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Protolytic dissociation of cyano derivatives of naphthol, biphenyl and phenol in the excited state: A review

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ABSTRACT

The excited state proton transfer (ESPT) has been extensively studied for hydroxyarenes, phenols, naphthols, hydroxystilbenes, etc., which undergo large enhancement of acidity upon electronic excitation, thus classified as photoacids. The changes of acidic character in the excited state of cyano-substituted derivatives of phenol, hydroxybiphenyl and naphthol are reviewed in this paper. The acidity constants pK_a in the ground state (S_0), pK_a^* in the first singlet excited state (S_1) and the change of the acidity constant in the excited state ΔpK_a for the discussed compounds are summarized and compared. The results of the acidity studies show, that the “electro-withdrawing” CN group in the molecules of naphthol, hydroxybiphenyl and phenol causes dramatic increase of their acidity in the excited state in comparison to the ground state. This effect is greatest for the cyanonaphthols (the doubly substituted CN derivatives are almost as strong as a mineral acid in the excited state), comparable for cyanobiphenyls, and smaller for phenol derivatives. The increase of acidity enables proton transfer to various organic solvents, and the investigation of ESPT can be extended to a variety of solvents besides water. The results of theoretical investigations were also presented and used for understanding the protolytic equilibria of cyano derivatives of naphthol, hydroxybiphenyl and phenol.

1. Introduction

Proton transfer is an important elementary step in many chemical and biological processes [1,2]. The excited state proton transfer (ESPT) has been extensively studied for hydroxyarenes, phenols, naphthols, hydroxystilbenes, etc., which undergo large enhancement of acidity upon electronic excitation [1–3]. Proton dissociation and acid–base equilibria in the excited state are strongly affected by substituents introduced in the aromatic ring. The introduction into the aromatic ring of the hydroxyarenes molecules an electron acceptor group, such as cyano, nitro or sulphonate groups, changes their acidity in both ground and excited states [4–9]. An aqueous medium is required for ESPT to take place in the case of simple phenols and naphthols, but substitution of electron withdrawing groups has greatly enhanced the photoacidity and made ESPT possible even in non-aqueous solvents [10–15]. The isomeric naphthols and their derivatives are prototypical photoacids whose excited-state behavior have been the subject of numerous publications. Several derivatives of 1- and 2-naphthol which possess electron-withdrawing cyano- or fluoroalkanesulfonyl substituents at 5- or 6-position have greatly enhanced excited-state acidities in water and also function as photoacids in polar and non-aqueous solvents [4,5,9,15–17]. This property of cyanonaphtols with one or two cyano groups is used to name these compounds “super” photoacids. A number of theoretical and experimental investigations have been carried out to understand the protolytic equilibria and proton transfer dynamics by taking 1- and 2-naphthols as the prototype for hydroxyaromatic compounds [18–27]. The donor-acceptor derivatives of biphenyl with hydroxyl and cyano substituents also demonstrate a strong photoinduced increase of acidity, similarly to cyano-derivatives of 2-naphthol [28,29]. Wehry et al. [30], Schulman et al. [31], Kaneko et al. [32] and Granucci et al. [33] have investigated the prototropic equilibria of phenols in ground and excited states. They reported that an increase of the acidity of *orto-* and *meta*-cyano derivatives was about 6 order of magnitude in the excited state in comparison to the ground state in an aqueous solution. The study of the acidity changes for monocyano- and dicyano-phenols in alcohol and water have shown that 3,4-dicyanophenol is the strongest acid among the investigated cyano-substituted phenols [34].

In this paper, the results of the acidity studies for cyano

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derivatives of 2-naphthol, biphenyl and phenol in the excited state are reviewed. The acidity constants pK$_a$ in the ground state (S$_0$), pK$_a^*$ in the first singlet excited state (S$_1$) and the change of the acidity constant in the excited state ΔpK$_a$ for the discussed compounds are summarized and compared. The results of theoretical investigations were also presented and used for understanding the protolytic equilibria of cyano derivatives of naphthol, hydroxybiphenyl and phenol.

2. Methods

2.1. Acid-base equilibria

The pKa of biphenyl cyano derivatives: 4-hydroxy-4′-cyanobiphenyl and 4-hydroxy-2,6-dimethyl-4′-cyanobiphenyl in the ground state was calculated using Eq. (1) [35].

$$pK_a = pH + \log[(\varepsilon - \varepsilon_{A-})/(\varepsilon_{HA} - \varepsilon)] \tag{1}$$

where: ε is the sum of the molar extinction coefficients of the solution mixture containing the anion A$^-$ and acid HA, ε_{A-} is the molar extinction coefficient of the pure anion A$^-$, and ε_{HA} is the molar extinction coefficient of HA.

