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Reinvestigation of solvent catalyzed ground-state reverse proton transfer in 7-hydroxyquinoline

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Abstract

The dynamics of the ground-state reverse proton transfer of 7-hydroxyquinoline have been reinvestigated in various alcohol solvents by pulse pump–cw probe transient absorption in combination with two-step laser-induced fluorescence measurements. The results show a nearly temperature-independent kinetic isotope effect for the reverse proton transfer in the ground state, consistent with the previous study. The overall proton transfer dynamics can be rationalized based on a kinetic derivation incorporating solvent reorganization forming a specific cyclic solvent/solute complex, and then the dissociation and actual proton transfer of this hydrogen bonded complex.

1. Introduction

Adiabatic excited-state proton transfer (ESPT) has been observed in a large number of organic molecules containing both acidic and basic functional groups [1–4]. The ESPT process usually involves transfer of a hydroxyl (or amino) proton to an acceptor such as a carbonyl oxygen or a nitrogen atom in the excited state, resulting in a large Stokes shifted proton-transfer (PT) tautomer emission. The rate of ESPT (k_{pt}^{*}) in an exergonic, unsymmetrical double potential well is usually on a fast time scale ($> 10^{9}$ s^{-1}), which may be dominated by a tunneling mechanism. The dynamics of the ground-state reverse proton transfer (GSRPT) have also received considerable attention. In certain ESPT molecules the rate of GSRPT is also ultrafast, and no metastable ground-state intermediate (i.e. the tautomer species) can be observed [5,6]. On the other hand, many molecules exhibiting ultrafast ESPT undergo slow GSRPT dynamics ($\ll 10^{9}$ s^{-1}) [7–9]. These ESPT molecules, in general, have no intramolecular hydrogen bond between acidic and basic functional groups. The excited-state proton transfer, therefore, takes place through the catalysis of solvent molecules. One prototype examined in this study is 7-hydroxyquinoline (7HQ). 7HQ exhibits a unique normal Stokes shifted emission ($\lambda_{max} \approx 375$ nm) in nonpolar as well as in polar, aprotic solvents at room temperature. In contrast, dual emission was observed in monohydroxyl alcohol solvents. In methanol the maxima of the normal species (enol form, see Fig. 1) and PT tautomer (keto form) emissions are at 375 and 520 nm, respectively. By a fluorescence titration study it has been concluded that the increase of the PT tautomer emission is indicative of the formation of a 2:1 alcohol/7HQ complex, and the rate of ESPT for the 2:1 alcohol/7HQ complex was calculated to be ≈ 5.0

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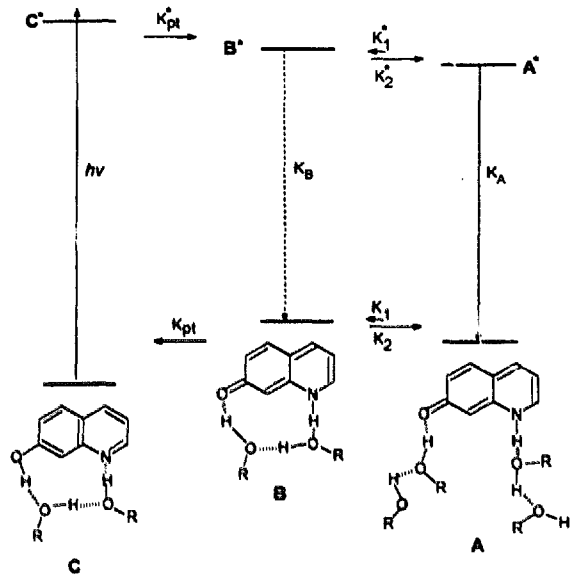

Fig. 1. The proposed proton transfer cycle of 7HQ in alcohol solvents, where **A** only represents one of the randomly solvated 7HQ. It is noted that Fig. 1 only depicts the complex **C** of the normal tautomer. Other types of alcohol/normal tautomer complexes in which the ESPT is prohibited during the lifetime of the excited state are not shown.

