unique non-exponential dependence of ESPT rate constants on temperature and pressure the authors developed an approximate stepwise two coordinate proton-transfer model that bridges the high-temperature proton tunneling limit and the low-temperature solvent controlled limit. Second are the studies of Pines et al. [21] and Huppert et al. [22] who investigated bimolecular reactions between hydroxyaromatic photoacids and carboxylates using femto- and picosecond time-resolved spectroscopies. By varying proton acceptor concentration and solvent viscosity the authors were able to separate and observe experimentally the diffusion- and reaction-controlled steps of the overall proton-transfer reaction.

Well-known reaction of the ESPT from pyranine to water [4a] was reinvestigated by Tran-Thi et al. using femtosecond fluorescence and absorption spectroscopies [20]. The authors have discovered two ultrafast steps (300 fs and 2.5 ps) which precede the relatively slow (87 ps) ESPT process. These intermediate steps were related to the solvation dynamics of the locally excited state and its subsequent relaxation to an intermediate electronic state. An intermediate with a lifetime of several picoseconds was observed for other ESPT systems [23].

The major goal of this study was to analyze kinetics and mechanism of excited-state proton transfer reactions of 2-octadecyl-1-naphthol (2O1N) in homogeneous solutions and compare them with the data obtained for 1-naphthol and derivatives of 2-naphthol in both homogeneous and micellar solutions [4c,e,10b,24]. Photodissociation kinetics of 1N and its derivatives is characterized by efficient proton-induced quenching [25]. Conceivable mechanisms include induced deactivation in the reaction complex caused by appearance of new modes promoting efficient internal conversion [26–28] in the vicinity of the transition state of the reaction and aromatic ring protonation in the geminate ion pair [4d,29,30].

Despite complications in the kinetic analysis, proton-induced deactivation of 1-naphthols appears to be useful in studying structural and environmental effects on the reaction rate and in elucidating the reaction mechanism in molecular organized systems. In the previous paper [24], we demonstrated how the rate constants of elementary steps of excited-state proton transfer reactions for 2O1N and the parent compounds can be evaluated in micellar solutions. Here, we report similar analysis of concentration-dependent steady-state and time-resolved fluorescence data for homogeneous solutions. Results obtained by using steady-state method are shown to agree well with the data obtained from picosecond measurements and time-dependent diffusion kinetics.



Scheme 1.

## 2. Experimental

1N (Merck) was purified by vacuum sublimation. The synthesis of 2O1N was described in the previous paper [24]. Sodium acetate was recrystallized from water and dried at 150 °C during two hours. HCl and NaOH were of analytical grade. Deionized water was used in all experiments. Ethanol was freed of water and other impurities according to the published procedure [31]. Acetonitrile (Merck) was used as received. All experiments were performed at room temperature (∼21–22 °C). pH values were measured with an ionometer I-120 (Russia) equipped with a glass electrode calibrated with standard aqueous buffers. Concentrations of 1N and 2O1N did not exceed 0.1 mM.

Absorption spectra were recorded with a Specord M-40 (Carl Zeiss Jena) or a Shimadzu UVPC-2101 spectrophotometer. Fluorescence spectra were measured with a Perkin-Elmer LS-50 luminescent spectrometer. Fluorescence decay curves were measured with time-correlated single-photon counting technique. A home-made instrument with an air flash lamp (FWHM ∼ 1 ns) and ORTEC electronics was used. The excitation wavelength of 313 nm was selected with an interference filter. Decay curves were analyzed by using a non-linear least-squares iterative deconvolution procedure.

## 3. Kinetic analysis

A simple kinetic scheme is often used to describe overall kinetics of proton transfer photoreactions of hydroxyaromatic compounds in homogeneous solutions [4]. For 1N and its derivatives, this scheme has to be modified to include quenching processes that are inherent in these compounds as shown in Scheme 1; where $k_1$ and $k_{-1}$ are the rate constants of *ArOH protolytic dissociation and *ArO$^-$ protonation; $\tau_0$ and $\tau'_0$ are the lifetimes of *ArOH and *ArO$^-$ in the absence of the protolytic reactions; $k_q$ and $k'_q$ refer to the rate constants of *ArOH and *ArO$^-$ quenching by hydronium ions, $k_d$ is the rate constant of radiationless deactivation competing with the adiabatic dissociation. Several mechanisms and pathways exist for diabatic proton quenching, such as induced internal conversion directly to the ground state and diabatic protonation of carbon atom (see Section 5 for more details). All the bimolecular rate constants ($k_{-1}$, $k_q$, and $k'_q$) would have apparent values including a mean activity coefficient of hydronium ions if uncorrected concentrations of a strong acid added would be used as [$H_3O^+$].

According to Scheme 1, fluorescence decay curves for *ArOH ($I$) and *ArO$^-$ ($I'$) are described by two-exponential functions:

$$I(t) = I_0 \left[ \exp\left(\frac{-t}{\tau_1}\right) + A \exp\left(\frac{-t}{\tau_2}\right) \right] \tag{1}$$

$$I'(t) = I'_0 \left[ \exp\left(\frac{-t}{\tau_2}\right) - \exp\left(\frac{-t}{\tau_1}\right) \right] \tag{2}$$

Decay times ($\tau_1$, $\tau_2$) and relative amplitude ($A$) can be expressed in terms of the reaction rate constants as:

$$\frac{1}{\tau_{1,2}} = \frac{\mu + \mu'}{2} \pm \left[ \frac{(\mu - \mu')^2}{4} + k_1 k_{-1}[H_3O^+] \right]^{1/2}, \tag{3}$$

$$A = \frac{1/\tau_1 - \mu}{\mu - 1/\tau_2}, \tag{4}$$

$$\mu = \frac{1}{\tau_0} + k_d + k_1 + k_q[H_3O^+] = \frac{1/\tau_1 + A/\tau_2}{1 + A} \tag{5}$$

$$\mu' = 1/\tau'_0 + (k_{-1} + k'_q)[H_3O^+] = 1/\tau_1 + 1/\tau_2 - \mu \tag{6}$$

$$k_1 k_{-1}[H_3O^+] = \mu\mu' - \frac{1}{(\tau_1\tau_2)} \tag{7}$$

Thus, all the rate constants can be determined from the plots of $\mu\mu'$ and $\mu\mu' - 1/(\tau_1\tau_2)$ against [$H_3O^+$], provided that $\tau_0$ and $\tau'_0$ are known.

At pH ∼ 5–8, all bimolecular processes involving hydronium ions are too slow to compete with any unimolecular process ($k_1$, $k_d$, $1/\tau_0$, and $1/\tau'_0$) so that *ArOH fluorescence decay becomes single exponential ($A \to 0$) with a lifetime $\tau_N$:

$$\frac{1}{\tau_1} = \frac{1}{\tau_N} = \frac{1}{\tau_0} + k_d + k_1 = \frac{1}{\tau} + k_1. \tag{8}$$

where $1/\tau = 1/\tau_0 + k_d$. The fluorescence kinetics of anionic species remains two-exponential with a rise time equal to the decay time of *ArOH ($\tau_1 = \tau_N$) and a decay time equal to the lifetime of the anion under direct excitation ($\tau_2 = \tau'_0$), if $\tau_0 < \tau'_0$. No significant deviation from single- or two-exponential fluorescence kinetics for *ArOH and *ArO$^-$ was found in our studies using the single-photon counting technique with a nanosecond time resolution. However, non-exponential decay of *ArOH fluorescence has been observed for some strong photoacids both in aqueous and non-aqueous solutions [4j,32,33]. This behaviour was rationalized within the framework of diffusion-controlled kinetics with a back-reaction boundary condition. A numerical solution of the Debye–Smoluchowski equation predicted for ArOH at pH ∼ 7 non-exponential fluorescence decay with asymptotic time dependence as $t^{-3/2}$. However, deviations from the single-exponential decay are significant only for very strong ($-\log(k_1/k_{-1}) = pK^* < 0.5$ in water) or multiply charged photoacids. According to Scheme 1, the fluorescence quantum yields of *ArOH ($\varphi$) and *ArO$^-$ ($\varphi'$) can be written as:

