Catalytic Roles of Water Protropic Species in the Tautomerization of Excited 6-Hydroxyquinoline: Migration of Hydrated Proton Clusters

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Fluorescence kinetic constants are measured as functions of wavelength, pH, hydrogen isotope, and temperature to understand proton transfers involved in the excited-state tautomerization of aqueous 6-hydroxyquinoline. Not only the detailed mechanism but also the individual catalytic roles of H_2O, H_3O^+, and OH^- in the tautomerization reaction have been determined. The variation of the relative contribution with pH is determined for each reaction pathway as well. Solvent structural dynamics is found to be important in the deprotonation of the enol group and in the migration of a hydrated proton cluster.

Introduction

Proton-transfer processes are elementary reactions of fundamental importance in chemistry and biology. Recent interests are on the dissociation dynamics of a proton from an acid[1−7] and on the dispersion dynamics of hydrated proton clusters in the bulk solvent.[8−10] Proton-transfer dynamics is determined by the size, structure, and motion of a solvent cluster as well as by the nature of a protropic group[1,11,12] while proton migration is controlled by solvent structural dynamics.[8,9,13]

The dynamics and mechanism of excited-state proton transfer to water have been often investigated with photoacids. 6-Hydroxyquinoline (6HQN) has extremely highly photoacidic and photobasic groups in acidic, basic, and neutral aqueous solutions.[14] 7-Hydroxyquinoline is known to form an intramolecular hydrogen-bonding chain, through which proton relay can take place during excited-state protropic tautomerization.[15,16] However, 6HQN cannot form an intramolecular hydrogen bond, owing to its geometry. Therefore, the proton transfers of 6HQN in aqueous solutions are controlled mainly by proton donation to solvent molecules and proton acceptance from solvent molecules. The mechanism of proton transfer to water is an enormously complicated problem. The most important feature controlling the extremely fast excited-state proton transfer into an aqueous medium is the formation of a specifically structured water cluster. Clusters of 4 ± 1 water molecules have been suggested as the proton acceptors of excited photoacids.[3] The proton-transfer results of various 1-naphthol and 2-naphthol derivatives have indicated that the apparent size of the water cluster also depends on the acidity of the proton donor.[1] Our investigation on the excited-state proton transfer of 6HQN can provide an important information about the proton-transfer mechanism in aqueous solution.

Hydroxyquinolines and their derivatives are extensively studied with both fundamental and practical interests.[14−20] As one hydroxyquinoline molecule has two protropic functional groups, four protropic species of a normal molecule (HQN), an enol-deprotonated anion ($^-$QN), an imine-protonated cation ($HQNH^+$), and an enol-deprotonated imine-protonated zwitterion ($^-QNH^+$) are equilibrated in aqueous hydroxyquinoline solution (Scheme 1). As the enol and imine groups of 6HQN and 7-hydroxyquinoline become more acidic and basic, respectively, in S_1 than in S_0,[14−19] photoexcitation drives excited-state tautomerization via enol deprotonation and imine protonation (Scheme 1). followed by ground-state reverse tautomerization.[17] Furthermore, the $^-QNH^+$ form of 6HQN at S_1 rapidly undergoes an intramolecular electron transfer from the deprotonated oxygen atom to the iminium ring to produce the quinoid form (QNH) (Scheme 1).[14]

Fluorescence kinetic profiles of 6HQN protropic species have been measured with the variations of wavelength, pH, hydrogen isotope, and temperature to understand the tautomerization mechanism of 6HQN at S_1. In this paper, we report the dynamics and roles of individual participations of H_3O^+, OH^-, and H_2O with pH variation for the first time to our knowledge.

Experimental Section

6HQN (98%) purchased from the Sigma was further purified via vacuum sublimation and column chromatography. 6^1HQN and 6^2HQN aqueous solutions were prepared by dissolving 6HQN in distilled water and in 99.9% ^2H_2O purchased from the Sigma, respectively. The p^1H and p^2H of 6HQN aqueous solutions were adjusted by adding ^{1}HCl or NaO^1H solution and ^{2}HCl or NaO^2H solution, respectively. The p^2H was corrected from the pH meter reading.[21] The concentration of 6HQN was 0.2 mM throughout the experiment. Sample temperature was controlled using a refrigerated bath circulator (Jeio Tech, RC-10V).

