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Direct Observation of Conformation-Dependent Pathways in the Excited-State Proton Transfer of 7-Hydroxyquinoline in Bulk Alcohols

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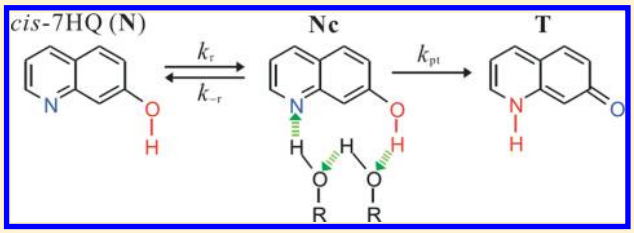
Supporting Information

ABSTRACT: The excited-state proton transfer (ESPT) of 7-hydroxyquinoline (7HQ) in bulk alcoholic solvents has been explored with variation of protic hydrogen atoms as well as alcohols. By measuring time-resolved kinetic profiles at two different excitation wavelengths, we have observed conformation-specific pathways in the ESPT of 7HQ. There are two possible rotamers of 7HQ according to the configuration of its hydroxyl group, which are *trans* and *cis*. On one hand, *trans*-7HQ cannot undergo proton transfer within its excited-state lifetime because the internal rotation of the hydroxyl group to form *cis*-7HQ hardly occurs. On the other hand, some *cis*-7HQ molecules exist as cyclic complexes of 7HQ·(alcohol)$_2$ at the moment of excitation, and the cyclic complexes can undergo ESPT rapidly via tunneling. However, the other *cis*-7HQ molecules should undergo solvent reorganization to form cyclic 7HQ·(alcohol)$_2$ complexes prior to intrinsic ESPT, and the solvent reorganization becomes the rate-determining step. In contrast to proton transfer, where intrinsic ESPT and solvent reorganization have been observed separately in time-resolved kinetic profiles, intrinsic deuteron transfer is too slow to be distinguished kinetically from solvent reorganization.



1. INTRODUCTION

Proton transfer is one of the most common and fundamental reactions in living organisms, and it plays an important role in a wide variety of biological and chemical phenomena.[1−8] In this regard, proton transfer has been attracting considerable attention. In particular, biological proton relay often takes place over a long distance, and hydrogen (H)-bonding solvent molecules such as water and amino acids mediate the proton relay by donating or accepting protons.[3−5,9,10] The dynamics of such long-ranged proton transport is determined mainly by the size, the structure, and the motion of mediating solvent molecules.[7,11−16] Thus, to understand the fundamental mechanisms of biological and chemical processes relevant to vital phenomena, it is essential to investigate the dynamics of solvent-mediated proton relay. According to the properties of mediating solvents, there are three possible manners how protons are transferred:[2] proton donation from an acid to a solvent molecule with subsequent proton scavenging by a base (protolysis), proton acceptance of a base from a solvent molecule with subsequent proton donation of an acid to the anionic solvent molecule (sovolysis), and direct proton relay from an acid to a base (direct exchange). In our previous papers, we have reported that proton transfer via a H-bonded water chain prefers to occur through protolysis,[16−19] whereas proton transfer via a H-bonded alcohol chain does through solvolysis.[15,20−22] Because of the different properties between water and alcohols, such as H-bonding abilities and proton-accepting/donating abilities, the mechanism of proton transport is dependent strongly on mediating solvents.

It is hard to explore the dynamics of biological proton transport in proteins directly due to the structural complexity as well as the massiveness of proteins.[4,5,10] Accordingly, a simplified biomimetic system is required to study the molecular mechanism and dynamics of biological proton transport in detail. Hydroxyquinolines, having two prototropic groups of photoacidic enol and photobasic imine, can be good experimental models to study biological proton-relay processes.[17−30] In particular, 7-hydroxyquinoline (7HQ) is well-known to undergo excited-state proton transfer (ESPT) via H-bonded solvent molecules;[17−22,26−30] two prototropic groups of 7HQ are too far from each other to donate or accept a proton directly, so that protic solvent molecules such as water or alcohol molecules are demanded to mediate proton transfer from the acidic enolic group to the basic imino group of 7HQ. On one hand, in an aqueous solution, proton relay is known to take place very fast through a systematically well-structured H-bond network;[1,14] the sequential, Grotthuss-type, proton transport of water occurs via interconversion between two hydration complexes of an Eigen cation and a Zundel cation.[18,19] Due to the unique properties of water such that each molecule can have as many as four H bonds, protons can be hydrated stably and transferred rapidly through well-organized H-bond chains in water. On the other hand, in an alcoholic solvent, it hitherto has been considered that intrinsic proton transfer can be hardly observed directly because solvent

