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ARTICLES

Picosecond Dynamics of the Photoexcited 6-Methoxyquinoline and 6-Hydroxyquinoline Molecules in Solution

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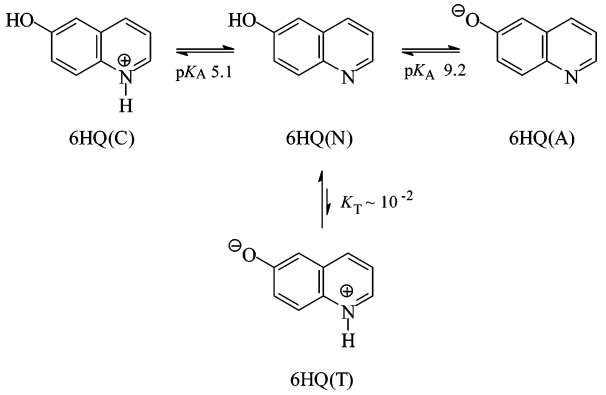
The photophysical properties of 6-methoxyquinoline (6MeOQ) and 6-hydroxyquinoline (6HQ) in organic solvents and in neutral, acidic, and alkaline aqueous solutions have been studied by picosecond transient absorption spectroscopy. The dynamics of photoinduced tautomerization by excited state proton transfer(s) arising in the case of 6HQ has been analyzed. Hydroxyl deprotonation of the cationic (quinolinium) form in acidic solution (pH 1.5) is 1 order of magnitude faster ($\tau_{dp} \sim 2.2$ ps) than imine protonation of the anionic (phenolate) form in 1 M KOH alkaline solution ($\tau_p \sim 30$ ps). In neutral solution, our results suggest a two-step process of initial proton release from the hydroxyl group followed by proton capture by the nitrogen atom with characteristic times close to the τ_{dp} and τ_p values, respectively.

1. Introduction

6-Hydroxyquinoline (6HQ) is an amphoteric bifunctional compound characterized by a weak acidic hydroxyl function ($pK_A = 9.2$) and a weak basic imine function ($pK_A = 5.1$) in the ground state.[1] A cationic (quinolinium) form 6HQ(C), an anionic (quinolinate) form 6HQ(A), and a neutral form 6HQ-(N) are thus predominantly present in acidic, alkaline, and neutral aqueous solutions, respectively, according to the acid−base equilibria displayed in Scheme 1. From a meticulous analysis of the absorption spectra, a very weak amount of a tautomeric form 6HQ(T) has also been suggested to coexist with the neutral form at pH 7 within an almost completely displaced equilibrium ($K_T = [6HQ(T)]/[6HQ(N)] \sim 10^{-2}$).[2−4]

SCHEME 1



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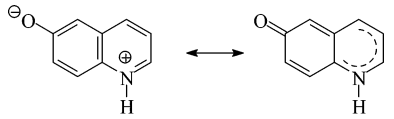
SCHEME 2



6HQ(T*)

The 6HQ(N), 6HQ(C), 6HQ(A), and 6HQ(T) species can be differentiated by the position of their lowest energy absorption band (326, 344, 358, and 408 nm, respectively[1,4]).

Extensive steady state fluorescence measurements as a function of the pH revealed that, in the excited state, both the acidity of the hydroxyl group and the basicity of the nitrogen atom are considerably enhanced in such a way that phenol deprotonation upon excitation of 6HQ(C) occurs in 10 M $HClO_4$ whereas pyridyl protonation upon excitation of 6HQ(A) arises in 12 M NaOH.[1] In neutral aqueous solution, the behavior of 6HQ upon excitation was suggested to result from both proton release to solvent molecules and proton capture from solvent molecules occurring simultaneously on both sites of the excited molecule. The essential stable form in an extremely large range of pH is thus the excited state of the tautomer, 6HQ(T*). It was assumed that the forward proton transfer processes were coupled to an intramolecular electron redistribution yielding a neutral quinonoid (ketonic) configuration, which strongly lowers the probability of the back proton transfers in the excited state (Scheme 2).[1]

Well distinguishable fluorescence emissions were identified for the excited state forms 6HQ(N*) (λ_{max} = 380 nm), 6HQ(C*) (λ_{max} = 450 nm), 6HQ(A*) (λ_{max} = 490 nm), and 6HQ(T*) (λ_{max} = 585 nm).[1,4] The excited tautomer being much less fluorescent than the 6HQ(C*), 6HQ(A*), and 6HQ(N*) forms,[1,5] the proton transfer can be considered as a quenching process. In organic solvents including alcohols, only the neutral form is present in both the ground and excited states, with fluorescence maxima ranging from 360 to 375 nm in acetonitrile and in alcohols.[5]

The almost unexplored dynamics of the excited state proton transfer in acidic, alkaline, and neutral aqueous solutions has been the object of two recent investigations by means of picosecond time-resolved fluorescence spectroscopy.[6,7] However, contradictory kinetic data are reported in these works, leading in particular to opposed conclusions concerning the chronology of the double proton transfer process in neutral water. The excited state dynamics of 6HQ remains thus mostly indeterminate. To obtain new information on this point, we have initiated a comprehensive analysis of the photophysics of 6HQ by using transient absorption spectroscopy with picosecond time resolution. We present in this paper some results obtained in the 0−1500 ps time domain in organic solvents and in aqueous solutions of various pH values. For comparison, we also give an analysis of the photophysics of the 6-methoxyquinoline molecule (6MeOQ), for which the acid−base properties are simpler because only the quinoline/quinolinium equilibrium is possible.[8,9]

2. Experimental Section

6-Hydroxyquinoline (Kodak) was recrystallized from ethyl ethanoate and 6-methoxyquinoline (Sigma) was purified by vacuum distillation. Acetonitrile, *n*-hexane, and methanol (Prolabo, spectrophotometric grade) were used as received. Potassium dihydrogen phosphate/disodium hydrogen phosphate buffer (0.1 M) aqueous solution of pH 7.00 at 25 °C (pH 7.02 at the 20 °C temperature of the experiments) was purchased from Crison Instruments and used as it. Acid and alkaline aqueous solutions were prepared from distilled and deionized water and redistilled perchloric acid (99.999%, Aldrich) and potassium hydroxide pellets (99.99%, Aldrich).