$$\varphi = \varphi_0 \frac{\tau}{\tau_0} \frac{1 + (k_{-1} + k'_{\mathrm{q}})\tau'_0[\mathrm{H_3O^+}]}{(1 + (k_{-1} + k'_{\mathrm{q}})\tau'_0[\mathrm{H_3O^+}])(1 + k_{\mathrm{q}}\tau[\mathrm{H_3O^+}]) + k_1\tau(1 + k'_{\mathrm{q}}\tau'_0[\mathrm{H_3O^+}])} \quad (9)$$

$$\varphi' = \varphi'_0 \frac{k_1\tau}{(1 + (k_{-1} + k'_{\mathrm{q}})\tau'_0[\mathrm{H_3O^+}])(1 + k_{\mathrm{q}}\tau[\mathrm{H_3O^+}]) + k_1\tau(1 + k'_{\mathrm{q}}\tau'_0[\mathrm{H_3O^+}])} \quad (10)$$

where $1/\tau = 1/\tau_0 + k_{\mathrm{d}}$, $\varphi_0 = k_{\mathrm{f}}\tau_0$ and $\varphi'_0 = k'_{\mathrm{f}}\tau'_0$ are fluorescence quantum yields of *ArOH and *ArO$^-$ in the absence of the excited-state protolytic reactions, $k_{\mathrm{f}}$ and $k'_{\mathrm{f}}$ are the radiative rate constants for *ArOH and *ArO$^-$. At pH ~ 5–8, the bimolecular processes can be neglected and one has for the fluorescence quantum yields:

$$\varphi_{\mathrm{N}} = \varphi_0 \frac{\tau}{\tau_0} \frac{1}{1 + k_1\tau} = \varphi_0 \frac{\tau_{\mathrm{N}}}{\tau_0} \quad (11)$$

$$\varphi'_{\mathrm{N}} = \varphi'_0 \frac{k_1\tau}{1 + k_1\tau} \rightarrow \varphi'_0 k_1 \tau_{\mathrm{N}} \frac{\tau'_{\mathrm{N}}}{\tau'_0} \quad (12)$$

where $\tau'_{\mathrm{N}}$ is the decay time of *ArO$^-$ at pH ~ 7. The fluorescence decay time of 1N anion is known to be slightly sensitive to solution pH [25,29]. This effect has been attributed to the presence of a small short-living component which results from geminate proton-induced fluorescence quenching at pH ~ 7 [25]. This component disappears at basic pH (direct excitation of the anion). Although we could not detect any significant deviation of the anion fluorescence decay from the single-exponential law, the *ArO$^-$ decay time at pH > 12 ($\tau'_0$) appeared to be slightly larger than that at pH ~ 7 ($\tau'_{\mathrm{N}}$). Therefore the fluorescence quantum yield was corrected for this difference as $\varphi'_0\tau'_{\mathrm{N}}/\tau'_0$.

The *ArOH fluorescence quantum yield ($\varphi_0$) and decay time ($\tau_0$) in the absence of the proton transfer are usually taken to be equal to the measured values in a highly acidic solution (pH < p$K_{\mathrm{a}}$*), where the excited-state protolytic equilibrium is shifted towards the neutral form. But it is practically impossible to measure these values for 1N derivatives in such a solution because of highly efficient proton-induced fluorescence quenching. Nevertheless, the photodissociation rate constant $k_1$ can be estimated from the fluorescence quantum yields and lifetimes (se Eq. (12)):

$$k_1 = \frac{(\varphi'_{\mathrm{N}}/\varphi'_0)(\tau'_0/\tau'_{\mathrm{N}})}{\tau_{\mathrm{N}}} \quad (13)$$

The rate constant $k_1$ can also be determined from the *ArO$^-$-to-*ArOH fluorescence quantum yield ratio in a given solution ($\varphi'_{\mathrm{N}}/\varphi_{\mathrm{N}}$) and in a solution where no photoprotolytic reaction occurs $(\varphi'_0/\varphi_0)_{\mathrm{s}}$. The latter quantity is determined under conditions of direct excitation of ArO$^-$ and ArOH. If we assume that the radiative rate constant ratio ($k_{\mathrm{f}}/k'_{\mathrm{f}}$) is practically insensitive to the solvent than we can write:

$$k_1 = \frac{(\varphi'_{\mathrm{N}}/\varphi_{\mathrm{N}})}{(\varphi'_0/\varphi_0)_{\mathrm{s}}} \frac{(\tau'_0/\tau_0)_{\mathrm{s}}}{\tau'_{\mathrm{N}}}, \quad (14)$$

where $(\tau'_0/\tau_0)_{\mathrm{s}}$ is the lifetime ratio in the selected solvent. In Eq. (14), one can use relative fluorescence intensities measured under conditions of identical excitation at the wavelength corresponding to an isosbestic point for all three solutions.

For molecules with relatively efficient proton-induced quenching, fluorescence data can be used to quantify the rates of elementary processes. Quantum efficiency of the adiabatic protolytic dissociation of *ArOH ($\eta$) and adiabatic protonation of *ArO$^-$ ($\eta'$) are defined as:

$$\eta = \frac{k_1}{k_1 + k_{\mathrm{d}}} \quad (15)$$

$$\eta' = \frac{k_{-1}}{k_{-1} + k'_{\mathrm{q}}} \quad (16)$$

Combining Eqs. (8), (14) and (15) one can also write:

$$\eta = \frac{(\varphi'_{\mathrm{N}}/\varphi'_0)(\tau'_0/\tau'_{\mathrm{N}})}{(1 - \tau_{\mathrm{N}}/\tau_0)} \quad (17)$$

$$\eta = \frac{(\varphi'_{\mathrm{N}}/\varphi_{\mathrm{N}})}{(\varphi'_0/\varphi_0)_{\mathrm{s}}} \frac{(\tau'_0/\tau_0)_{\mathrm{s}}}{(1/\tau_{\mathrm{N}} - 1/\tau_0)\tau'_{\mathrm{N}}}. \quad (18)$$

The sum of the apparent rate constants of the *ArO$^-$ protonation and proton-induced quenching ($k_{-1} + k'_{\mathrm{q}}$) can be determined directly from a slope of the plot of fluorescence quantum yield ratio versus [H$_3$O$^+$]:

$$\frac{(\varphi\varphi'_{\mathrm{N}})}{(\varphi_{\mathrm{N}}\varphi')} = 1 + (k_{-1} + k'_{\mathrm{q}})\tau'_{\mathrm{N}}[\mathrm{H_3O^+}] \quad (19)$$

Eqs. (9)–(12) can be rewritten in a form that enables separate determination of $k_{-1}$ and $k'_{\mathrm{q}}$, if $k_1\tau_{\mathrm{N}} = (\varphi'_{\mathrm{N}}/\varphi'_0)(\tau'_0/\tau'_{\mathrm{N}})$ is known:

$$\frac{(\varphi_{\mathrm{N}}/\varphi - 1)}{[\mathrm{H_3O^+}]} = k_{\mathrm{q}}\tau_{\mathrm{N}} - \frac{k_1\tau_{\mathrm{N}}k_{-1}\tau'_0(\varphi_{\mathrm{N}}\varphi')}{(\varphi\varphi'_{\mathrm{N}})} \quad (20)$$

One can obtain $k_1$ and $\eta'$ from a plot of $\varphi'/\varphi$ versus $\varphi_{\mathrm{N}}/\varphi$:

$$\frac{(\varphi'/\varphi)}{(\varphi'_0/\varphi_0)}(\tau'_0/\tau_0)_{\mathrm{s}} = k_1\tau'_{\mathrm{N}} + \frac{\varphi_{\mathrm{N}}/\varphi - 1}{\eta'} \quad (21)$$