$\times 10^9$ s^{-1} with a barrier height of 0.54 kcal/mol in the methanol solution [7]. Other nonspecifically solvated 7HQ does not undergo proton transfer within the life span of the excited state, resulting in normal emission. The rate of reverse proton transfer in 7HQ was first reported to be 2.8×10^5 s^{-1} with a significantly large energy barrier of 4.2 kcal/mol in neat methanol at room temperature [7]. The dynamics of GSRPT for 7HQ, in comparison to that of ESPT, are slower by more than four orders of the magnitude. Subsequently, the existence of the long-lived ground-state tautomer species was further confirmed by Terazima and Azumi by a thermal lensing experiment, and the relative energy of each state was calculated [10]. Based on a significant deuterium isotope effect on the rate of the GSRPT and the fact that the activation energy does not vary, Varma and co-workers [9] concluded that the slow dynamics of the GSRPT were due to the thermally activated solvent reorganization forming a solute–alcohol complex in a suitable configuration for the proton transfer. Recently, various ratios of (*n*)alcohol/(*m*)7HQ tautomer complexes in the ground state have been trapped and studied by their luminescence properties in inert gas matrix isolated conditions [11,12].

The slow recovery process during a proton transfer cycle has been one focus in our studies [13–16] based on the prospect of developing efficient photon storage systems. In this Letter, the mechanism of the GSRPT for 7HQ has been carefully reinvestigated by an ultra sensitive pulse-probe/cw-pump differential transient absorption system in combination with an intensified diode array coupled two-step laser-induced fluorescence (TSLIF) measurement. Our results lead to a GSRPT mechanism incorporating formation, dissociation and actual proton transfer of a specific 2 : 1 solvent–solute complex. This mechanism is fundamentally in agreement with the proton-transfer picture proposed by Varma and co-workers [9] but with a clearer rephrase based on a rational kinetic derivation.

2. Experimental

2.1. Material

7HQ (Eastman Kodak) was recrystallized three times from ethanol. The purity was checked by the fluorescence excitation spectrum. 7-hydroxy(*d*)-quinoline (7DQ) was prepared by dissolving 7HQ in methanol-*d* solvent. Methanol-*d* was then vaporized under reduced pressure (< 10 mm Hg). The alcohols and their deuterium (O–D) isotopes (Aldrich) were of spectrograde quality and were used without further purification.

2.2. Measurements

For the pulse-pump/cw-probe transient absorption measurement a pulse laser (Nd : YAG 266 nm, 8 ns) and a cw Ar^+ laser (454.5 nm) are used as the pump and probe excitation sources, respectively. The probe laser beam was divided into collimated sample and reference beams. The intensity of each beam was monitored by a separate silicon photodiode of < 1.0 ns response time (EG & G model SGD-444). Prior to photolysis both reference and sample Ar^+ beams were adjusted by the thin film polarizer so that the dc voltages of the two diodes are balanced (i.e.

dc = 0). The time-dependent transient absorbance $A(t)$ can be expressed as $A(t) = \log\{I_0/[I_0 - I(t)]\}$ where I_0 is the probe laser intensity when no pump pulse is applied to the sample and is a constant value throughout the time-resolved measurement. $I(t)$ is the difference signal between sample and reference beams, and is obtained directly from the output of the differential diodes when the sample is excited by the pump laser. By applying a dichroic mirror, the pump and probe pulses are coaxially passed through the sample cuvette. With an average of 200 shots an absorbance of 1.0×10^{-4} can be detected. Details of the pulse-pump/pulse-probe transient absorption and two-step laser-induced fluorescence (TSLIF) have been elaborately described elsewhere [17]. With a combination of filters and dichroic mirrors (Fig. 2) the decay of the transient absorption and TSLIF can be measured under an identical configuration. For obtaining the temperature-dependent dynamics of the transient absorption and TSLIF, the sample was placed in a home-made quartz dewar through which cold N_2 gas flowed. By careful adjustment of the N_2