The subpicosecond transient absorption experiment has been already described.[10] Briefly, it was carried out by using a 1 kHz Ti−sapphire laser system based upon a Coherent (MIRA 900D) oscillator and a BM Industries (ALPHA 1000) regenerative amplifier. This system was set in a femtosecond configuration for all the absorption measurements. Tripling the initial 90 fs pulses at 800 nm (0.5 mm BBO crystal) provided the pump excitation at 266 nm. Its power was limited to 10−20 μJ per pulse (1.0−2.0 mJ/cm^2). A probe white light continuum pulse was generated at 800 nm in a CaF_2 plate. The probe pulse was delayed in time relative to the pump pulse using an optical delay line (Microcontrol Model MT160-250PP driven by an ITL09 controller, precision ±1 μm). The overall time resolution (fwhm of the pump−probe intensity cross-correlation) is estimated to be about 300 fs from the two-photon (pump + probe) absorption signal in pure hexane. The time dispersion of the continuum light over the 300−700 nm region of analysis is about 0.8 ps. The transmitted light was analyzed by a CCD optical multichannel analyzer (Princeton Instrument LN/CCD-1340/400-EB detector + ST-138 controller). The variation of optical density (ΔOD) was obtained as the ratio of the pump + probe signal to the probe-only signal. Samples were circulating in a flow cell with 2.5 mm optical path length. Data collection times were 3 min (~180 000 pump−probe sequences). In all measurements, the pump−probe polarization configuration was set at the magic angle. The sample concentration was typically 10^{-3} M. The characteristic times related to the spectral changes were obtained from exponential fit of the observed kinetics.

Corrected fluorescence spectra were obtained with a SLM 8000 C spectrofluorometer. Decay times were measured with a multifrequency phase-modulation fluorometer (Spex Fluorolob-Tau 3). Ludox was used as the scattering solution. The data were analyzed by a nonlinear least-squares method using Globals software (Globals Unlimited, University of Illinois at Urbana-Champaign, Laboratory for Fluorecence Dynamics). The concentration of the solutions was of the order of 2×10^{-5} M.

3. Results and Discussion

3.1. Photophysics of 6MeOQ. The fluorescence spectra of 6MeOQ have been reported and analyzed in various solvents and the acid−base kinetics of the excited state in aqueous solutions has been determined.[8,9] In organic solvents (acetonitrile, alcohols) and in alkaline aqueous solution, the neutral molecule presents a single emission at 365 ± 15 nm. In pure water, both the neutral and protonated forms are in equilibrium in the ground state (pK_A = 5.2) and two emission bands were observed at 370 and 440 nm, respectively. From time-resolved and steady state fluorescence measurements,[9] the basicity of the nitrogen atom appeared considerably enhanced upon excitation, and proton abstraction from water takes place. The excited state decay time of the neutral form and the fluorescence rise time of the protonated form were found in the range 1.7−1.9 ns. An excited state protonation rate of 3.5×10^6 M^{-1} s^{-1} (pK^* = 11.8) was deduced.

We have recorded the transient absorption spectra of 6MeOQ in acetonitrile, *n*-hexane, methanol, buffered aqueous solution at pH 7.00, and aqueous solutions of $HClO_4$ at pH 5 and 1.5, and of KOH at pH 14, as a function of the pump−probe time delay (0−1500 ps time range) following subpicosecond laser

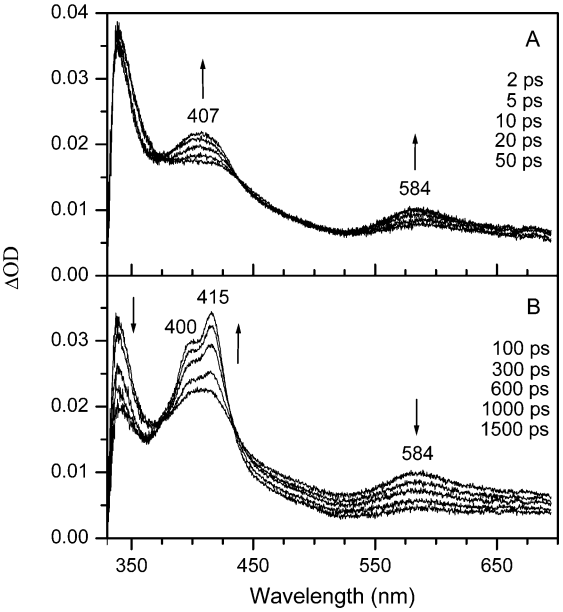


Figure 1. Transient absorption spectra of 6MeOQ in acetonitrile after excitation at 266 nm: (A) from 2 to 50 ps; (B) from 100 to 1500 ps. Vertical arrows indicate the signal evolution. The main band wavelengths (nm) are given.

excitation at 266 nm. Complementary time-resolved fluorescence measurements in the nanosecond time domain were also performed.

Figure 1 shows typical absorption spectra obtained in acetonitrile for different time delays in the 2−50 ps (part A) and 100−1500 ps (part B) time domains. Vertical arrows indicate the signal evolution. The 2 ps spectrum exhibits a broad band maximizing at 340 nm and extending in the red region with two weaker, rough maxima around 400 and 600 nm. Below 340 nm, the transient absorption signal drops abruptly and becomes extremely noisy. This effect, observed at all times and in all solvents, corresponds clearly to the complete extinction of the probe light due to its absorption by the unexcited 6MeOQ molecules that constitute a strong filter below 340 nm ($\lambda_{max}(S_0 \rightarrow S_n) = 329$ nm[8]). From 2 to 50 ps, the main absorption band does not change significantly in intensity and position but the two secondary absorptions rise notably while they become sharper and narrower, leading to well-defined bands at 407 and 584 nm. From 50 to 1500 ps, both the 340 and 584 nm bands decay whereas the structureless band at 407 nm evolves into a sharp absorption with two resolved maxima at 400 and 415 nm. The presence of isosbestic points at 375 and 435 nm indicates that the 50 ps spectrum characterizes the precursor of the final species described by the 400/415 nm absorption. Although the 1500 ps time window of the experiment is too narrow to allow any accurate kinetic measurement of events longer than ∼400 ps, we notice that the intensity of the 340 and 584 nm bands at 1500 ps is about half that observed initially, which is consistent with the order of magnitude of the fluorescence lifetime (1.3 ns) that we measured for 6MeOQ in acetonitrile. Accordingly we ascribe the initial absorption spectrum in Figure 1 (peak maxima at 340, 407, and 584 nm) to the lowest excited singlet state, S_1, and the final spectrum (400, 415 nm) to the triplet state, T_1.