Absorption spectra were obtained using a UV−vis spectrophotometer (Sinco, S-2040). Fluorescence spectra were obtained using a home-built fluorometer, which consisted of a 75-W Xe lamp (Acton Research, XS 432), 0.15-m and 0.30-m monochromators (Acton Research, Spectropro 150 and 300), and a photomultiplier tube (Acton Research, PD 438). Static fluorescence spectra were not corrected for the wavelength-dependent variation of detector sensitivity.

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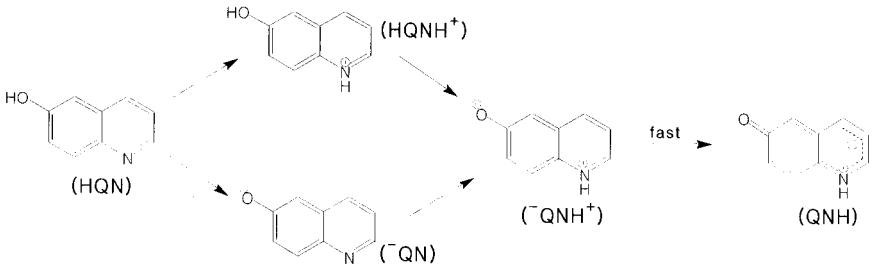
SCHEME 1: Excited-State Tautomerization of Aqueous 6HQN



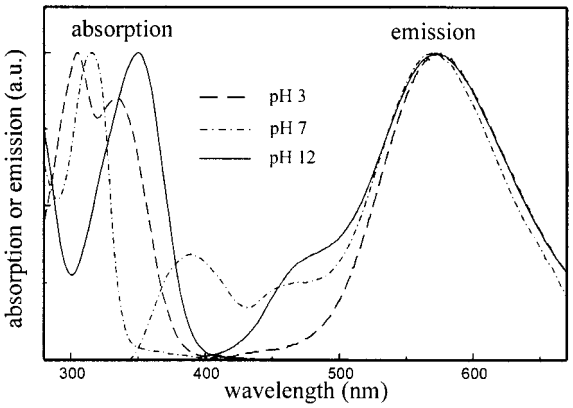


Figure 1. Absorption and emission spectra at 22 °C of 6HQN aqueous solutions at designated pHs.

An actively/passively mode-locked Nd:YAG laser (Quantel, YG 701) with the pulse duration of 25 ps was employed for picosecond fluorescence kinetic measurements. Samples were excited by 320-nm pulses generated from a Raman shifter, which was filled with 20-atm methane gas and pumped by 266-nm laser pulses. Fluorescence was collected from the front surface of the sample excitation for all static and time-resolved fluorescence measurements. Fluorescence kinetic profiles were obtained using a 10-ps streak camera (Hamamatsu, C2830) attached with a CCD (Princeton Instruments, RTE−128-H). Fluorescence kinetic constants were extracted by fitting measured kinetic profiles to computer-simulated kinetic curves convoluted with the instrument temporal response functions.

Results and Discussion

Aqueous 6HQN solutions at pH 7 show multiple emission bands originating from its various protropic species (Figure 1). The emission at 380 nm is normal fluorescence, and it is emitted from HQN. The emission at 450 nm is from $^{-}$QN and HQNH^{+}, and it will be called intermediate fluorescence. Last, the emission at 580 nm originating from QNH is quinoid fluorescence. The intermediate fluorescence at pH 3 originates entirely from HQNH^{+}, while that at pH 12 results from $^{-}$QN. Figure 1 shows that the intermediate emission is much smaller at pH 3 than at pH 12. This is due to the fact that the cationic fluorescence decays much faster than the anionic fluorescence (vide infra).

Figure 2 shows that both the formation and decay times of aqueous 6HQN at 22 °C and pH 7 increase as monitored fluorescence wavelength increases or as hydrogen isotope mass increases. These indicate that proton-transfer kinetics involved in the excited-state tautomerization of aqueous 6HQN can be monitored by measuring fluorescence kinetics with our temporal resolution. Table 1 shows the kinetic time constants of the normal, intermediate, and quinoid fluorescence at various pHs and isotopes. It is noteworthy that the ^{1}H/^{2}H kinetic isotope effect (KIE) of the fluorescence kinetics varies very significantly with sample pH and emission wavelength.