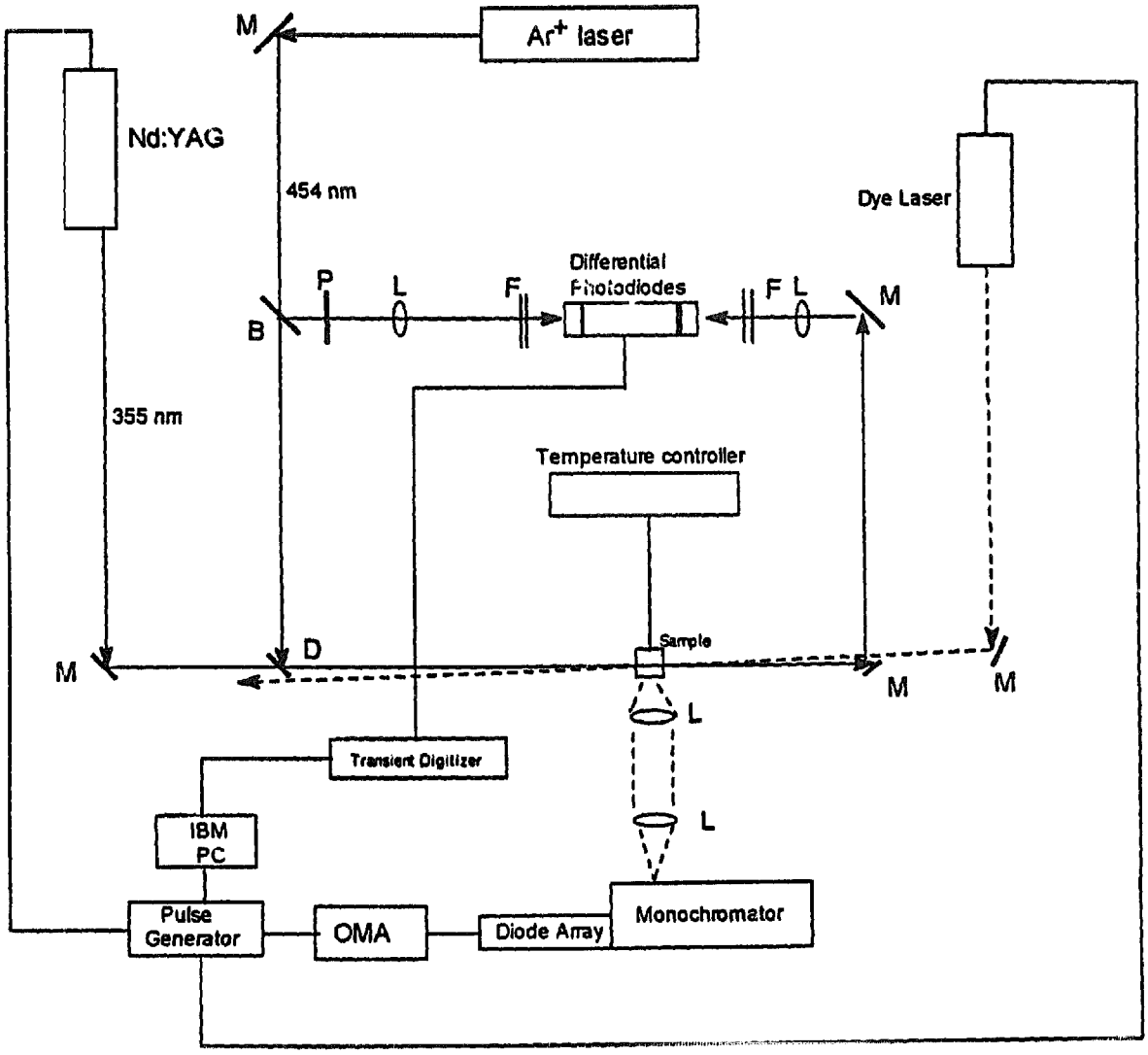

Fig. 2. The experimental setup for the measurements of pulse pump–cw probe transient absorption and pulse pump–pulse probe TSLIF. M: mirror, F: filter, D: dichroic mirror, L: lens, B: beam splitter, P: polarizer, OMA: optical multichannel analyzer.

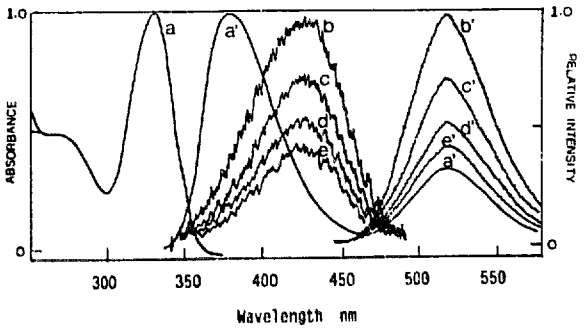

Fig. 3. UV absorption (a) and emission spectra (a') of 7HQ in methanol. Transient absorption ((b)–(e)) and TSLIF ((b')–(e')) of 7HQ in methanol at various delay times between pump (266 nm) and probe pulses (white light pulse for transient absorption, 440 nm dye laser for TSLIF). (b (b')) 200 ns; (c (c')) 1.5 μs; (d (d')) 2.5 μs; (e (e')) 3.0 μs.

gas flow rate, a constant temperature with ±0.2°C/min fluctuation could be maintained during the measurement.