The evolution of the transient absorption spectra of 6MeOQ upon photoexcitation in *n*-hexane and methanol was found similar to that shown in Figure 1 for the acetonitrile solution. The S_1 state decay time (or T_1 state appearance time) measured from these spectra in *n*-hexane (250 ps) is much shorter than in

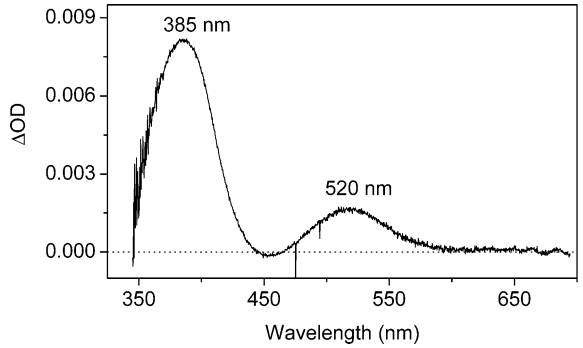


Figure 2. Transient absorption spectrum of 6MeOQ in $H_2O/HClO_4$ solution (pH 1.5) at a delay time of 10 ps following excitation at 266 nm.

acetonitrile. In contrast, a longer fluorescence lifetime (3.04 ns) was reported in methanol.[9] The increase of the S_1 state lifetime on going from *n*-hexane to acetonitrile, and then to methanol, was found to be accompanied by a decrease of the triplet state yield and an increase of the overall fluorescence intensity. Such a solvent effect, usual in nitrogen heterocyclic compounds, has been shown[11] to result from a stronger vibronic coupling between the close-lying lowest $n\pi^*$ and $\pi\pi^*$ excited states in nonpolar solvents than in polar solvents, favoring nonradiative processes. On the other hand, a short-time evolution comparable to that characterizing the 0−50 ps absorption spectra in acetonitrile (Figure 1, part A) was observed in methanol but not in *n*-hexane. According to the fact that the 266 nm pump excitation wavelength is in resonance with an excited state S_n higher than the S_1 state, this evolution could be due to the internal conversion process, $S_n \rightarrow S_1$. However, it looks more like a band narrowing effect than the appearance of a new spectrum. It seems thus more reasonable to ascribe the observed 0−50 ps spectral evolution to some kind of relaxation in the excited S_1 state. Its specific observation in polar solvents suggests that it characterizes the S_1 state solvation dynamics. Indeed, a notable increase in polarity being expected in going from S_0 to S_1, an important rearrangement of the solvent cage structure must take place in polar solvents.[12−14]

In an alkaline aqueous solution of 1 M KOH, where both the ground state and excited S_1 state are unprotonated, the time evolution of the transient absorption spectra of 6MeOQ following photoexcitation was found to be similar to that observed in organic solvents but the T_1 state yield was still lower than that in methanol. In $H_2O/HClO_4$ solution at pH 1.5, where the protonated form of 6MeOQ is dominant in the ground and excited states, a new transient absorption spectrum is observed upon excitation with a main band at 385 nm and a weaker one at 520 nm (Figure 2). No significant changes in band shape and intensity were noticed on the 0−1500 ps time domain, which can be correlated to the long fluorescence lifetime ($\tau =$ 23 ns, $\lambda_{max} = 438$ nm) that we measured in these conditions. This absorption spectrum is thus ascribed unambiguously to the excited S_1 state of the protonated molecule. A very slight but reproducible negative ΔOD is remarked in the 455 nm region, which corresponds nearly to the position of the fluorescence emission. The spectrum observed in this region results thus from a superposition of transient absorption and stimulated emission (gain) signals. In solutions of intermediate pH 5−7 (data not shown), the passage from the excited state absorption spectrum of the neutral species to that of the protonated one was clearly manifested by the disappearance of the strong band around 340 nm and the substitution of the 584 nm band by the 520 nm one. At 1500 ps, the intensity of the unprotonated excited state

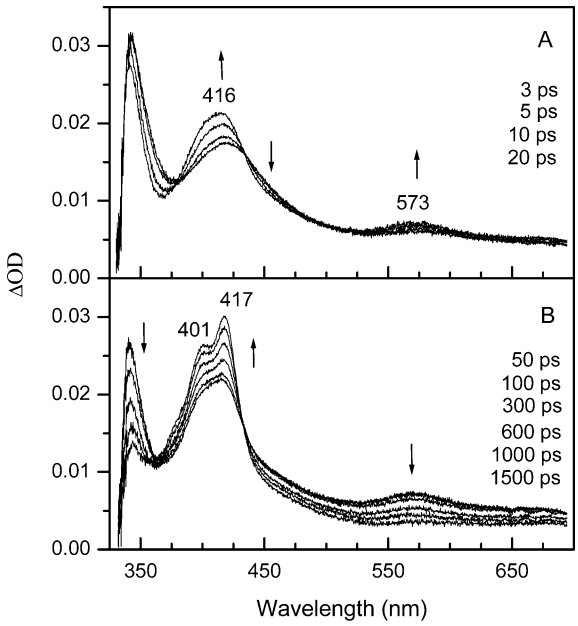


Figure 3. Transient absorption spectra of 6HQ in acetonitrile after excitation at 266 nm: (A) from 3 to 20 ps; (B) from 50 to 1500 ps. Vertical arrows indicate the signal evolution.

spectrum was about half that observed initially. This evolution is in agreement with the fluorescence decay time of 1.9 ns reported for the neutral species in pure water.[9] In the 380−420 nm region, the spectral evolution appears more complex as the S_1 state of the neutral molecule, the S_1 state of the protonated molecule, and the T_1 state produced from the former in competition with the proton transfer process have overlapping absorption bands around 400 nm.