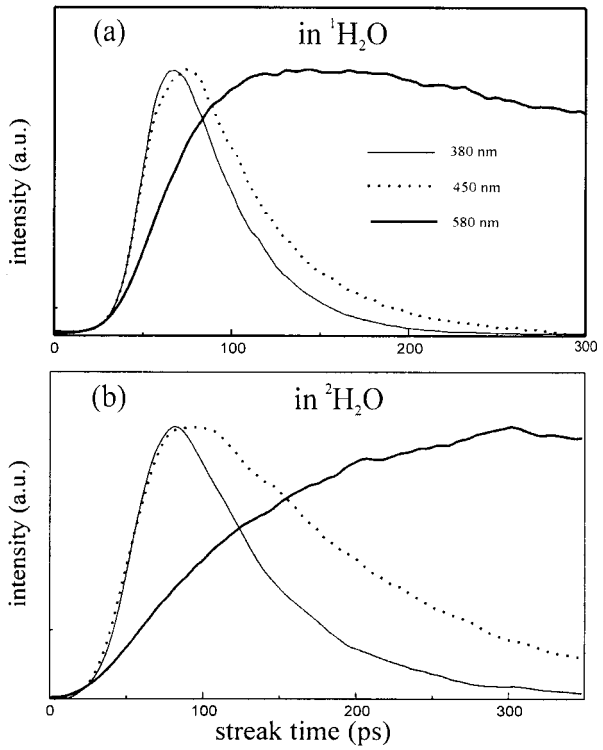


Figure 2. Typical fluorescence kinetic profiles at indicated wavelengths of 6HQN at pH 7 in $^{1}H_2O$ (a) and $^{2}H_2O$ (b) at 22 °C.

TABLE 1: Fluorescence Time Constants at 22 °C and Kinetic Isotope Effect[a]

monitored wavelength (nm)	solvent	pH	rise time(ps)	decay time(ps)	kinetic isotope effect[a]
380	$^{1}H_2O$	7	*b*	25	2.5
	$^{2}H_2O$		*b*	65	
450	$^{1}H_2O$	7	*c*	45	3.0
	$^{2}H_2O$		*c*	145	
450	$^{1}H_2O$	11	*b*	46	2.8
	$^{2}H_2O$		*b*	150	
450	$^{1}H_2O$	3	*b*	10	1.0
	$^{2}H_2O$		*b*	10	
580	$^{1}H_2O$	7	46	2300	3.0
	$^{2}H_2O$		150	4000	

[a] Average values obtained from the data in Figure 3. [b] Instant. [c] Not instant but still too fast to be resolved.

We have measured the temperature dependence of 6HQN fluorescence kinetics at various emission wavelengths, pHs, and hydrogen isotopes in order to understand the complicated processes involved in the excited-state tautomerization of aqueous 6HQN better (Figure 3). The intermediate emission decay time is 10 ps at pH 3 and does not change with

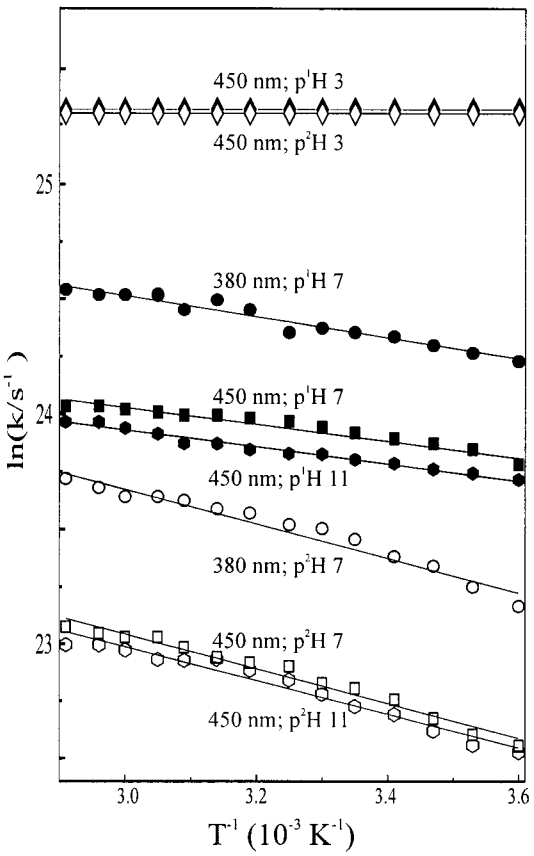


Figure 3. Arrhenius plots for the fluorescence decay rates of 6HQN aqueous solutions at indicated wavelengths and pHs. The p^1Hs and p^2Hs were measured in ^1H_2O and ^2H_2O, respectively, at 22 °C. The lower three plots of ^2H_2O solutions are not quite linear, becoming steeper at lower temperature. Although this may suggest that tunneling becomes more significant at lower temperature, we have ignored the nonlinearity because of our poor signal-to-noise ratios.