3. Results

Figs. 3b–3e show the 266 nm laser-induced transient absorption spectrum of 7HQ in methanol. The maximum of the transient absorption at 430 nm is ≈ 3200 cm^{-1} red-shifted (peak-to-peak) with respect to the normal $S_0 \rightarrow S_1$ transition (330 nm, Fig. 3a). The spectral features and transient absorption maximum did not vary with respect to the delay time, indicating that only one transient species exists. Since its decay is not affected by the presence of molecular oxygen, the contribution of a triplet state species can be ruled out. When probed by a second pulse laser in the transient absorption region a laser-induced tautomer fluorescence maximum at 520 nm was observed (Fig. 3b'–3e'). The excitation spectrum of the TSLIF (tuned from 410 to 460 nm) with a maximum intensity at 430 nm is identical with the transient absorption spectrum. Therefore, the assignment of the 430 nm transient absorption to the $S_0 \rightarrow S_1$ transition of the PT tautomer [7,9] is indisputable. The dynamics of the decay measured by TSLIF are similar to those of the transient absorption. For example, the lifetime of the transient species in methanol is measured to be 3.9 ± 0.4 μs by TSLIF. This value, within experimental error, is consistent with that measured by the transient absorption (4.21 ± 0.06 μs). However, due to the fluctuation (e.g. homogeneity and intensity) of the pulse lasers, curve fitting of the dynamics of the decay will be performed mainly based on the results of the transient absorption using the pulse-pump (266 nm)/cw (Ar^+, 454 nm)-probe technique. In methanol-*d* solvent the decay of the PT tautomer is significantly slower than that in methanol. At 298 K, the ratio of the rate of the decay between methanol and methanol-*d*, K^{H}_{obs}/K^{D}_{obs} was calculated to be 5.7 ± 0.3. A large kinetic isotope effect was also observed in ethanol. For comparison, dynamics of the GSRPT for various alcohols obtained in this work and previous literature are listed in Table 1.

As reported by Itoh et al. [7] and Varma and co-workers [9], we also observed significant temperature-dependent decay dynamics for the ground-state PT tautomer from 298 to 230 K [1]. The straight line obtained by plotting k_{obs} versus $1/T$ in various

[1] Since the polyhydrated 7HQ, in which the ESPT is prohibited is thermally more stable than the 2:1 alcohol/7HQ complex, the transient absorbance of the PT tautomer is very weak at temperatures < 220 K.

Table 1
The activation energy and frequency factor of GSRPT of 7HQ in methanol and ethanol and their O–D isotopes

Solvent	τ (μs, 298 K)		E_{obs} (kcal/mol)		A_{obs} (298 K) × 10^{-8} s^{-1}	
	this work	literature	this work	literature [a]	this work	literature
methanol	4.21 ± 0.06	3.5 [b], 4.1 [c], 3.7 [d]	5.1 ± 0.4	4.2 [b], 5.1(±0.1) [c]	(16 ± 2.0)	16(±3.0) [c]
methanol-*d*	23.86 ± 0.10	24 [b], 23.0 [c], 30 [b]	5.2 ± 0.3	5.5 [b], 5.3(±0.1) [c]	(2.8 ± 0.3)	2.7(±0.3) [c]
ethanol	11.21 ± 0.05	10.6 [c]	5.9 ± 0.4	5.9(±0.1) [c]	(24 ± 3.0)	23(±3.0) [c]
ethanol-*d*	39.30 ± 0.10	38.8 [c]	6.1 ± 0.4	6.0(±0.2) [c]	(5.8 ± 0.4)	6(±1.0) [c]