3.2. Photophysics of 6HQ. Transient pump−probe spectra of 6HQ in acetonitrile, methanol, buffered aqueous solution at pH 7.00, alkaline aqueous solution of 1 M KOH, and acid solutions of 3×10^{-2} M and 12 M $HClO_4$ were recorded in the 0−1500 ps time delay range. In most cases, these spectra resulted from the superimposition of transient absorption (positive ΔOD) and of bleaching or stimulated emission (negative ΔOD) signals. Complementary nanosecond time-resolved fluorescence experiments were also carried out. Measurements in HCl solutions were excluded from the present discussion because an undesirable, ultrafast reaction of quenching of the lowest excited state of 6HQ by the chloride anion was observed.

Organic Solvents. Figure 3 shows typical spectra obtained in acetonitrile. The time evolution of these spectra is similar in all aspects to that described above for 6MeOQ in the same solvent (Figure 1) and characterizes thus the $S_1 \rightarrow T_1$ intersystem crossing process. The shape, position, kinetics, and short-time relaxation dynamics of the observed bands are nearly the same for 6HQ and 6MeOQ, which indicates that the nature and structure of the S_1 and T_1 states are comparable in both compounds. As a confirmation, the fluorescence spectrum of 6HQ in acetonitrile ($\lambda_{max} = 359$ nm, not shown) is similar to that of 6MeOQ. Moreover, the transient absorption spectra obtained for 6HQ in methanol are still characteristic of the $S_1 \rightarrow T_1$ process but are indicative of a lower T_1 state yield compared to that in acetonitrile, as for 6MeOQ. The 6HQ and 6MeOQ molecules thus exhibit quite identical photophysical behavior in organic solvents.

Alkaline Aqueous Solution. In aqueous solutions, the evolution of the transient spectra of 6HQ after photolysis is much more complex than in organic solvents and quite different from that

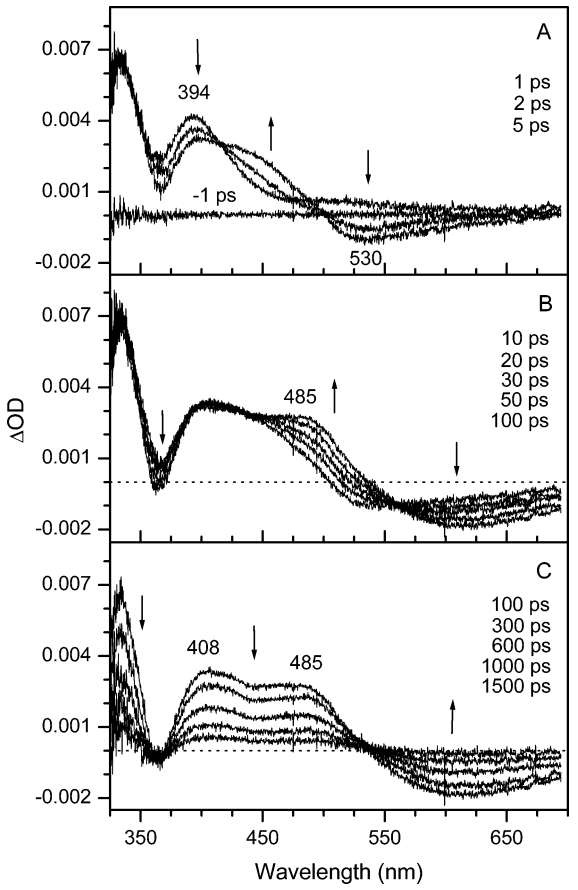
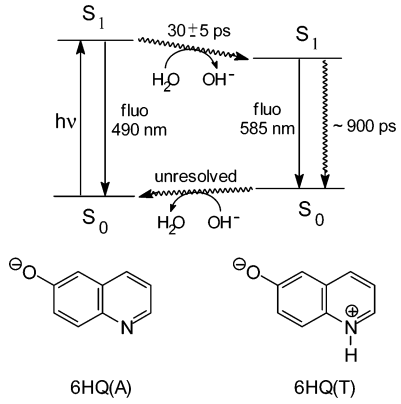


Figure 4. Transient absorption spectra of 6HQ in H_2O + 1 M KOH after excitation at 266 nm: (A) from 1 to 5 ps; (B) from 10 to 100 ps; (C) from 100 to 1500 ps. Vertical arrows indicate the signal evolution. The spectral contribution of the solvated electron produced by two-photon ionization has been subtracted (see the text).

observed for 6MeOQ. For clarity, it is convenient to divide the 0−1500 ps time domain in different parts. Figure 4 shows spectra recorded after excitation of the quinolinate form 6HQ-(A) in a solution of 1 M KOH from 1 to 5 ps (part A), 10 to 100 ps (part B), and 100 to 1500 ps (part C). These spectra have been processed so as to remove the spectral contribution of the solvated electron (broad absorption band starting around 350 nm and peaking at ∼700 nm, with an OD_{max} value of ∼0.002) that is inevitably produced from two-photon excitation of the water solvent at alkaline pH. This treatment was done by subtracting the spectra recorded in a pure KOH/water solution from those obtained in the presence of 6HQ. By repeating the measurements for various pump excitation intensities, which allows varying considerably the yield of water ionization, we checked that the photophysics of 6HQ was independent of the electron concentration and thus not affected by the presence of electrons within the 0−1500 ps time range. The deep and narrow gorge remarked in Figure 4 at all times at about 360 nm corresponds to the position of the lowest energy absorption of the ground state anion 6HQ(A).[1,4] It is thus likely due to a bleaching signal. The 1 ps spectrum (part A) displays a sharp absorption band peaking below 350 nm and a weaker one at 394 nm. This spectrum undergoes a fast evolution until 5 ps, with a broadening of the 394 nm band that shifts to 398 nm and the appearance of a hole at 530 nm (5 ps spectrum). Then, up to 100 ps, a new absorption band grows at 485 nm whereas the 398 nm band shifts to 408 nm. In addition, the negative band at 530 nm is replaced by a new one around 610 nm. An isosbestic point is present at 560 nm. The exponential fit of the