TABLE 2: Activation Energies and Preexponential Factors Obtained from Figure 3

monitored wavelength (nm)	solvent	pH	activation energy (kJ mol^{-1})	preexponential factor (s^{-1})
380	^1H_2O	7	3.9	2.0×10^{11}
	^2H_2O		6.2	2.0×10^{11}
450	^1H_2O	7	3.1	8.0×10^{10}
	^2H_2O		6.3	1.0×10^{11}
450	^1H_2O	11	3.1	8.0×10^{10}
	^2H_2O		6.1	9.0×10^{10}
450	^1H_2O	3	0.0	1.0×10^{11}
	^2H_2O		0.0	1.0×10^{11}

temperature. (Furthermore, the observed amplitude at zero delay time did not change with temperature. This indicates that the observation of the temperature independence is not due to the limit of our temporal resolution.) Moreover, the KIE of the deprotonation from the hydroxyl group of $HQNH^+$ is unity (Table 1). All these suggest that the deprotonation takes place rapidly with negligible activation energy and that the solvent motion controls the deprotonation process of $HQNH^+$ at S_1. The imine protonation (46 ps at 22 °C) of $^-$QN, monitored at 450 nm at pH 11, is slower than the enol deprotonation of $HQNH^+$ and shows a measurable activation energy of 3.1 kJ mol^{-1}. The rate and temperature dependence of intermediate emission decay at pH 7 are very similar to those at pH 11, indicating that the intermediate emission at neutral pH originates dominantly from $^-$QN. However, a slightly faster rate, compared

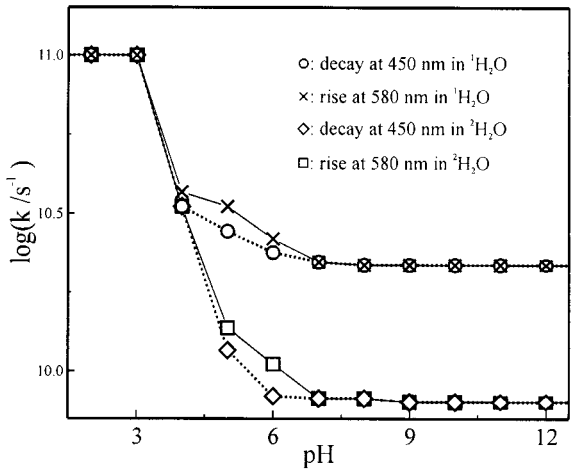


Figure 4. pH-dependent logarithmic fluorescence rate constants of 6HQN aqueous solutions at 22 °C. The observed rises of the 580-nm quinoid fluorescence are faster than the observed decays of the 450-nm intermediate fluorescence at weakly acidic conditions in particular.

with that at pH 11, suggests that emission from $HQNH^+$ may also contribute to the intermediate emission at pH 7 slightly. The deprotonation of HQN hydroxyl group, monitored at 380 nm, takes 25 ps at 22 °C, and its activation energy is as large as 3.9 kJ mol^{-1}.

It is noteworthy that the deprotonation from the hydroxyl group of $HQNH^+$ is faster with an activation energy much smaller than that of HQN. The additional positive charge in $HQNH^+$ obviously enhances the acidity of the hydroxyl group significantly and makes it easier to form a water cluster, which is essential for deprotonation.[22−27] Since the intermediate emission decay time is 10 ps at pH 3 and this deprotonation process is controlled entirely by the solvent motion, the formation of a water cluster appropriate for the deprotonation would take place about 10 ps. Water clusters are reported[5−7,11,12] to be necessary for proton transfers to/from H_2O. The KIE of the enol deprotonation for HQN is 2.5, while that of the imine protonation for $^-$QN is 2.8. These values are larger than the KIE of proton mobility (1.4) originating from the hydrogen bond cleavage of water.[10] The enol deprotonation of HQN and the imine protonation of $^-$QN are slower than the formation of the water cluster, and their KIEs are larger than 1.4. These suggest that these two processes are activation-controlled and that tunneling might be important. The protonation to the imine group of HQN from H_2O never occurs, probably due to the highest activation energy among the possible proton transfers of the excited-state tautomerization. This suggests that at S_1 the acidity of the hydroxyl group is much larger than the basicity of the pyridinyl moiety.