Thereafter, $k_{-1}$ and $k'_{\mathrm{q}}$ can be determined. The values of $k'_{\mathrm{q}}$ and $k_{\mathrm{q}}/k_1$ can also be determined separately from the data plotted as:

$$\frac{(\varphi'_0/\varphi' - 1) - (\varphi'_{\mathrm{N}}/\varphi' - 1)(\varphi\varphi'_{\mathrm{N}})/(\varphi'\varphi_{\mathrm{N}})}{[\mathrm{H_3O^+}]} = k'_{\mathrm{q}}\tau'_0 + \frac{k_{\mathrm{q}}}{k_1}\frac{\varphi\varphi'_{\mathrm{N}}}{\varphi'\varphi_{\mathrm{N}}} \quad (22)$$

If $k_{\mathrm{q}}/k_1 \ll k'_{\mathrm{q}}\tau'_0$, Eqs. (10), (12), (19) and (22) can be combined into

$$\frac{\varphi'_0}{\varphi'} - 1 = \frac{1}{k_1\tau} + k'_{\mathrm{q}}\tau'_0[\mathrm{H_3O^+}] + \frac{(k_{-1} + k'_{\mathrm{q}})\tau'_0[\mathrm{H_3O^+}]}{k_1\tau} \quad (23)$$

$$(\varphi_0'/\varphi' - 1) - \frac{(\varphi_0'/\varphi_N' - 1)(\varphi\varphi_N')}{(\varphi'\varphi_N)} = k_q'\tau_0'[H_3O^+] \qquad (24)$$

In this work, relative fluorescence intensities were used instead of quantum yields because no change in the spectral shape was observed under all experimental conditions. The $ArO^-$ fluorescence intensity corresponding to $\varphi_0'$ (see below) was measured at pH > 12. An isosbestic point with the longest wavelength was selected for excitation ($\lambda_{ex} = 309$ and 308 nm for 1N and 2O1N, respectively, in an MeCN–$H_2O$ mixture, 2:1, v/v) in order to calculate the fluorescence quantum yield ratio directly from the intensity ratio. The $^*ArO^-$ fluorescence intensity ($I'$) was corrected for the overlap of *ArOH and $^*ArO^-$ fluorescence spectra:

$$I' = I'_{exp} - I_{exp}\left(\frac{i_0'}{i_0}\right), \qquad (25)$$

where $I'_{exp}$ and $I_{exp}$ are the experimental values of the fluorescence intensities at the $^*ArO^-$ and *ArOH emission maxima, $i_0'$ and $i_0$ are the *ArOH fluorescence intensities measured at the same wavelengths as $I'_{exp}$ and $I_{exp}$, respectively. The corresponding intensities in the emission spectra of the protonated form of 1N and 2O1N in hexanol or ethanol (no excited-state protolytic dissociation occurred in these solvents) were used to correct the anion spectra according to Eq. (25).

## 4. Results

### 4.1. Ground state pK

The ground-state acidity constants of 1N and its derivative were determined in a MeCN-EkO mixture (2:1, v/v) by using fluorescence and absorption titration. The p$K$ values

Table 1
Kinetic parameters of the protolytic photoreactions of 1N and 2O1N

| Compound | 1N | 1N | 2O1N |
|---|---|---|---|
| Solvent | $H_2O$[a] | MeCN–$H_2O$ (2:l) | MeCN–$H_2O$ (2:l) |
| $I'_N/I_N$ | >50 | 1.78 | 0.91 |
| $\varphi'_N/\varphi'_0$ | 0.76 | 0.39 | 0.33 |
| $\tau_N$ (ns) | 0.033 | 0.80 | 0.53 |
| $\tau'_N$ (ns) | 7.6 | 12.4 | 10.1 |
| $\tau'_0$ (ns) | 8.0 | 13.8 | 10.8 |
| p$K$ | 9.2 | 11.9 | 12.5 |
| $k_1$ ($ns^{-1}$) | 25[b], >20[c] | 0.49[b], 0.44[c] | 0.65[b], 0.28[c] |
| $\eta$ | 0.81[b], >0.66[c] | 0.46[b], 0.41[c] | 0.38[b], 0.16[c] |
| $k_{-1} + k'_q$ ($M^{-1}$ $ns^{-1}$) | 101 | 37[d] | 30[d] |
| $k_{-1}$ ($M^{-1}$ $ns^{-1}$) | 68 | 12[e], 9[f], 9[g] | 7[e], 5[f], 6[g] |
| $k'_q$ ($M^{-1}$ $ns^{-1}$) | 33 | 25[e], 28[f], 28[g] | 23[e], 25[f], 24[g] |
| $\eta'$ | 0.67 | 0.33[e], 0.25[f] 0.25[g] | 0.23[e], 0.17[f], 0.20[g] |
| p$K$* | 0.4 | 1.3–1.4 | 1.0–1.3 |
| $k_q$ ($M^{-1}$ $ns^{-1}$) | 6 | 3[e] | 2[e] |
| $k_{NR}/k_{SEP}$ | 0.2–0.5 | 1.2–1.4 | 1.6–5.1 |
| $k_{NR}/k_{-R}$ | 0.5 | 2.1–3.1 | 3.3–5.0 |
| $k_{-R}/k_{NR}$ | 0.5–1.0 | 0.4–0.7 | 0.3–1.6 |
| $k_R$ ($ns^{-1}$) | 42–62 | 1.1–1.5 | 0.8–5.0 |
| $k_{REC}$ ($M^{-1}$ $ns^{-1}$) | 170–240<br>(74–85)[h] | 35–58<br>(40–44)[h] | 34–44<br>(40–44)[h] |
| $k_{-R}$ ($ns^{-1}$)[i] | 55 | 75 | 75 |
| $k_{NR}$ ($ns^{-1}$) | 27 | 150–230 | 250–380 |
| $k_{SEP}$ ($ns^{-1}$) | 50–110<br>(35–48)[h] | 110–200<br>(11–13)[h] | 50–230<br>(11–13)[h] |
| $k_{REC}/k_{SEP}$ ($M^{-1}$) | 1.3–5.2<br>(1.5–2.4)[h] | 0.2–0.5<br>(3.1–4.1)[h] | 0.2–0.9<br>(3.1–4.1)[h] |

[a] From Refs. [29a,b].

[b] $k_1 = (I'_N/I'_0)(\tau'_0/\tau'_N)/\tau_N$ see Eq. (14).

[c] $k_1 = \{(I'_N/I_N)/(I'_0/I_0)_s\}(\tau'_0/\tau_0)_s/\tau'_N$, see Eq. (15); $(I'_0/I_0)_s = 0.64$ and 0.54 for 1N and 2O1N, respectively, in absolute ethanol; $(\tau'_0/\tau_0)_s = 1.9$ and 1.6 for 1N and 2O1N, respectively, in absolute ethanol.

[d] From the data plotted according to Eq. (20).

[e] $k_{-1}$ and $k_q$ from the data plotted according to Eq. (21), $k'_q$ from the difference between $(k_{-1} + k'_q)$ and $k_{-1}$.

[f] $k_{-1}$ from slopes of the plots in the coordinates corresponding to Eqs. (20) and (24).

[g] $k'_q$ from the slopes of the plots in the coordinates corresponding to Eq. (25), $k_{-1}$ from the difference between $(k_{-1} + k'_q)$ and $k'_q$.

[h] Calculated by using the standard expressions for the diffusion-controlled rate constants: $k_{REC} = [4\pi N_A Ad/1000][\delta/(e^{\delta}-1)]$ and $k_{SEP} = [3D/a^2][\delta/(1-e^{-\delta})]$, where $\delta = -e^2/(4\pi\varepsilon_0\varepsilon aRT)$, $D = 1.0 \times 10^{-4}$ and $4.2 \times 10^{-5}$ $cm^2/s$ for $H_2O$ and MeCN–$H_2O$ [41], respectively, $a = 5.5$–7 Å, $T = 295$ K, $\varepsilon = 78.4$ and 51.4 for $H_2O$ and MeCN–$H_2O$ [39], respectively.