SCHEME 3



decay kinetics at 610 nm and of the rise kinetics at 485 nm leads to the same characteristic time of 30 ± 5 ps. The short-wavelength region is not significantly modified in this 10−100 ps period. Finally, from 100 to 1500 ps, one observes the concomitant disappearance of all signals, i.e., the 350, 408, and 484 nm absorptions and the 610 nm hole, with an approximate decay time of 900 ps. An isosbestic point is again noticed at 535 nm between the negative and positive signals during the decay kinetics. All these observations attest that the 100 ps spectrum in Figure 4 corresponds to a single transient species, the precursor of which is characterized by the 5−10 ps spectrum.

We ascribe the 100 ps spectrum to the excited state tautomer, 6HQ(T*), as the negative band at 610 nm corresponds without ambiguity to the stimulated emission ($S_1 \rightarrow S_0$) of the excited tautomer, the only species emitting in this region. The apparent bathochromic shift of this band relative to the position of the 6HQ(T*) fluorescence ($\lambda_{max} = 580$ nm) can be explained by the superimposition of the positive transient signal due to the tautomer $S_1 \rightarrow S_n$ absorption in the high energy side of the emission band. Accordingly, we ascribe the 5−10 ps spectrum to the precursor excited state 6HQ(A*) produced initially from the excitation of the ground state anion 6HQ(A). This assignment is confirmed by the presence of a negative signal around 530 nm, which is likely due to the stimulated emission of the excited quinolinate 6HQ(A*). Its shift relative to the 6HQ(A*) fluorescence ($\lambda_{max} = 490$ nm) can be attributed, as above, to the fact that the spectra in Figure 4 result from overlapping $S_1 \rightarrow S_n$ absorption and $S_1 \rightarrow S_0$ emission signals in the 400−500 nm region. In this regard, we suggest that the spectral evolution observed in the 0−5 ps time scale is due to some kind of relaxation dynamics of the excited state 6HQ(A*) such as solvation or vibrational/conformational relaxation. The absence of any transient signal after decay of the excited state tautomer 6HQ(T*) indicates that the molecules recover directly the initial ground state anionic form 6HQ(A). We conclude that the electronic relaxation of 6HQ(T*) mainly by radiationless decay is instantaneously followed by the ground state deprotonation of the quinolinium group, 6HQ(T) → 6HQ(A), which is not surprising in highly basic medium. Indeed, from the values of the activity coefficient reported for OH^- (1 M) in water[15] and of its diffusion coefficient,[16] the pseudo-first-order rate for the diffusional recombination ($6HQ(T) + OH^- \rightarrow 6HQ(N) + H_2O$) can be estimated to be 1.4×10^{10} s^{-1}. This is much faster ($\tau =$ 74 ps) than the preceding step of radiationless deactivation of 6HQ(T*) ($\tau = 900$ ps). Scheme 3 provides a summarized description of the reaction process.

It must be noted that, if the excited state back proton transfer was to be observed, the above diffusional rate constant of 1.4×10^{10} s^{-1} would hold and an equilibrated reaction 6HQ(A*) $+ H_2O \rightleftarrows$ 6HQ(T*) $+ OH^-$ should be envisaged in the excited state. In this case, the 30 ps rise time value found for 6HQ(T*) would result from both the forward and backward proton transfer kinetics. However, as will be seen below, a similar rise time value is found in neutral aqueous solution where the diffusional process of back proton transfer cannot occur during the 6HQ(T*) lifetime due to the low concentration in OH^-. Moreover, the 6HQ(T*) decay time in 1 M KOH (∼900 ps) is comparable to the decay time in neutral solutions (∼800 ps). These analogies indicate that the rise and decay kinetics of 6HQ(T*) are not affected by the OH^- concentration; i.e., the reverse proton transfer reaction does not occur, even in 1 M NaOH. The 30 ps characteristic time corresponds thus actually to the excited state imine protonation reaction, 6HQ(A*) → 6HQ(T*). This time is slightly shorter than the 46 ps decay time reported for the 6HQ(A*) fluorescence in alkaline aqueous solution (pH 11).[6] The lack of proton back-recombination even at high OH^- concentration is consistent with the previous assumption[1] that the stable form of the excited tautomer dominantly corresponds to a ketonic configuration (Scheme 2). In fact, this configuration of 6HQ(T*) is characterized by a reduced charge separation and an attenuated quinolinium acidity compared to the zwitterionic form.[1] Interestingly, the excited state imine protonation is much faster in 6HQ(A) (30 ps) than in 6MeOQ (1.9 ns[9]). This large difference confirms the previous statement that the negative charge of the oxy group in 6HQ(A*) enhances considerably the basicity of the nitrogen atom.[1]