[a] The data unit (kJ/mol) taken from Ref. [9] has been converted to kcal/mol.
[b] Ref. [7]. [c] Ref. [9]. [d] Ref. [10]

alcohols satisfies the classical Arrhenius behavior given by the formula

$$k_{obs}(T) = A_{obs} \exp[(-\Delta E_{obs}/k_B T)], \quad (1)$$

where k_B is the Boltzmann constant and A_{obs} is a pre-exponential factor. Within experimental error our transient absorption measurement shows no isotope dependence of the activation energy (Table 1). For example, the activation energy, ΔE_{obs}, was calculated to be 5.1 ± 0.3 and 5.2 ± 0.3 kcal/mol in methanol and methanol-*d*, respectively, consistent with Varma and co-workers' result [9]. In comparison, Itoh et al. [7] have reported a difference in ΔE_{obs} of 1.3 kcal/mol between methanol and methanol-*d*. This discrepancy is believed to be due to the experimental uncertainty. A difference of 1.3 kcal/mol only causes a small change of the slope (E_{obs}/k_B) in the plot of ln k_{obs} versus $1/T$ within a small temperature variation (footnote 1). Therefore, experimental uncertainty introduced at any temperature may result in a different curve fitted ΔE_{obs} value. For this reason, we have put forth a great deal of effort in the time-resolved measurements to reduce the experimental uncertainty to a minimum. This includes applying the smallest exciting power to reduce the thermal lensing and shock wave effects, normalizing the laser pulse intensity, and maintaining constant temperature in the solution during the period of data acquisition. At this stage, our data reconfirm Varma's results [9].

4. Discussion

The temperature independence of the energy barrier is intriguing since it does not fit, as stated by Varma and co-workers, within the principles of classical transition state theory. If the energy barrier is directly associated with the migration of the proton from N–H of 7HQ keto form and O–H through the relay of 2 solvent molecules (Fig. 1), the observed kinetic isotope effect (k^H_{obs}/k^D_{obs}) should mainly result from the difference in the zero-point energy. On the contrary, the key factor for the difference between k^H_{obs} and k^D_{obs} at each temperature results from a difference in the pre-exponential factor A_{obs} (Table 1). In order to explain their GSRPT results, especially in the kinetic solvent isotope studies, Varma and co-workers [9] proposed a two-step mechanism to achieve the tautomerization. The first step is to reach thermally induced fluctuations in a single structurally well defined conformation of the complex suitable for the double proton transfer. The second step involves tunneling from the occupied zero vibrational levels in the double-minimum well. The first step is isotope independent and temperature dependent and its activation energy must be related to structural reorganization of the alcohol molecules in the complex to achieve a hydrogen-bonded cyclic structure. The second step is dominated by the tunneling process from the zero vibrational level. In a small temperature range the tunneling process is nearly temperature independent, but strongly isotope dependent if it only associates with the O–H vibration modes. The essence of this mechanism, according to Varma and co-workers [9,18,19], is that a fast pre-equilibrium is established in which the relative population, $p(T)$, of the initial tunneling level is temperature dependent and stationary. Therefore, the overall rate constant is $p(T)k$(tunnel).

Based on the fundamental frame of solvent reorganization coupled GSRPT dynamics proposed by Varma and co-workers [9] we have derived the GSRPT dynamics in 7HQ from the kinetics standpoint. The overall GSRPT can be depicted in Eq. (2) (see below) incorporating the formation of a specific 2:1 alcohol/7HQ (keto form) hydrogen bonded complex (**B**) from a randomly solvated 7HQ keto form (**A**), and actual proton transfer from **B** to the solvated normal form (enol form) of 7HQ (**C**) (the proposed configuration for each solvated complex is shown in Fig. 1),

$$\mathbf{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \xrightarrow{k_{pt}} \mathbf{C}. \quad (2)$$

The kinetic expression for [**A**] and [**B**] can thus be written as

$$d[\mathbf{A}]/dt = -k_1[\mathbf{A}] + k_2[\mathbf{B}] \quad (3)$$

and

$$d[\mathbf{B}]/dt = k_1[\mathbf{A}] - (k_2 + k_{pt})[\mathbf{B}]. \quad (4)$$

Since the dynamics of GSRPT are much slower than that of ESPT ($k_{pt} > 10^9$ s^{-1}) and the fluorescence decay ($k_f > 10^8$ s^{-1}), at the initial delay time of 50 ns in our measurement the ground state tau-

tomer should be completely populated before its decay. Applying the Laplace transformation, the decay kinetics of **A** and **B** can be expressed by

$$[\mathbf{A}] = [\mathbf{A}]_0\left[g_1\, e^{-r_1 t} - g_2\, e^{-r_2 t}\right],$$

$$[\mathbf{B}] = [\mathbf{A}]_0\left[k_1/(r_1 - r_2)\right]\left[e^{-r_2 t} - e^{-r_1 t}\right],$$