[i] $k_{-R} = \Omega/\tau_D$, $\Omega = 0.49$, $\tau_D = 8.8$ ps and 6.4 ps for $H_2O$ and MeCN–$H_2O$, respectively [40,66].

were calculated as mean values from three linear plots of $\log(\alpha/(1-\alpha))$ versus pH. The degree of ArOH dissociation, $\alpha = [\mathrm{ArO}^-]/([\mathrm{ArO}^-] + [\mathrm{ArOH}])$, was determined from $\mathrm{ArO}^-$ absorption, ArOH and $\mathrm{ArO}^-$ fluorescence intensities (data not shown). To compare p$K$ values in bulk water and in aqueous acetonitrile, the measured pH values were corrected to the hydrogen ion activity referred to the standard state in the mixed solvent [34]:

$$\mathrm{p}a_\mathrm{H} = \mathrm{pH} - (E_\mathrm{j} - \log\gamma_\mathrm{H}) \tag{26}$$

where $E_\mathrm{j}$ is the liquid junction potential and $\log\gamma_\mathrm{H}$ is the transfer activity coefficient of the proton (the medium effect on hydrogen ions). For the MeCN–$H_2O$ mixture, a $(E_\mathrm{j} - \log\gamma_\mathrm{H})$ value of −0.53 was obtained by interpolating data from Ref. [34a]. The p$K$ values are presented in Table 1.

### 4.2. Excited-state protolytic reactions in aqueous acetonitrile

The rate constants for the alkyl derivative cannot be measured in bulk water because of extremely low solubility of this compound. We chose an MeCN–$H_2O$ mixture with a volume ratio of 2 because pronounced protolytic photodissociation both of 1N and 2O1N was observed in this mixture, fluorescence decay times could be reliably measured with our single-photon counting instrument, and such a mixture with an aprotic solvent appeared to be a better model for the micellar interior [24].

Fluorescence spectra of 1N and 2O1N in aqueous acetonitrile at various HCl concentrations are presented in Fig. 1. In contrast to bulk water, strong fluorescence of neutral species ($\lambda_\mathrm{fl} = 364$ and 365 nm for 1N and 2O1N) was observed in aqueous MeCN at neutral pH. The emission maximum of the 1N anion ($\lambda_\mathrm{fl} = 465$) showed a blue shift relative to that in bulk water ($\lambda_\mathrm{fl} = =490$ nm). Similar observation of 2O1N anion emission' solvatochromism was impossible because of low solubility of 2O1N in water. Adding HCl to naphthol solutions caused the $^*\mathrm{ArO}^-$ fluorescence to be strongly quenched but the *ArOH emission to be only slightly increased. This was attributed to efficient quenching of $^*\mathrm{ArO}^-$ (and *ArOH) by hydronium ions (see Scheme 1).

Fluorescence decay curves of 1N and 2O1N at neutral pH were practically single exponential (more than 97% of the decay) with lifetimes ($\tau_\mathrm{N}$) of 0.80 and 0.53 ns, respectively. The fluorescence kinetics of anionic species was well described by a two-exponential function (Eq. (3)), the rise time was close to the *ArOH decay time. These results confirmed the validity of Scheme 1 for the protolytic dissociation in these solutions. The $\tau_\mathrm{N}$ value for 1N compares well with that reported for mixed solutions with an organic solvent concentration of 66.67% v.: 0.8–0.9 ns for MeCN and EtOH, 0.51 ns for MeOH (obtained by interpolating experimental data from Refs. [29,35,36]).

Values of $k_1$ and $\eta$ calculated from stationary and time-resolved fluorescence data (see Eqs. (13)–(18)) are in reasonably good agreement (Table 1). The bimolecular rate constants $k_{-1}$, $k'_\mathrm{q}$, $k_\mathrm{q}$ and the quantum efficiency $\eta'$ were determined from the relative fluorescence intensities plotted according to Eqs. (20)–(25). The measured quantities were corrected for a kinetic activity coefficient, $F = (f_\pm)^2$, in order to obtain the values independent of experimental conditions and to make possible their comparison with data in bulk water [4a,37]. The mean activity coefficient, $f_\pm$, for 1,1-electrolyte was calculated according to the Debye–Hückel equation and was adjusted to the molar scale for the sake of generality [38]:

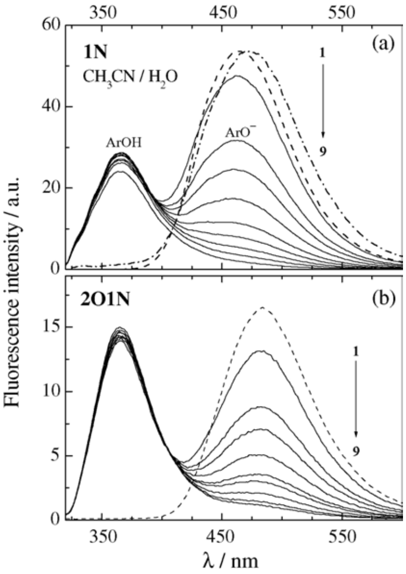


Fig. 1. Fluorescence spectra of 1N (a) and 2O1N (b) in the MeCN–$H_2O$ mixture (2:1, v/v) in the presence of NaOH (∼0.01 M, dashed lines) or HCl (solid lines). Arrows with numbers refer to $\mathrm{ArO}^-$ fluorescence and represent an increase in HCl concentration, which was 0 (1), 0.0016 (2), 0.0032 (3), 0.0063 (4), 0.0125 (5), 0.025 (6), 0.05 (7), 0.1 (8) and 0.25 M (9) for both compounds. The spectra in basic solutions were multiplied by a factor of 0.4. The dashed-dotted line corresponds to 1N fluorescence spectrum in bulk water at neutral pH.

$$-\log f_\pm = \frac{1.82 \times 10^6 (\varepsilon T)^{-3/2}\sqrt{C}}{1 + 50.3(\varepsilon T)^{-1/2} l \sqrt{C}} + \log\left[1 + C\frac{2M_1 - M_2}{1000 d_0}\right] \tag{27}$$

where $C$ is the molar concentration of hydrochloric acid, $T = 294$ K the absolute temperature, $\varepsilon$ is the dielectric constant, which was estimated to be equal to 51.4 for 66.7% aqueous acetonitrile [39,40], $l$ representing the "ion-size" parameter is taken to be 0.5 nm [38], $M_1 = (w_{\mathrm{H_2O}}/M_{\mathrm{H_2O}} + (1 - w_{\mathrm{H_2O}})/M_{\mathrm{MeCN}})^{-1}$ and $M_2 = M_{\mathrm{HCl}}$ are the solvent and solute molecular weights, $w_{\mathrm{H_2O}}$ is the water weight fraction in the mixture, $d_0$ is the solvent density taken to be equal to the solution density (0.87 g/cm$^3$) [41]. Fig. 2a shows the $^*\mathrm{ArOH}$-to-$^*\mathrm{ArO}^-$ fluorescence quantum yield ratio plotted against $F[\mathrm{H_3O^+}]$, where $[\mathrm{H_3O^+}]$ is taken to be equal to the HCl concentration.

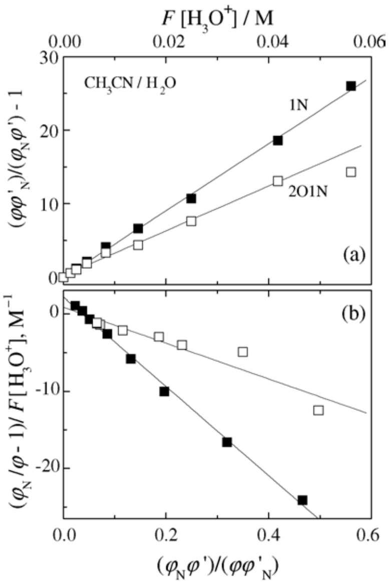


Fig. 2. Plots of $(\varphi\varphi'_N)/(\varphi_N\varphi') - 1$ vs. $F[H_3O^+]$ (a) an $(\varphi_N/\varphi - 1)/F[H_3O^+]$ vs. $(\varphi_N\varphi')/(\varphi\varphi'_N)$ (b) for 1N (solid symbols) and 2O1N (open symbols) in the MeCN–$H_2O$ mixture (2:1, v/v).