The observed formation of quinoid emission is faster in both ^1H_2O and ^2H_2O than the observed decay of intermediate emission in weakly acidic solutions in particular (Figure 4). Since the quinoid species does not exist at all in S_0 at the moment of excitation, its fluorescence cannot rise faster than the intermediate decay unless there is another faster channel. Considering Figures 3 and 4, we propose that the excited-state tautomerization at 22 °C consists of several pathways, as shown in eqs 1−4 and that the relative contributions of the individual pathways are dependent on pH.

$$\mathrm{HQN} \xrightarrow[25\ \mathrm{ps}]{H_2O\ H_3O^+} {}^-\mathrm{QN} \xrightarrow[\mathrm{fast}]{H_3O^+\ H_2O} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (1)$$

$$\mathrm{HQN} \xrightarrow[25\ \mathrm{ps}]{H_2O\ H_3O^+} {}^-\mathrm{QN} \xrightarrow[46\ \mathrm{ps}]{H_2O\ OH^-} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (2)$$

$$\mathrm{HQNH}^+ \xrightarrow[10\ \mathrm{ps}]{H_2O\ H_3O^+} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (3a)$$

$$\mathrm{HQN} \xrightarrow[\mathrm{Fast}]{H_3O^+\ H_2O} \mathrm{HQNH}^+ \xrightarrow[10\ \mathrm{ps}]{H_2O\ H_3O^+} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (3b)$$

$${}^-\mathrm{QN} \xrightarrow[46\ \mathrm{ps}]{H_2O\ OH^-} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (4a)$$

$$\mathrm{HQN} \xrightarrow[\mathrm{Fast}]{OH^-\ H_2O} {}^-\mathrm{QN} \xrightarrow[46\ \mathrm{ps}]{H_2O\ OH^-} {}^-\mathrm{QNH}^+ \left(\xrightarrow[\mathrm{fast}]{} \mathrm{QNH}\right) \quad (4b)$$

Since all the rate constants must be the same regardless of apparent kinetic variation with pH, we can calculate the individual fractional contributions of f_{Nf}, f_{Ns}, f_C, and f_A for eqs 1−4, respectively, assuming the following relations at every measured pH:

$$1 = f_{Nf} + f_{Ns} + f_C + f_A \quad (5)$$

$$\tau_I/\mathrm{ps} = (46f_{Ns} + 10f_C + 46f_A)\,(f_{Ns} + f_C + f_A)^{-1} \quad (6)$$

While eq 5 is trivial, eqs 6 and 7 show that observed

$$\tau_Q/\mathrm{ps} = (25f_{Nf} + 46f_{Ns} + 10f_C + 46f_A) \quad (7)$$

$$\frac{\tau_N}{\tau_I} \times \frac{A_N}{A_I} = \frac{25f_{Nf} + 25f_{Ns}}{46f_{Ns} + 10f_C + 46f_A} \times \frac{(\nu_{380})^3}{(\nu_{450})^3} \times \frac{S_{380}}{S_{450}} \quad (8)$$

intermediate decay time (τ_I) and quinoid rise time (τ_Q) are the weighted averages of respectively involved times. The left and right parts of eq 8 indicate the observed and calculated ratios, respectively, of normal emission intensity to intermediate emission intensity. τ and A are the observed emission lifetime and initial intensity, respectively, of each shown species, while ν and S are the frequency and the experimental sensitivity factor, respectively, at each shown wavelength. It is assumed in eq 8 that the Einstein coefficients of spontaneous normal and intermediate emission are the same except the cubic dependence to emission frequency because the fluorescence is emitted from the same aromatic ring chromophore for all the protropic species involved. Each fraction should of course be no smaller than 0 and no bigger than 1.

For the first time to our knowledge, we are presenting the detailed individual catalytic roles of H_2O, H_3O^+, and OH^- as functions of pH for the excited tautomerization reaction of 6HQN in water (Figure 5). If the normal species is excited more efficiently at 320 nm than the other protropic species, the tautomerization will be catalyzed dominantly by H_2O following the pathways of eqs 1 and 2 in the broad pH region of 3.7−9.9. Since 6HQN exists mostly as $HQNH^+$ below pH 3.7 and $^-$QN above pH 9.9 at the moment of excitation, the tautomerization occurs following eqs 3 and 4 outside the pH region of 3.7−9.9. It is notable that the tautomerization is catalyzed faster by H_2O (eq 1) than by OH^- (eq 4b). In the pathway of eq 1, the release of a proton from the enol group initiates the formation