where

$$g_1 = (k_1 - r_2)/(r_1 - r_2),$$

$$g_2 = (k_1 - r_1)/(r_1 - r_2),$$

$$r_1 = \tfrac{1}{2}\Big\{(k_1 + k_2 + k_{pt}) + \left[(k_1 - k_2 - k_{pt})^2 + 4k_1k_2\right]^{1/2}\Big\},$$

$$r_2 = \tfrac{1}{2}\Big\{(k_1 + k_2 + k_{pt}) - \left[(k_1 - k_2 - k_{pt})^2 + 4k_1k_2\right]^{1/2}\Big\}.$$

The **A** → **B** process involves the reorganization of any nonspecifically solvated 7HQ keto form to a very specific 2:1 alcohol/7HQ cyclically hydrogen bonded **B** species, resulting in a large negative entropy value (ΔS_{ab}). On the other hand, it is reasonable to assume that the enthalpy difference, ΔH_{ab}, between **A** and **B** is small. This can be rationalized by the fact that the solvation effects, such as hydrogen bonding interaction and dipole–dipole interaction, should be similar between the solvated **A** and **B** species. Accordingly, the free energy ΔG_{ab} ($= \Delta H_{ab} - T\Delta S_{ab}$) is expected to have a large positive value which mainly results from the large negative change of the entropy from **A** to **B**. In the later section, the entropy associated with the **A** → **B** process will be extracted experimentally to support this viewpoint. Since $\Delta G_{ab} = -RT\ln(k_1/k_2)$, a large positive ΔG_{ab} value indicates that $k_2 \gg k_1$. As a result g_1 is calculated to be negligible while $g_2 \approx -1$. Under this condition the time-dependent concentration of complex **B** can also be neglected due to the negligibly small value of $k_1/(r_1 - r_2)$ which is $\approx k_1/(k_2 + k_{pt}) \approx 0$. Hence, the only species contributing to the observed decay kinetics is species **A** and its decay dynamics can be simplified to

$$[\mathbf{A}] = [\mathbf{A}]_0\, e^{-r_2 t}. \tag{5}$$

The rate of decay for the randomly solvated species **A**, according to Eq. (5) is single exponential which is in agreement with the experimental results. The value of r_2 is a key factor for the following discussion. Based on the condition that $k_1 \ll k_2$, r_2 can be simplified to

$$r_2 = k_{obs} = k_1k_{pt}/(k_2 + k_{pt}). \tag{6}$$

The rate of relaxation of solvated **B** to the randomly solvated 7HQ (**A** species), k_2, can be treated as a regular solvent relaxation process. In the case of methanol the average rate of solvent relaxation has been reported to be in the range of $(1.5\text{–}3.0)\times 10^{11}$ s^{-1} at ambient temperature [20–22]. Unfortunately, in Eq. (6) the actual proton transfer rate, k_{pt}, cannot be determined independently. Therefore, an attempt has been made so that k_{pt} is on the same order of magnitude as the rate of excited state proton transfer, k_{pt}^*. This assumption is valid as long as the potential hypersurface along the proton transfer coordinate is not drastically different between the ground and excited states. It has been concluded that the ESPT takes place solely from a 2:1 methanol/7HQ cyclic complex [7,9] and the proton transfer process is the rate limiting step. Therefore, $k_{obs}^* \approx k_{pt}^*$, which has been measured to be in the range of 5.88×10^9 s^{-1} [7] and 5.00×10^9 s^{-1} [9] in the methanol solution. As a result, $k_{pt} \ll$ the rate of solvent relaxation k_2 ($\approx 10^{11}$ s^{-1}), and Eq. (6) can be rewritten to

$$r_2 = k_{obs} = k_1k_{pt}/k_2 = K_{eq}k_{pt} = k_{pt}\exp(\Delta G_{ab}/RT). \tag{7}$$