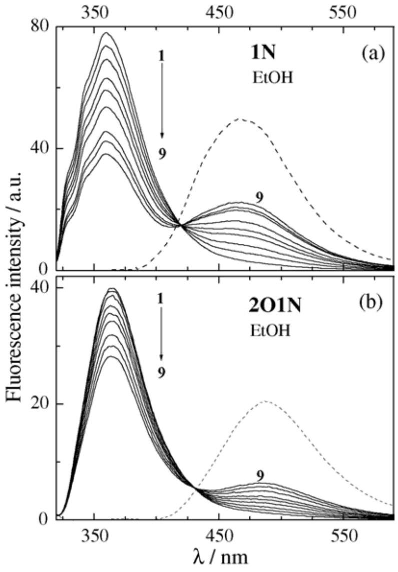


Fig. 3. Fluorescence spectra of 1N (a) and 2O1N (b) in EtOH in the presence of 0.01 M NaOH (dashed lines) or MeCOONa (solid lines). Arrows with numbers refer to ArOH fluorescence and represent an increase in MeCOONa concentration, which was 0 (1), 0.0075 (2), 0.015 (3), 0.03 (4), 0.045 (5), 0.06 (6), 0.09 (7), 0.12 (8) and 0.15 M (9) for both naphthols.

For 1N and 2O1N, we obtained $(k_{-1} + k'_q)\tau'_0$ values of 455 and 304 $M^{-1}$, respectively. To separate the rate constants $k_{-1}$ and $k'_q$ the fluorescence quantum yields were plotted according to Eq. (20) (Fig. 2b) and Eq. (21) (data not shown). The data indicated that the inequality $k_q/k_1 \ll k'_q\tau'_0$ was valid for these systems. Therefore, relative fluorescence quantum yields $\varphi_N/\varphi$ and $\varphi'_N/\varphi'$ can be plotted also in the co-ordinates corresponding to Eqs. (23) and (24). Good linear fits in such co-ordinates (not shown) and the similar values of the rate constants calculated in different ways confirmed the validity of our approach. The data obtained are collected in Table 1.

### *4.3. Excited-state protolytic reactions in absolute ethanol*

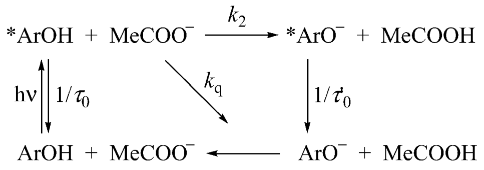
Fluorescence spectra of 1N and 2O1N in absolute EtOH at various concentrations of MeCOONa are depicted in Fig. 3. Only UV-emission of the protonated form ($\lambda_{fl}$ = 360 and 365 nm for 1N and 2O1N, respectively) was observed in the absence of proton acceptor. Increasing the acetate concentration resulted in a decrease of the *ArOH fluorescence intensity and an increase in the intensity of the blue emission corresponding to $*ArO^-$ ($\lambda_{fl}$ = 466 and 488 nm for 1N and 2O1N, respectively). The *ArOH fluorescence decay curves remained single exponential in the presence of sodium acetate, the decay time decreased with MeCOONa concentration. No change in naphthol absorption spectra was detected in the presence of MeCOONa up to the highest concentration used (0.15 M). The effects observed were described by Scheme 2, where $k_2$ is the excited-state proton-transfer rate constant, and $k_q$ is the rate constant of *ArOH quenching by $MeCOO^-$. The overall concentration of acetic acid in EtOH solution of sodium acetate appears to be very low and no backward reaction in the excited-state is observed.

According to Scheme 2, the apparent rate constants can be determined from the *ArOH ($\varphi$) and $*ArO^-$ ($\varphi'$) fluorescence quantum yields or from the *ArOH fluorescence decay time ($\tau$):

$$\frac{(\varphi'\varphi_0)}{(\varphi'_0\varphi)} = k_2\tau_0\left(\frac{\tau'}{\tau'_0}\right)[\mathrm{MeCOO^-}] \tag{28}$$

$$\frac{\varphi_0}{\varphi} = \frac{\tau_0}{\tau} = 1 + (k_2 + k_q)\tau_0[\mathrm{MeCOO^-}] \tag{29}$$

where $\tau'/\tau'_0$ is introduced to correct for the difference in $*ArO^-$ lifetimes under conditions of the excited-state reaction and of direct excitation. Plots in the coordinates corresponding to Eqs. (28) and (29) are shown in Fig. 4. Sodium acetate in EtOH was assumed to be completely dissociated. No correction to a non-unity activity coefficient of the acetate ion was done. Practically the same slope for the plots of the relative fluorescence quantum yield and decay time (not shown) provided evidence for the absence of static quenching in this system. Fluorescence decay times and rate constants for 1N and 2O1N in EtOH are collected in Table 2. A rather small difference in the slopes obtained



Scheme 2.

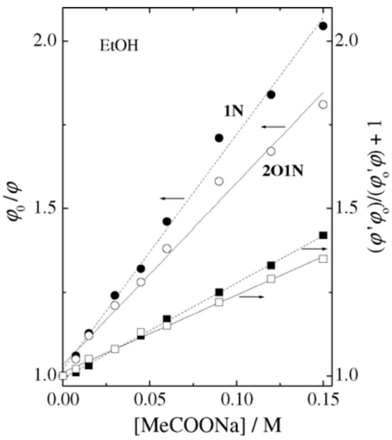


Fig. 4. Plots of $\varphi_0/\varphi$ (circles) and $(\varphi_0\varphi')/(\varphi\varphi'_0)+1$ (squares) vs. MeCOONa concentration in ethanol solution of 1N (solid symbols) and 2O1N (open symbols).

Table 2
Kinetic parameters of excited-state proton transfer from naphthols to acetate anion in absolute ethanol[a]

| Compound | 1N | 2O1N | 2N[b] | 1O2N[b] |
|---|---|---|---|---|
| $\tau_0$ (ns) | 5.0 | 3.3 | 6.5 | 8.4 |
| $\tau'_0$ (ns) | 9.5 | 5.3 | 8.4 | 11.2 |
| $k_2$ ($M^{-1}$ $ns^{-1}$) | 1.1 | 0.7 | 0.5 | 0.4 |
| $k_q$ ($M^{-1}$ $ns^{-1}$) | 0.3 | 0.2 | 0.2 | 0.1 |
| $\eta$ | 0.8 | 0.8 | 0.7 | 0.8 |

[a] Uncertainties in the rate constants are ∼10%.
[b] From Ref. [10b].

from $\varphi_0/\varphi$ and $((\varphi'/\varphi_0)/\varphi'_0\varphi)$ plots pointed out to relatively low efficiency of the acetate-induced quenching ($k_q < k_2$). In other words, the quantum efficiency of the proton transfer between excited naphthols and acetate-ion was rather high ($\eta = k_2/(k_2 + k_q) = 0.7$–$0.8$).