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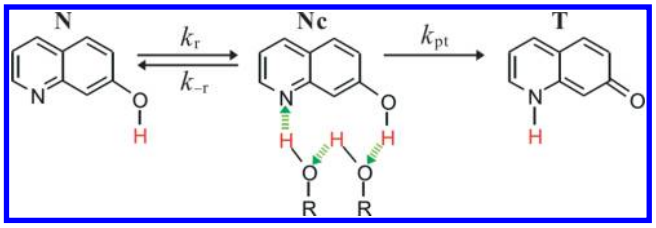
reorganization, which takes place prior to intrinsic proton transfer to form a proper conformation, becomes the rate-determining step.[27−29] For this reason, some isolated systems have been employed to explore intrinsic proton transfer directly. For example, in an aprotic nonpolar medium such as *n*-heptane, a 7HQ molecule and two alcohol molecules form a cyclic complex of 7HQ·(alcohol)$_2$ stably in the ground state, and upon excitation, the cyclic complex can undergo ESPT rapidly.[20,22] However, in a bulk alcohol, solvent reorganization to form the cyclic complex takes place prior to intrinsic ESPT, and it becomes the rate-determining step of overall ESPT.[27,28] Thus, the direct observation of intrinsic ESPT is usually interfered by solvent reorganization.

In a bulk alcohol, a two-step ESPT mechanism, shown in Scheme 1, has been widely discussed:[21,27−29,31] the first step is

Scheme 1. Excited-State Triple Proton Transfer of 7HQ in a Bulk Alcohol



solvent reorganization (k_r) of the normal species (**N**) of 7HQ to form a cyclically H-bonded 7HQ·(alcohol)$_2$ complex (**Nc**), and the second step is the intrinsic proton transfer (k_{pt}) of **N** via H-bonded alcohol molecules to produce the tautomeric species (**T**) of 7HQ. In one limit, if solvent reorganization is the rate-determining step, the overall ESPT rate constant (k_{PT}) of 7HQ becomes k_r. In the opposite limit, if an equilibrium ($K = k_r/k_{-r}$) between solvent reorganization and solvent randomization (k_{-r}) is rapid compared with k_{pt}, k_{PT} is independent of solvent dynamics and is expressed as Kk_{pt}. The static role of solvation is reported to be $k_{PT} = k_{pt}\exp(-\Delta G/k_BT)$ in the manner of the transition-state theory,[32] where ΔG is the Gibbs free energy of **Nc** formation. Solvation to form an appropriate precursor configuration is generally believed to be prerequisite to efficient proton tunneling.[18,20,32]

Here we report the direct observation of conformation-specific ESPT pathways of 7HQ in bulk alcohols (Scheme S1 of the Supporting Information). There are two possible rotamers of 7HQ according to the configuration of its hydroxyl group; *cis*-**N** can undergo ESPT whereas *trans*-**N** cannot. Some of *cis*-**N** conformers exist as cyclically H-bonded complexes of 7HQ·(alcohol)$_2$, that is, **Nc**, already at the moment of excitation, and **Nc** can undergo ESPT rapidly via tunneling (Scheme S1a of the Supporting Information). However, the other *cis*-**N** conformers, which remain as 7HQ monomers, 1:1 7HQ-alcohol complexes, or noncyclically H-bonded 1:2 7HQ-alcohol complexes, need to form **Nc** via solvent reorganization before undergoing intrinsic proton transfer (Scheme S1b of the Supporting Information).