Generally, the measurements of photoacids excited-state acidities (pKa*) are based on the analysis of fluorescence properties of the neutral hydroxyaromatic compound, HA, and its conjugate base, A$^-$. The HA in the excited state is a stronger acid than in the ground state if the absorption or emission spectrum of the conjugate base displays a bathochromic shift relative to that of the conjugate acid [36,37]. This thermodynamic cycle is described by the Főrster equation (Eq. (2)), where pKa* = ΔG$_a^*$/2.3RT is the ground (excited)-state acidity constant and h$\nu_{1(2)}$ is the energy of the 0–0 electronic transition for the conjugate acid (base) [38]. A more useful treatment is to take hν_1 and hν_2 as the averages of the absorption and fluorescence transitions of each acid and base species (Eqs. (3) and (4)).

$$pK_a^* = pK_a - (h\nu_1 - h\nu_2)/2.3RT \tag{2}$$

$$\tilde{\nu}_{00}^{A-} = \frac{\tilde{\nu}_{A-}^{a} + \tilde{\nu}_{A-}^{f}}{2} \tag{3}$$

$$\tilde{\nu}_{00}^{HA} = \frac{\tilde{\nu}_{HA}^{a} + \tilde{\nu}_{HA}^{f}}{2} \tag{4}$$

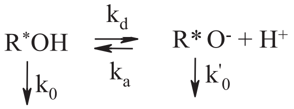
The change of the acidity constant (ΔpK$_a$) in the excited state was calculated using the Eq. (5):

$$\Delta pK_a = \frac{Nhc}{2,3RT}\left(\tilde{\nu}_{00}^{A^-} - \tilde{\nu}_{00}^{HA}\right) = \frac{0,625}{T}\left(\tilde{\nu}_{00}^{A^-} - \tilde{\nu}_{00}^{HA}\right) \tag{5}$$

where: T is the temperature on the Kelvin, $\tilde{\nu}_{00}^{A-}$ and $\tilde{\nu}_{00}^{HA}$ are the energies (cm^{-1}) of the 0–0 transitions for the anion A$^-$ and the neutral acid HA, $\tilde{\nu}_{A-}^{a}$ and $\tilde{\nu}_{HA}^{a}$ are the wavenumbers of the absorption band maxima of the anion A$^-$ and the neutral acid HA, $\tilde{\nu}_{A-}^{f}$ and $\tilde{\nu}_{HA}^{f}$ are the wavenumbers of the fluorescence maxima of these species.

Hydroxyarenes undergo a number of processes in addition to fluorescence and excited-state proton transfer (ESPT), such as proton-induced quenching and homolytic OH bond cleavage to produce radicals, studied most extensively for 1-naphthol and phenol derivatives. The presence of competing processes and incomplete excited-state equilibrium may lead to erroneous results in determination of pKa* by fluorescence titration [17].

In the case of hydroxyaryls (HA≡ROH, where R is an aromatic ring system) the acid form dominates in the ground state, and it is converted to an excited R*OH molecule by photoexcitation. The R*OH undergoes a reaction of ESPT to solvent according to the following scheme:



The dissociation rate constant of R*OH is $k_{d.}$ The dissociation process generates the (R*O$^-$/H$^+$) ion pair at their “contact” distance, a, from which they may associate with the rate constant k_a. The separation of the partners over the distance r requires overcoming an attractive electrostatic potential $V(r) = -(R_D/r)$ (R$_D$ is the Debye (Onsager) distance, when r = R$_D$ the Coulomb interaction equals to the thermal energy). Both excited species, R*OH and R*O$^-$, decay to their ground state in a few nanoseconds, by a combination of radiative and nonradiative processes (rate constants k$_0$ and k$'_0$, respectively).

Using this approach, which considered the diffusion equation generalized to the Debye-Smoluchowski equation (DSE), the overall acid constant (equilibrium dissociation constant) is expressed with Eq. (6) [8,17,39].

$$pK_a^* = -\log[(k_d \exp(-R_D/a))/k_a] \tag{6}$$

where: a is the contact distance, k_d and k_r are the dissociation and recombination rate constants, R_D is the Debye (Onsager) distance.

2.2. Dipole moments in the excited state

The experimental dipole moments for biphenyl cyano derivatives: 4-hydroxy-4′-cyanobiphenyl and 4-hydroxy-2,6-dimethyl-4′-cyanobiphenyl in the first excited singlet state were calculated on the basis of solvatochromic analysis using the solvent shifts of the fluorescence spectra with the ground state dipole moments obtained on the basis of the semi-empirical calculations (Eq. (7)) [40].

$$hc\tilde{\nu}_f = -\frac{\mu_E(\mu_E - \mu_G)}{2\pi\varepsilon_0\ a^3}\Delta f + const$$
$$\text{where:}\quad \Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\cdot\frac{n^2\ - 1}{2n^2 + 1} \tag{7}$$

In Eq. (1), $\tilde{\nu}_f$ – the maximum of the fluorescence band, ε_0 – the dielectric constant in vacuum, μ_E, μ_G – the dipole moments of the solute in the excited and ground state, respectively, h and c – the Planck constant and the velocity of light, ε – the static dielectric constant of the solvent and n – the refractive index of solvent. The Onsager cavity radius a is taken as 6 Å in analogy to similar biphenyls [41].

2.3. Quantum chemical calculations

Semiempirical AM1 calculations on gas phase 2-naphthol and its cyano derivatives (for both acid and basic forms) in their first 3 singlet states were performed using the AMPAC 6.55 package [7,42]. Electron density distributions and dipole moments of cyano hydroxybiphenyl molecules in their ground and excited states were calculated based on AM1 method calculations [29]. All AM1