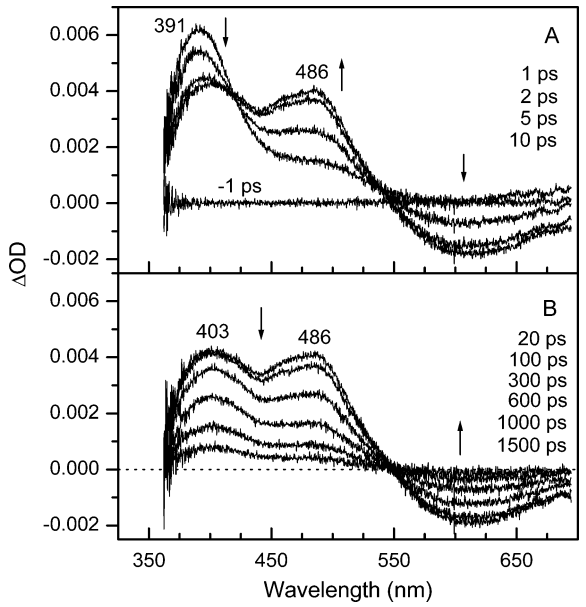
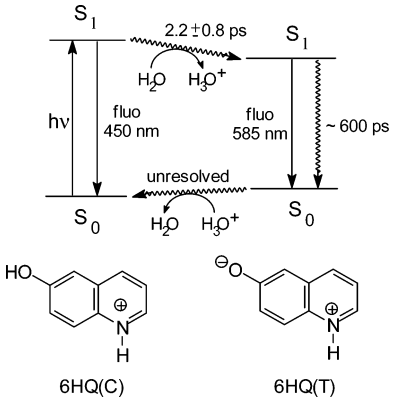


Figure 5. Transient absorption spectra of 6HQ in $H_2O/HClO_4$ at pH 1.5 after excitation at 266 nm: (A) from 1 to 10 ps; (B) from 20 to 1500 ps. Vertical arrows indicate the signal evolution.

Acid Aqueous Solutions. Figure 5 shows the transient spectra obtained after excitation of the quinolinium form 6HQ(C) in an aqueous solution of 3×10^{-2} M $HClO_4$ (pH 1.5) within the 0−10 ps (part A) and 20−1500 ps (part B) time windows. The shortest time spectrum presents a strong absorption band at 391 nm and a shoulder around 500 nm. This spectrum decays within 10 ps and leads to a new spectrum with two absorption maxima at 403 and 486 nm and a negative signal at 610 nm. This evolution is described by two isosbestic points at 420 and 540 nm and a characteristic time of 2.2 ps. Then, all the bands, positive and negative, disappear simultaneously (isosbestic point at 550 nm) with a rate constant of $\sim(600 \text{ ps})^{-1}$. The absence of signal below 360 nm is due to the entire extinction of the probe light by the residual ground state cation 6HQ(C) that absorbs

SCHEME 4



strongly in this region ($\lambda_{max} = 313$ and 344 nm[1,4]). At a $HClO_4$ concentration of 12 M, a single spectrum was observed, nearly constant in shape and intensity from 0 to 1500 ps, and similar to that recorded at 1 ps for the 3×10^{-2} M $HClO_4$ solution. In these conditions, a fluorescence ($\lambda_{max} = 446$ nm) lifetime of 24 ns was measured.

The final transient spectrum observed in Figure 5 (10−1500 ps) presents the same spectral characteristics as that found in alkaline solution (Figure 4, 100−1500 ps). It corresponds thus to the excited state tautomer 6HQ(T*). The precursor spectrum (1 ps spectrum in Figure 5) is logically ascribed to the parent excited state 6HQ(C*) produced initially by direct excitation of the ground state cation 6HQ(C). This assignment is confirmed by the fact that only this parent excited state spectrum is present in an extremely acidic medium (12 M $HClO_4$) where the deprotonation of the hydroxyl group is not expected to occur.[1] The absence of perceptible decay of the 6HQ(C*) absorption spectrum within the 0−1500 ps time range in such an acidic solution is consistent with its long fluorescence lifetime. The high rate of excited state hydroxyl deprotonation measured at pH 1.5 ($\tau = 2.2$ ps) cannot be suspected of being significantly affected by the reprotonation kinetics because the maximum pseudo-first-order rate of back proton transfer, estimated from the proton diffusion coefficient in water,[16] is much slower (1.5×10^9 s^{-1}, $\tau = 670$ ps).

The ultrafast character of the deprotonation process is in agreement with a previous prediction, from the comparison of the photoinduced acid−base properties of the 6- and 7-hydroxyquinolinium ions, that the rate of proton ejection in 6HQ(C*) must be notably higher than the 5.5×10^{10} s^{-1} value ($\tau = 18$ ps) measured for 7HQ(C*) at pH 2.[17] On the other hand, as in alkaline solution, no transient signal is detected after decay of the 6HQ(T*) spectrum. This observation implies that proton capture by the oxy group $-O^-$ of the tautomer to yield back the initial cationic species, 6HQ(T) → 6HQ(C), follows immediately its deactivation to the ground state. A global description of the reaction process is given in Scheme 4.

This reaction scheme is the counterpart of Scheme 3 in acidic media. The excited state tautomer formation in acidic solution is faster than in alkaline solution as the rate of phenol deprotonation in the former case is notably higher than the rate of imine protonation in the latter case. This result is consistent with the observation by Kim et al. that the cationic fluorescence at pH 3 decays faster than the anionic fluorescence at pH 12.[6] However, the 10 ps fluorescence decay time of 6HQ(C*) at pH 3 reported by these authors is much longer than the 2.2 ps time of phenol deprotonation in Scheme 4. A possible explanation for this discrepancy is that the asserted 10 ps value was limited by the instrument temporal resolution, not specified in ref 6.