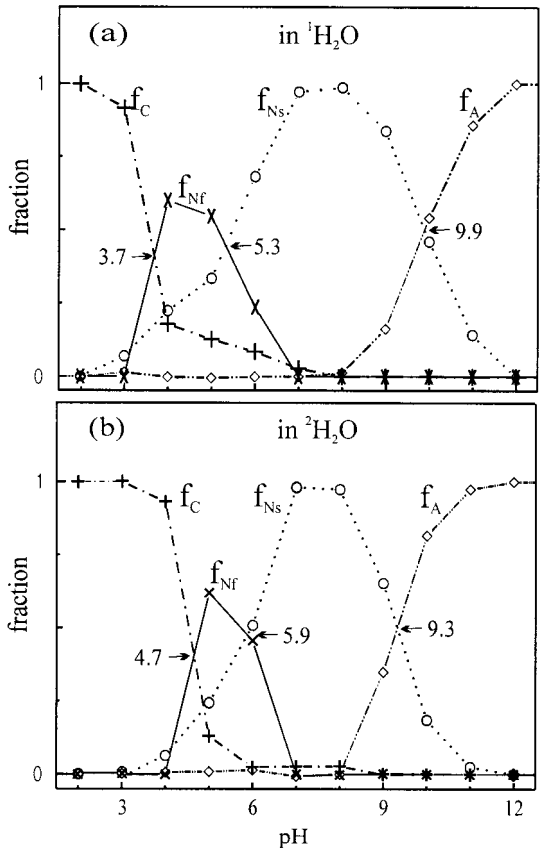


Figure 5. pH-dependent fractional pathway contributions at 22 °C of 6HQN excited-state tautomerization in ^1H_2O (a) and ^2H_2O (b).

of a hydrated proton cluster, which, via migration, participates directly in the protonation of pyridinyl moiety over a long distance within a very short period of time. This can be explained by the fact that $^{-}$QN formed in eq 1 does not have a hydrated proton cluster from the bulk solvent within the reactive cross section of the pyridinyl moiety. If there are such protons near the nitrogen atom of the imine group, the pathways of eq 3 will dominate the process of eq 1. The pH regions following both the processes of eqs 1 and 2 become narrower with the heavier hydrogen isotope. This also supports the fact that the intermediate formation steps of eqs 3 and 4 are diffusion-controlled.

Simulation studies have shown that proton diffusion does not occur via hydrodynamic Stokes diffusion of a rigid complex but via migration of a structural defect due to continual interconversion between covalent and hydrogen bonds.[9] A proton migrates as $H_9O_4^+$ converts to $H_5O_2^+$ by a structural defect displaced over a distance of $\sim$5 Å. The proton in the $H_9O_4^+$ or $H_5O_2^+$ complex is reported[8,9] to be strongly hydrogen-bonded and delocalized. Solution fluctuation modulates the proton transfer barrier and determines the migration path to occur. The proton in the initially generated water cluster migrates within a few picoseconds to another cluster near the nitrogen atom of the imine group via a few structural defects. This explains the reason why the observed quinoid emission formation is faster than the observed intermediate emission decay in the pH range of 4−6, as seen in Figure 4.

We have also found that the 10% (in v) water-mixed methanol solution of 6HQN shows normal and quinoid emission bands with a slight intermediate fluorescence band. However, the 10% (in v) water-mixed acetonitrile solution of 6HQN shows normal and intermediate fluorescence bands with a negligibly small quinoid emission band. (Neither intermediate nor quinoid emission is observable from water-free methanol and acetonitrile solutions of 6HQN.) These observations indicate that a water cluster is necessary for the enol deprotonation to form a hydrated proton cluster ($H_{2n+1}O_n^+$) and $^{-}$QN species and that a hydrogen-bond network is also necessary for the dissociated proton to hop from a water molecule to another and finally to the nitrogen atom of the imine.[28,29] Although a further study is urgent to understand the details, these observations support qualitatively the reaction pathway of eq 1. The observation of f_{Nf} with pH variation provides experimental evidences on the roles of water clusters and proton hopping for an exited state proton-transfer reaction in water.

Conclusions

The dynamics and relative importance of the individual catalytic processes of water protropic species in the excited-state tautomerization of aqueous 6HQN have been measured as functions of pH, temperature, fluorescence wavelength, and hydrogen isotope. One of the processes is attributed to the formation of a hydrated proton cluster[1−7] from the enol deprotonation and the subsequent relay of the proton to the immine group through a few structural defects. Our results provide experimental evidences on the recent idea that the extremely fast proton transfer in water occurs by the continuous formations and breakages of hydrogen bonds involved in water clusters.[8−10]

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