## 5. Discussion

### 5.1. Ground-state acidity constants

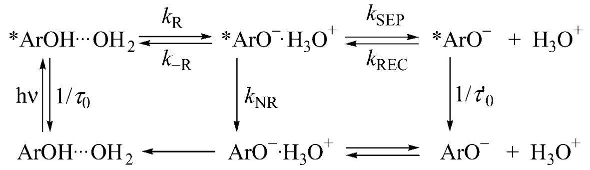
In the ground state, 2O1N was found to be a weaker acid ($\Delta pK = 0.6$) than the parent compound. An effect of the octadecyl substituent was even larger for 2-naphthol. Apparent p$K$ values of 13.0 and 11.9 were obtained for 1-octadecyl-2-naphthol (1O2N) and 2-naphthol (2N) in the MeCN–$H_2O$ mixture (2:1, v/v) [42]. Previously we have reported p$K$ values of 9.9 and 9.1 for these compounds in CTAB micelles [10b]. It is well known that alkyl substituents slightly decrease the acidity of hydroxyaromatics. Ground-state p$K$ values of 9.45, 9.70 and 9.64 were determined for 2-naphthol, 6-methyl-2-naphthol and 7-methyl-2-naphthol, respectively, in water [43a]. p$K$ values of 14.36, 14.90, 14.48 and 14.54 for phenol, 2-methylphenol, 3-methylphenol and 4-*t*-butylphenol in MeOH [44] provide another example of the alkyl group effect. A decrease in the naphthol acidity constant caused by the octadecyl group appeared to be slightly larger than that caused by smaller alkyl substituents.

According to Semi-empirical MO calculations [45] and ab initio calculations [46] (HF/3–21G level) relatively high π-electron density exists in position 2 of 1N and position 1 of 2N in the ground state. Semi-empirical calculations [47] gave formal charges of −0.0470 and −0.0467 at the carbon atoms in these positions in 1- and 2-methoxynaphthalenes. Some suppression of the protolytic dissociation is therefore expected when an electron-donating group is bounded to the carbon atom in such a position.

An increase of p$K$ for 1- and 2-naphthols in the aqueous MeCN solution relative to neat water appeared to be similar to that observed for other hydroxyaromatics and carboxylic acids ($\Delta pK = 2.5$–$2.7$). The p$K$ shift was larger in MeCN solutions in comparison to alcohol solutions of the same dielectric constant ($\Delta pK = 1.2$–$1.4$) [44,48–52]. Higher p$K$'s were also found for phenols and carboxylic acids in neat MeCN [50,51] as compared to MeOH [44,48], although both solvents have similar dielectric constants. A difference between the acidity constant of an acid AH in a mixed or non-aqueous solution ($pK_s$) and that in neat water ($pK_w$) can be expressed in terms of Gibbs free energies ($\Delta_w^s G$) of proton and anion transfer from water (w) to a particular solvent(s) [38,53]:

$$\begin{aligned}2.3RT(pK_s - pK_w)\\ &= \Delta_w^s G(H^+) + \Delta_w^s G(A^-) - \Delta_w^s G(AH)\\ &\approx \Delta_w^s G(H^+) + \Delta_w^s G_{es}(A^-), \qquad (30)\end{aligned}$$

where $\Delta_w^s G_{es}(A^-)$, is an electrostatic term of the free energy of $A^-$ transfer. The electrostatic component of the anion free energy of transfer as a function of solvent polarity appeared to be well described by the Born equation [35b,38,44,53a] with a similar value of the anion radius for different compounds and solvents. This term is therefore independent of the organic solvent nature. However, an extremely small value of the anion radius must be taken to obtain quantitative agreement with experimental data for large organic acids [35b,53a]. This results in a very strong decrease of the dissociation constant with the organic solvent concentration in binary mixtures. The Gibbs energy of proton transfer into a pure organic solvent or binary mixture is completely non-classical (does not obey Born equation) [53,54]. For aqueous MeOH it changes only by 1 kJ $mol^{-1}$ upon increasing the alcohol concentration up to 80% *w*., whereas for EtOH mixtures it reaches a minimum value of ca. −5 kJ $mol^{-1}$ at an alcohol concentration of ∼65% w. and than goes up to 11 kJ/mol in the absolute alcohol [54]. According to Groves and Wells [53b], $\Delta_w^s G(H^+)$ in MeCN–$H_2O$ mixtures decreases monotonously with MeCN concentration and reaches a minimum (−7 kJ $mol^{-1}$) at 35% w. A further increase in the MeCN concentration results in a strong increase of the Gibbs energy of transfer for proton. Therefore, a p$K$ difference of ∼2.5 (corresponds to 15 kJ $mol^{-1}$) between 66.7% v. acetonitrile and bulk water



Scheme 3.

may be attributed to positive free energies of transfer both for proton and naphtholate anion.

### 5.2. *Some features of protolytic photodissociation mechanism for 1-naphthol derivatives*

The results obtained in this study for 2O1N together with the data for 1N are discussed in terms of formal kinetic parameters and medium effects on the rate constants. According to a general scheme of acid-base reactions [55], excited-state protolytic dissociation of aromatic hydroxycompounds can be described by Scheme 3: here, $k_R$ and $k_{-R}$ are the rate constants of the forward and backward proton transfer along a hydrogen bond. The rate constants $k_{SEP}$ and $k_{REC}$ refer to the separation and formation of a reactive hydrogen-bonded ion-pair, which is usually assumed to consist of a base molecule and a protonated water molecule separated by 2–3 hydrogen-bonded water molecules. The latter two rate constants are estimated by using the steady-state approximation for diffusion-controlled reactions. Decay of all three species should be taken into account in kinetic analysis of excited-state reactions. The rate constant $k_{NR}$ corresponds to radiationless decay of the reactive ion-pair. Typically, emission from the ion pair can be neglected.

Scheme 3 takes into account the radiationless deactivation observed for 1N and its derivatives [4c,25,29]. Reaction kinetics is independent of actual mechanism(s) of the deactivation. Scheme 3 predicts multi-exponential decay of *ArOH and $^*ArO^-$ fluorescence even at neutral pH. However, single-exponential decay should be observed for the neutral form of very weak ($k_R/k_{-R} \ll 1$) and very strong photoacids ($k_R/k_{-R} \gg 1$) at pH ~ 5–8. When $k_R/k_{-R} \approx 1$, single exponential decay of the ArOH fluorescence should also be observed provided that $k_{SEP}/k_{-R} \gg 1$. Thus, Scheme 1 should give a good description of the overall dissociation kinetics for many photoacids provided that diffusion steps can be approximated by conventional kinetics with time-independent rate constants. Deviations from the single-exponential rate law as predicted by Scheme 3 should be distinguished from intrinsically non-exponential kinetics predicted by Debye–Smoluchowski equation with the reversible-reaction boundary condition [32]. However, the latter type of kinetics could be observed only for a few strong photoacids.

Quantum efficiency of the adiabatic protolytic dissociation, $\eta$, which is determined from the fluorescence quantum yields at low concentration of hydronium ions, can be expressed as

$$\eta = \frac{k_1}{k_1 + k_d} = \frac{k_{SEP}}{k_{SEP} + k_{NR}} \tag{31}$$

Contrary, quantum efficiency of the adiabatic protonation of $^*ArO^-$ by hydronium ions ($\eta'$) is determined from $\varphi$ and $\varphi'$ at high concentration of hydronium ions:

$$\eta' = \frac{k_{-1}}{k_{-1} + k'_q} = \frac{k_{-R}}{k_{-R} + k_{NR}}, \tag{32}$$

Eqs. (31) and (32) can be used to evaluate some rate constants introduced in Scheme 3.