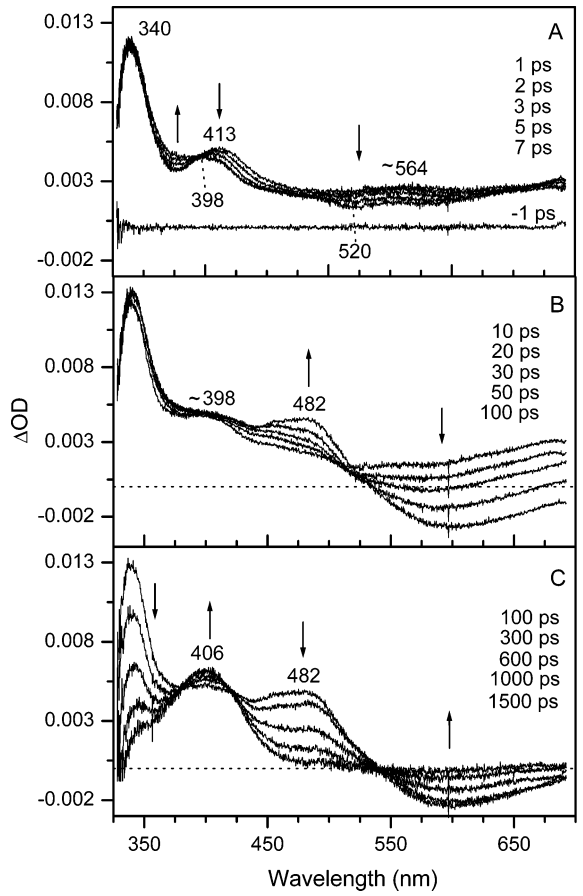


Figure 6. Transient absorption spectra of 6HQ in pH 7 buffer aqueous solution after excitation at 266 nm: (A) from 1 to 7 ps; (B) from 10 to 100 ps; (C) from 100 to 1500 ps. Vertical arrows indicate the signal evolution. The spectral contribution of the solvated electron produced by two-photon ionization has been subtracted.

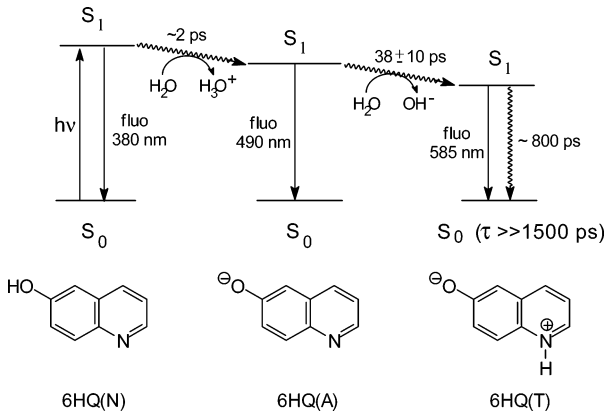
Neutral Aqueous Solution. The transient absorption spectra measured after excitation of the neutral form 6HQ(N) in a buffered aqueous solution at pH 7 are displayed in Figure 6 for the 0−7 ps (part A), 10−100 ps (part B), and 100−1500 ps (part C) time domains. The spectral transformations are less clear than in the alkaline or acidic solutions because a larger number of transient signals contribute to the spectra. They can be roughly divided into four steps. The initial spectrum produced upon excitation (part A, 1 ps spectrum) shows two absorption bands at 340 and 413 nm, and a much weaker one at about 564 nm. This spectrum evolves within 7 ps with a shift of the 413 nm band to 398 nm and the appearance of a depression at 520 nm. An isosbestic point is noticed at 398 nm. Then, from 10 to 100 ps (Figure 6, part B), a new absorption band at 482 nm rises and a broad negative signal at 600 nm deepens (characteristic time 38 ± 10 ps). The 350−420 nm region does not undergo major changes. Finally (Figure 6, part C), the concomitant decay of the 340 and 482 nm absorption and 600 nm negative signals from 100 to 1500 ps is accompanied by the appearance of a new absorption band at 406 nm (approximate characteristic time of 800 ps). Isosbestic points are observed on both sides of the peak maximum, at 381 and 422 nm. Similar spectral evolution and kinetics were observed in pure, deionized water in the absence of buffer.

The 1 ps spectrum corresponds manifestly to that found at short time in acetonitrile (Figure 3, part A) and can thus be ascribed to the excited neutral species 6HQ(N*) produced by direct excitation of the ground state neutral molecule 6HQ(N), the predicted preponderant form at pH 7.[1] In these conditions,

a bleaching signal is expected at 326 nm, that is, outside our spectral window. The hollowed part of the spectrum around 375 nm might result partly from the stimulated emission band of 6HQ(N*) (fluorescence $\lambda_{max} = 380$ nm). The 100 ps spectrum (Figure 6, part B) corresponds unambiguously to the 6HQ(T*) species already characterized in the acidic and alkaline solutions. Its precursor spectrum (part A, 7 ps spectrum) shows some similarities (absorption maxima around 340 and 398 nm, stimulated emission signal at ca. 520 nm) with the precursor spectrum of the excited state tautomer in alkaline solution (10-ps spectrum in Figure 4), that is, the excited state quinolinate 6HQ(A*) spectrum. The difference of band shape in the 300−400 nm region between the neutral and alkaline solutions is well explained by the absence, at pH 7, of the 6HQ(A) bleaching responsible for the strong negative band observed at 360 nm in KOH 1 M. According to this assignment, the 1−7 ps and 10−100 ps spectral changes observed in neutral solution can be correlated to the excited state dynamics of phenol deprotonation, 6HQ(N*) → 6HQ(A*), and subsequent imine protonation, 6HQ(A*) → 6HQ(T*), respectively. Finally, while in acidic and alkaline media, the excited tautomer was observed to decay without giving rise to any perceptible transient species, a strong residual transient absorption at 406 nm appears in the neutral solution upon disappearance of the 6HQ(T*) spectrum. Although this band is nearly located at the position of the $T_1 \rightarrow T_n$ absorption band of 6HQ in organic solvents (1500 ps spectrum in Figure 4), its assignment to the T_1 state seems doubtful for two reasons: intersystem crossing from the tautomer S_1 state should yield the triplet tautomer, which is not expected to absorb at the same energy as the triplet state of the neutral form (the $S_1 \rightarrow S_n$ absorption and $S_1 \rightarrow S_0$ emission undergo significant bathochromic shifts on going from the neutral to the tautomer form). On the other hand, considering the fact that the tautomer S_1 lifetime is comparable at every pH value (750 ± 150 ps), there is no reason for the tautomer intersystem crossing process to be particularly efficient in neutral solution but completely inefficient in acidic or alkaline solutions. We thus prefer to assign the residual 406 nm absorption band to the ground state tautomer, 6HQ(T), presumed to absorb at 408 nm.[4] The much higher stability of this species in neutral water ($\tau \gg 1500$ ps) than in acidic or alkaline solutions is consistent with the low pK_A values (∼7) reported for the two equally probable ground state equilibrated reactions 6HQ(T) + $H_2O \rightleftarrows$ HQ(C) + OH^- and 6HQ(T) + $H_2O \rightleftarrows$ HQ(A) + H_3O^+.[4] For comparison, in the case of pyranine, the ground state back proton transfer reaction from the anion produced by photoinduced pH jump to the initial neutral form (p$K_A = 7.2$) was found to take place in the microsecond time scale.[18] The whole photophysical behavior of 6HQ in water is summarized in Scheme 5.