It should be noted that Eq. (7) is derived without the requirement of a fast pre-equilibrium between **A** and **B**. Since the effect of zero-point energy cancels out between k_1 and k_2, ΔG_{ab} is apparently isotope independent. If k_{pt} is a thermally assisted process, i.e. k_{pt} is proportional to $\exp(-\Delta E_{pt}/RT)$ (where ΔE_{pt} is the activation energy associated with the proton transfer reaction), the temperature-dependent term in Eq. (7) becomes $\exp[-(\Delta G_{ab} + \Delta E_{pt})/RT]$. Since the proton-transfer reaction involves the simultaneous rupture of a N–H bond in 7HQ keto form and two O–H bonds of the solvent molecule, ΔE_{pt} must be isotope dependent. If the observed kinetic isotope effect k_{obs}^{H}(in methanol)/k_{obs}^{D}(in methanol-*d*) of 5.7 results from the difference in zero-point vibrational energy, the difference between ΔE_{pt}^{D} and ΔE_{pt}^{H}

should be 1.03 kcal/mol which is in contrast to the measured nearly isotope-independent ΔE_{obs} value. Therefore, the dynamics of ground-state reverse proton transfer reaction, k_{pt}, is not a thermally activated process but most probably, as proposed by Varma and co-workers [9], through a tunneling mechanism which should be nearly temperature independent within a small range of temperature variations but is isotope dependent. As a result, comparing Eqs. (1) and (7), the pre-exponential factor A_{obs} corresponds to the proton tunneling rate k_{pt}, and the experimentally calculated ΔE_{obs} is essentially ascribed to be the free energy (ΔG_{ab}) between **A** and **B**. For the case of methanol, ΔG_{ab} is calculated to be 5.1 ± 0.4 kcal/mol. Assuming that ΔH_{ab} is negligibly small, ΔS_{ab} is calculated to be -18.8 eu, consistent with an expected large negative value. The observed kinetic isotope effect solely depends on the pre-exponential term k_{pt}, i.e. $k^{H}_{obs}/k^{D}_{obs} = A^{H}_{obs}/A^{D}_{obs} = k^{H}_{pt}/k^{D}_{pt}$. The pre-exponential factor A_{obs} which is equivalent to k_{pt} in Eq. (7) is calculated to be 1.6×10^{9} s^{-1} (see Table 1) in methanol and is $\ll k_2$, supporting the validity of our original assumption. Furthermore, k_{pt} is on the same order of magnitude as k^{*}_{pt}, indicating that the assumption of $k_{pt} \sim k^{*}_{pt}$ is valid.

In principle, there are two major parameters which direct the proton tunneling rate: the barrier height and the proton-transfer distance. Since the solvent catalyzed proton transfer in 7HQ keto form involves either concurrent or sequential breakage of two O–H and one N–H bonds, the relatively low proton tunneling rate and large isotope substitution effect may be due to a relatively large barrier height and an overall greater proton transfer distance. Unfortunately, since the actual potential energy surface along the proton transfer reaction coordinates is not known, a theoretical approach to calculate the proton (or deuterium) tunneling rate is not possible at this stage. It should be noted that for the above derivation we simply treated the proton tunneling process independent of temperature in a small temperature range (298–220 K). Theoretically, temperature dependence of the proton tunnelling should be significant at low temperatures. However, limited by the existence of small concentration of the 2:1 alcohol/7HQ hydrogen bonded complex at < 220 K, the temperature-dependence of k_{pt} cannot be verified.

Finally, the mechanism of populating the nonspecific solvated species **A** in the ground state is also quite intriguing. The overall proton-transfer cycle originates from the excitation of a ground-state 2:1 alcohol/normal tautomer (enol form) complex **C** (see Fig. 1). Due to the identical tautomer emission spectra between non-time-resolved and TSLIF measurements, it is believed that the excitation of the 2:1 solvent/7HQ (enol form) complex **C** undergoes an adiabatic proton transfer resulting in a 2:1 solvent/PT tautomer complex $\mathbf{B}^{*}$. Subsequently, fast solvent relaxation takes place before the spontaneous relaxation of $\mathbf{B}^{*}$ ($k^{*}_{2} \gg k_{B}$), giving rise to a nonspecific polyhydrated $\mathbf{A}^{*}$. This process, similar to the $\mathbf{B} \rightarrow \mathbf{A}$ process, is believed to be highly exergonic and the rate may be limited by the solvent relaxation time. The reverse process, $\mathbf{A}^{*} \rightarrow \mathbf{B}^{*}$, is negligible ($k^{*}_{2} \gg k^{*}_{1}$), similar to that proposed in the GSRPT dynamics (vide supra). As a result, the observed PT tautomer emission solely results from relaxation of $\mathbf{A}^{*}$, generating the initial populated randomly solvated **A** species.

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