Apparent rate constants used in Scheme 1 and Eqs. (3)–(24) can be expressed through rate constants of elementary reactions presented in Scheme 3 as

$$k_1 = \frac{k_R k_{SEP}}{k_{-R} + k_{NR} + k_{SEP}} = \frac{k_R}{(1/\eta + k_{-R}/k_{SEP})} \tag{33}$$

$$k_{-1} = \frac{k_{-R} k_{REC}}{k_{-R} + k_{NR} + k_{SEP}} = \frac{k_{REC}}{[1 + (k_{SEP}/k_{-R})/\eta]} \tag{34}$$

using common steady-state approximation ($d[^*ArO^- \cdot H_3O^+]/dt \approx 0$), Eqs. (31)–(32), and definitions of $k_1$, $k_{-1}$ $k_q$, and $k'_q$ according to Scheme 1. It is important to note that, in the presence of efficient deactivation in the ion pair, the ratio of the rate constants, $k_1/k_{-1}$, is still equal to the excited-state acidity constant $K^*$:

$$\frac{k_1}{k_{-1}} = \left(\frac{k_R}{k_{-R}}\right)\left(\frac{k_{SEP}}{k_{REC}}\right) = K^*. \tag{35}$$

The *ArOH decay time, $\tau_N$, depends on the radiationless decay rate and may be substantially shorter than $1/k_1$:

$$\frac{1}{\tau_N} = \frac{1}{\tau_0} + \frac{k_1}{\eta} = \frac{1}{\tau_0} + \frac{k_R(k_{SEP} + k_{NR})}{k_{-R} + k_{NR} + k_{SEP}}. \tag{36}$$

The ratios $k_{NR}/k_{SEP}$ and $k_{NR}/k_{-R}$ can be quantified using experimental data (see Eqs. (15), (16), (31) and (32)):

$$\frac{k_{NR}}{k_{SEP}} = \frac{1}{\eta} - 1 = \frac{k_d}{k_1} \tag{37}$$

$$\frac{k_{NR}}{k_{-R}} = \frac{1}{\eta'} - 1 = \frac{k'_q}{k_{-1}} \tag{38}$$

Thereafter, $k_{-R}/k_{SEP}$ can be evaluated and used to calculate the rate constants, $k_R$ and $k_{REC}$, according to Eqs. (33) and (34). The results obtained for 2O1N and 1N are presented in Table 1. Similar two-step kinetic scheme was used in Ref. [56] to analyze protolytic photodissociation of 4-methyl-7-hydroxyflavylium in micelles. Recently it was suggested to include a “loose” hydrogen-bonded complex into Scheme 3, therefore making ESPT a three-step process [57].

### *5.3. Excited-state protolytic dissociation in aqueous acetonitrile*

The dissociation rate of hydroxyarenes in mixed solutions was shown to depend very nonlinearly on the water concentration [35,36,58–60]. This was initially attributed to water structure breaking, which results in a dilution of large water clusters acting as a proton acceptor. However, recent time-resolved studies [23,59,61,62] demonstrated an important role of single water molecules and water dimers in the photodissociation of ArOH and $ArNH_3^+$ in various aqueous mixtures.

The excited-state protolytic dissociation of 1N derivatives in aqueous MeCN has some specific features (Table 1). The acidity constant of 2O1N in the singlet excited state is slightly larger than that for 1N. In contrast, 2O1N in the ground state is weaker acid than the parent compound. The rate constant of the protolytic photodissociation of 2O1N is close to that for 1N. Quantum efficiencies of the adiabatic excited-state dissociation of *ArOH and protonation of $^*ArO^-$ in the mixed solvent were found to be rather low (0.2–0.5). A decrease of the acidity constant of excited 1N in aqueous acetonitrile compared to neat water ($\Delta pK \approx 1.0$) was much smaller than that in the ground state ($\Delta pK = 2.7$). This suggested a much smaller free energy of transfer for the excited naphtholate anion, $\Delta_w^s G(^*A^-)$ (see Eq. (30)). The difference can be attributed to greater delocalization of the charge over the aromatic system in the excited anion as compared the ground-state species.

Enhancement of 2O1N acidity relative to 1N in the singlet excited state as compared to the ground one is probably caused by essentially different electronic structures of these two states. Semi-empirical calculations [47] gave a formal charge close to zero for a carbon atom in position 2 of 1-methoxynaphthalene in the singlet excited state ($^1L_a$). As mentioned above, in the ground state it was a position of high electron density. Such a decrease in the electron density should result in a much smaller effect of an electron-donating group in position 2 on the acidity constant in the excited state relative to the ground state. For 2-methoxynaphthalene, a change in the formal charge at position 1 was much smaller upon excitation to $^1L_b$ state [47]. A similar action of an alkyl group on the ground and excited state may therefore be expected. The fast that the electron density in the first excited singlet state is not localized in the same position as in the ground state causes difference in acidity between substituted phenols [63] and naphthols [64] in the ground versus excited states. The difference in p$K^*$ between 2O1N and 1N was also consistent with a difference in the fluorescence spectra of these compounds and their anions. Emission maxima of 2O1N and its anion in aqueous MeCN were shifted by 10 and 30 nm relative to those for 1N. According to the Förster cycle [4a,65], $\Delta pK = pK - pK^*$ should be larger by ∼1 unit (∼6 kJ mol$^{-1}$) for 2O1N than for 1N. This difference more than compensated the larger ground-state p$K$ of 2O1N. Zero–zero transition energies for ArOH and $ArO^-$ were estimated from mean values of the fluorescence and absorption maxima without correction to an energy loss due to solvent and solute relaxation upon excitation. The relaxation term was expected to have similar values for the alkyl naphthols and the parent compound.

The overall rate constant ($k_{-1} + k'_q$) for the interaction of $^*ArO^-$ with hydronium ions in aqueous MeCN appeared to be only slightly smaller than $k_{REC}$ calculated from steady-state diffusion kinetics (see Table 1). In contrast, the diffusion rate constant in water was significantly smaller than the sum ($k_{-1} + k'_q$) reported for 1N. It is worth mentioning that there exist significant discrepancies in the published data for the reaction of 1N anion with protons. In Table 1 we presented the data of Webb et al. [29] that are generally in good agreement with the results of other groups. However, their value of ($k_{-1} + k'_q$) is likely to be overestimated because they used proton concentrations that were overcorrected: for a kinetic activity coefficient, $F = (f_\pm)^2$, and for a thermodynamic coefficient, $\sim f_\pm$. Harris and Selinger [43c] reported a $k'_q$ value of 28 M$^{-1}$ s$^{-1}$, which was practically the same as that shown in Table 1, but their value of $k_{-1}$ (14 M$^{-1}$ ns$^{-1}$) was surprisingly small.

Good linear correlations between $\log k_1$ and p$K^*$ were observed for different photoacids in aqueous solution [4c,e,f,g,l]. The existence of such correlations is evident from Eqs. (33) and (35), which can be written as

$$\log k_1 = \log k_{REC} - pK^* - \log\left[1 + \frac{k_{SEP} + k_{NR}}{k_{-R}}\right] \qquad (39)$$

For 2-naphthol derivatives and many other hydroxyaromatic compounds, $k_{NR} \ll k_{sep}$ and the last term in Eq. (39) is rather small so that $\log k_1$ plotted against p$K^*$ gives a straight line with the slope of −1 and $\log(k_{REC}/M^{-1}s^{-1}) \approx 10.8$ (see Ref. [24]). The rate constant $k_{REC}$ obtained from kinetic data was close to the theoretical value in aqueous MeCN and exceeded that in $H_2O$ by a factor of 2–3. This discrepancy in water is likely due to inaccurate values of the rate constants ($k_{-1} + k'_q$) in water.

For the compounds studied, $pK^* > 0$ and the protonation of $^*ArO^-$ was therefore exergonic. In such systems, $k_{-R}$ should be close to the reciprocal Debye relaxation time of the solvent ($\tau_D$ = 8–9 ps in water, 6 ps in MeCN–$H_2O$ 2:1, v/v) [36,41,66]. The value of $k_R$ for 1N in water was very close to $1/\tau_D$ of the solvent scaled with a steric factor $\Omega = 0.49$ [36] (see Table 1). In contrast, $k_R$ in MeCN–$H_2O$ was much smaller than $\Omega/\tau_D$. This indicates an endergonic reaction of proton transfer in the mixed solvent ($k_R/k_{-R} < 1$). A remarkable decrease of $k_R$ observed for 1N in aqueous MeCN in comparison to $H_2O$ corresponds to a change in the Gibbs free energy of proton transfer reaction by ∼6–9 kJ mol$^{-1}$.