This reaction scheme implies that the photoinduced acidity of the hydroxyl group is notably higher than the photoinduced basicity of the imine group. This conclusion is consistent with the above observation that, in the excited state, hydroxyl deprotonation in acidic solution is faster than imine protonation in alkaline solution. It also agrees with the conclusions expressed by Kim et al. from time-resolved fluorescence measurements.[6] In fact, these authors already proposed a two-step reaction scheme in neutral aqueous solution, starting with the hydroxyl deprotonation process. However, some kinetic parameters (fluorescence rise times and decay times) reported in this work differ notably from those determined from absorption in the present account (Scheme 5). The fluorescence decay time of 6HQ(A*) (45 ps) and rise time of 6HQ(T*) (46 ps)[6] correspond approximately to the 38 ps value measured here for the 6HQ-

SCHEME 5



(A*) → 6HQ(T*) process. However, the 25 ps decay time claimed for the initial 6HQ(N*) fluorescence seems notably overestimated in regard to the ∼2 ps value found above (see Scheme 5) for the 6HQ(N*) → 6HQ(A*) process. This 25 ps lifetime appears also in manifest contradiction with the observation in the same report[6] that the fluorescence growth of 6HQ(A*) is too fast to be resolved and appears closely superimposed on that, instantaneous and thus limited by the instrumental response, of 6HQ(N*). According to the above two-step reaction mechanism, the 6HQ(N*) decay and 6HQ(A*) appearance should have identical kinetics. This contradiction is still more perceptible if we consider the results obtained in D_2O,[6] where the 6HQ(N*) decay time is reported to be extended to 65 ps and the 6HQ(A*) rise is still closely fitting the instrument-limited rise of the 6HQ(N*) species.

As discussed above, the 38 ± 10 ps characteristic time found for the excited state protonation of the anionic form, 6HQ(A*) → 6HQ(T*), in neutral solution correlates approximately with the 30 ± 5 ps value measured for the same reaction in 1 M KOH alkaline solution (see Scheme 3). More surprisingly, the about 2 ps characteristic time found for the hydroxyl deprotonation in neutral solution (6HQ(N*) → 6HQ(A*) reaction in Scheme 5) corresponds nearly to the 2.2 ps time determined for this process in acidic solution at pH 1.5 (6HQ(C*) → 6HQ(T*) reaction in Scheme 4). This result is unexpected because, whereas an enhancement of the imine basicity was observed on going from 6MeOQ* to 6HQ(A*) due to charge donation by the anionic oxy group, a higher hydroxyl acidity is likely to occur in 6HQ(C*) compared to 6HQ(N*) due to charge withdrawing effect induced by the cationic pyridinium moiety.[1,6] In this respect, the observation of identical and ultrafast deprotonation rates for the excited neutral and cationic forms, 6HQ(N*) and 6HQ(C*), suggests that the determinant parameter governing the proton transfer is not the proton acceptor character of the excited solute but rather the dynamics of solvent reorientation and solvent/solute interaction via H-bonding.

4. Conclusion

The 6MeOQ and 6HQ dynamics in solution following pulse excitation at 266 nm has been investigated by picosecond transient absorption measurements. In organic solvents, both molecules have similar photophysical behaviors essentially characterized by the $S_1 \rightarrow T_1$ intersystem crossing deactivation. In aqueous solutions, the 6HQ molecule shows a specific pH-dependent reactivity of intermolecular proton transfers to and/or from the water solvent that confirms the reaction schemes of photoinduced tautomerization established earlier from steady state emission studies.[1] In alkaline solution (1 M KOH),

protonation of the nitrogen atom in excited 6-oxyquinoline anion 6HQ(A*) leads to the excited tautomer, 6HQ(T*), with a characteristic time of 30 ± 5 ps. The lack of excited state back-reaction confirms the ketonic structure of 6HQ(T*). In acidic solution (pH 1.5), deprotonation of the hydroxyl group in excited 6-hydroxyquinolinium cation 6HQ(C*) to yield the 6HQ(T*) excited tautomer takes place within 2.2 ± 0.8 ps. Finally, in neutral aqueous solution (pH 7), our results suggest that two consecutive proton transfers occur: a preliminary step of fast hydroxyl deprotonation in excited 6-hydroxyquinoline 6-HQ-(N*) producing the 6HQ(A*) species ($\tau \cong 2$ ps) is followed by imine protonation to generate the 6HQ(T*) excited tautomer ($\tau = 38 \pm 5$ ps).

In all cases, the tautomer deactivation occurs in about 1 ns. In alkaline and acidic media, it is immediately followed by the ground state reaction of reverse proton transfer yielding the starting ions, 6HQ(A) and 6HQ(C), respectively. The lifetime of the 6HQ(T) tautomer (∼0.5−1.0 ns) is shorter than the lifetime (a few tens nanoseconds) of the 6HQ(C) cation in extremely acid solution ([$HClO_4$] > 11 M) and 6HQ(A) anion in extremely basic solution ([NaOH] > 10 M[1]) or than the lifetime of 6-HQ(N) in organic solvent (1.5−3 ns). However, the difference cannot account for the drastic decrease in fluorescence intensity observed[1] on going from the cationic, anionic, or neutral form to the tautomeric form. The low fluorescence yield of the tautomer is thus attributable to a very slow radiative deactivation process, which suggests small oscillator strength for the electronic transition between the ground state (zwitterionic form) and excited state (ketonic form) of the tautomer.

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