It is possible to estimate rate constants of induced radiationless decay in the reactive hydrogen-bonded ion pair ($k_{NR}$) and ion-pair separation ($k_{SEP}$) from the values of $k_{NR}/k_{SEP}$ and $k_{NR}/k_{SEP}$ if one assumes that $k_{-R} = \Omega/\tau_D$. The results collected in Table 1 showed that strong retardation of the protolytic dissociation in aqueous MeCN relative to bulk water was mainly caused by an approximately 40-fold decrease of $k_R$. A decrease of $k_{SEP}$ by a factor of 2–4 also contributed to a smaller value of $k_1$ in mixed solution. The rate constant $k_{NR}$ was significantly larger in aqueous MeCN than in $H_2O$. A substantial difference in ($k_{NR}/k_{-R}$) for the mixed solvent and bulk water suggested that mechanisms of the radiationless decay in the reactive complex are not directly related to a proton-transfer reaction. No significant difference in $k_{NR}$ was found for 1N and 2O1N. Very high values of $k_{NR}$ and $k_{SEP}$ indicated the absence of a substantial activation energy both for radiationless decay and diffusion separation.

Our data demonstrate that the long-chain alkyl group in 2O1N has no specific effect both on thermodynamics and kinetics of proton transfer reactions and no peculiar *ortho*-effect [67] could be observed. Same effect was observed in micellar solutions [24]. The alkyl substituent seems not to disrupt the structures of $(H_2O)_n$ and $(H_2O)_nH^+$ that act as proton acceptor and donor, respectively.

It is of interest to compare our analysis of proton transfer kinetics for 1N derivatives with that based on numerical solution of the Debye–Smoluchowski equation with a back-reaction boundary condition. The values of $k_{SEP}$ (50–110 $ns^{-1}$) and $k_{NR}$ (27 $ns^{-1}$) obtained in this study from the data of Webb et al. for 1N in water are in very good agreement with the analogous rate constants (48, 26 $ns^{-1}$) reported by Pines et al. [25] from picosecond decay kinetics and fluorescence quantum yields. However, our estimates of the rate constants for the proton transfer steps ($k_R$ = 42–62 $ns^{-1}$, $k_{-R} = 55\,ns^{-1}$) were by a factor of ~2 larger than those obtained by Pines et al. Additional work is needed to clarify the origin of these discrepancies. The fact that the rate constant for the backward proton-transfer reaction estimated by using time-dependent diffusion kinetics was substantially smaller than that predicted from the dielectric relaxation time is of particular concern.

### *5.4. Excited-state proton transfer in absolute ethanol*

For 1N and many other aromatic hydroxycompounds ($pK^* > 0$ in water), the excited-state protolytic dissociation in bulk organic solvents is too slow to compete with excited-state deactivation. A stronger proton acceptor should be added to observe excited-state proton transfer in such solvents.

In our previous paper [10b] we have reported the rate constants for the excited-state proton-transfer reactions between 2N derivatives and acetate anion in absolute ethanol. These data together with our results for 1N derivatives are presented in Table 2. We found that all these rate constants vary in a rather narrow range (0.4–1.1 $M^{-1}\,ns^{-1}$). The same reaction of 2N in water-alcohol mixtures was extensively studied [4a,37,68,69]. The reported values of $k_2$ in water (2.0–2.9 $M^{-1}\,ns^{-1}$) approach a diffusion-controlled limit expected for reactions with highly negative free energies. The free energy of $-11\,kJ\,mol^{-1}$ could be estimated for this reaction in water from a difference in p*K* of acetic acid (4.8) and excited 2N (2.8). A good linear correlation between the rate constant and reaction free energy was observed only for strongly endergonic reactions. The reaction of acetate anion with excited naphthols ($pK^* = 0–3$ in water) provides therefore little information on relative excited-state acidities in water.

Equilibrium constants for the protolytic dissociation of carboxylic acid and phenols are known to decrease substantially in alcohols [44,48,49,52]. For acetic acid in EtOH a p*K* value of 10.3 was reported [48]. A ground-state p*K* of 13.9 was determined for 1N in MeOH [48b]. A similar shift by ~3–4 units was reported for ground- and excited-state p*K* of 5-cyano-2-naphthol in MeOH and EtOH [70]. These data suggest that the free energy of the reaction between excited naphthols and acetate anion may be more negative in EtOH. However, some authors asserted that the p*K* difference between phenol and acetic acid (hence the reaction free energy) remained practically the same in water, methanol, acetonitrile, dimethylformamide and increased in dimethylsulfoxide [44,48,52]. We found that the proton-transfer rate constant for the reaction of 1N and 2N with acetate anion in absolute EtOH differed only by a factor of 2.2, whereas $pK^*$ likely varied by more than 2 units. This suggests that kinetics of this reaction falls within a region that is intermediate between diffusion control and thermodynamic control.

The efficiency of the adiabatic proton transfer from *ArOH to acetate anion, $\eta$, was found to be high. This showed a significant decrease of the deactivation rate in $^*ArO^-{\cdot}HOOCMe$ in EtOH as compared to $^*ArO^-{\cdot}H_3O^+$ in water and aqueous MeCN.

## 6. Conclusions

2O1N was found to be a promising fluorescent probe that can be used to explore proton transfer processes in a wide variety of reaction media including mixed solutions and molecular organized systems.

Most important feature of 1-naphthol derivatives is a competition of adiabatic excited-state proton transfer with deactivation of the excited state which decreases a quantum yield of adiabatic proton-transfer reaction. This deactivation complicates kinetic analysis, yet provided a deeper insight into mechanisms of the excited-state proton-transfer reactions. Protolytic photodissociation of 1-naphthol derivatives was analyzed within the framework of a kinetic model that included fast deactivation of excited naphtholate anion in the geminate ion pair which can be attributed to promoted internal conversion and/or protonation of the excited aromatic nucleus. The rate constants of the protolytic photodissociation ($k_1$) for 1N and 2O1N in aqueous MeCN were close to each other. A decrease of $k_1$ in the mixed solvent relative to that in neat water was caused by strong reduction of the rate constant of proton transfer in a hydrogen-bonded complex ($k_R$), and by an increase in the efficiency of the proton-induced deactivation (larger ratio $k_{NR}/k_{SEP}$). Proton-induced quenching in the reactive ion pair ($k_{NR}$) decreased the quantum efficiency of the adiabatic reaction of 1N derivatives. Our data also showed that the deactivation rate constant, $k_{NR}$, increased significantly in less polar environment of the MeCN–$H_2O$ mixture.

Practically no deactivation was observed when excited-state proton transfer between 1-naphthols was studied in ethanol using acetate ion as a proton acceptor. This suggested the nature of a proton acceptor is an important factor in the deactivation mechanism. The rate constants for proton transfer from excited 1- and 2-naphthols and their alkyl derivatives to acetate anion were found to have similar values. These indicated that these reactions are in a kinetic regime, which is intermediate between the diffusion and thermodynamic control. Therefore, this reaction is not suitable for a comparison of the reactivity of these naphthols in non-aqueous media.

A decrease in the ground- and excited-state acidity constants of 1N in aqueous MeCN as compared to $H_2O$ was consistent with available estimates of the Gibbs free energies of transfer for proton and naphtholate anion from water to a particular solvent. A considerably smaller increase of p$K$ in the excited state ($\Delta pK^* \approx 1.0$) relative to that in the ground state ($\Delta pK^* \approx 2.7$) suggests smaller free energy of transfer for the excited naphtholate anion what can be attributed to greater delocalization of the charge over the aromatic system in the excited anion as compared the ground-state.

The difference in effects of the same long-chain alkyl substituent in position 1 of 2N and position 2 of 1N on the acidity of the ground and singlet excited states indicated much greater decrease of electron density in the position 1 rather than in position 2 of excited naphthalene ring what hided much weaker effect of the alkyl substituent for 1-naphthol derivative. Electron-donating alkyl group caused some decrease of the acidity of the ground state of 2O1N and of both ground and singlet excited states of 1O2N relative to parent naphthols but some increase of the acidity of the singlet excited state of 2O1N.

No specific effects of a long-chain alkyl substituent in the ortho-position to the hydroxy group could be revealed from our kinetic data in both mixed aqueous solutions and micellar systems. This suggests that solvation of the reactive group and the solvent structure in its vicinity are not changed in the presence of a large alkyl group in the naphthol.

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