2. EXPERIMENTAL SECTION

7HQ (99%) was used as purchased from Acros while alcohols (ROH, anhydrous, ≥99.5%), purchased from Sigma-Aldrich, were stored over molecular sieves of 4 Å for 24 h prior to use. The protic hydrogen atom of 7HQ was exchanged with a ^{2}H (D) atom to prepare deuterated 7HQ (7DQ) by dissolving 7HQ in a deuterated alcohol (ROD, isotopic purity ≥99.5%). The concentration of 7HQ was kept to be 0.1 mM in every alcohol. Absorption spectra were measured with a UV/vis spectrophotometer (Scinco, S3100). Emission and excitation spectra were obtained using a home-built fluorometer consisting of a Xe lamp of 75 W (Acton Research, XS432) with a monochromator of 0.15 m (Acton Research, Spectrapro150) and a photomultiplier tube (Acton Research, PD438) attached to a monochromator of 0.30 m (Acton Research, Spectrapro300). To obtain time-resolved fluorescence kinetic profiles, a mode-locked Nd:YAG laser (Quantel, Pizzicato) with the pulse duration of 25 ps was employed for excitation, and a streak camera of 10 ps (Hamamatsu, C2830) attached to a CCD detector (Princeton Instruments, RTE128H) was used for detection. Samples were excited with the third-harmonic pulses (355 nm) of the laser or with 315 nm pulses generated from a Raman shifter, filled with CH_4 gas of 15 atm and pumped by the fourth-harmonic pulses (266 nm) of the laser. Emission wavelengths were selected by combining band-pass and cutoff filters. Fluorescence kinetic constants were extracted by fitting kinetic profiles to computer-simulated exponential curves convoluted with instrument response functions. All the measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of 7HQ with variation of alcohols. The band maximum of the absorption spectra appears

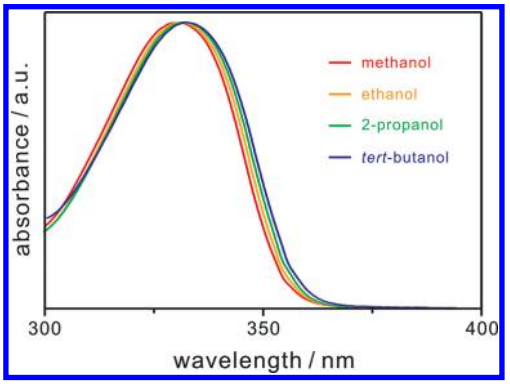


Figure 1. Maximum-normalized absorption spectra of 0.1 mM 7HQ in indicated alcohols.

around 330 nm and shifts to the blue by 1.8 nm as the solvent changes from *tert*-butanol (ε = 12.5 at 25 °C) to methanol (ε = 33.0 at 25 °C), showing weak hypsochromic solvatochromism with increase of the solvent polarity (Table 1). One would expect that the $^1(\pi,\pi^*)$ absorption band shifts to the red, rather than to the blue, as the solvent polarity increases. Thus, we suggest that $^1(n,\pi^*)$ transition also contributes to the absorption band of 7HQ. On the other hand, neither the absorption band of **T**, which would presumably appear around 410 nm,[17] nor the absorption band of any cationic or anionic intermediate species, which would presumably appear around 370 nm,[33] was observed in all the explored alcohols. This indicates that, even in polar protic solvents of alcohols, proton transfer to form **T*** does not take place in the ground state; only **N** exists in the ground state.

The excitation of **N** at 330 nm gives largely Stokes-shifted fluorescence at 520 nm, which arises from the formation of **T***, as well as dominant **N*** fluorescence at 380 nm without

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Table 1. Solvent-Dependent Rate Constants for the ESPT of 7HQ in Diverse Alcohols

alcohol	ε^a	η^a (cP)	α^b	β^b	k_f^{-1c} (ps)	k_s^{-1d} (ps)
methanol	33.0	0.54	0.93	0.62	54	190
ethanol	25.3	1.07	0.83	0.77	62	380
1-propanol	20.8	1.94	0.84	0.90	70	490
1-butanol	17.8	2.54	0.84	0.84	74	560
2-propanol	20.2	2.04	0.76	0.95	79	530
tert-butanol	12.5	4.31	0.68	1.01	94	620

[a]Dielectric constant (ε) and viscosity (η) of alcohols at 25 °C.[34] [b]Proton-donating (α) and -accepting abilities (β), which indicate the acidity and the basicity, respectively, of alcohols.[35−37] [c]Observed fast-rise times of **T*** fluorescence. [d]Observed slow-rise times of **T*** fluorescence.

showing intermediate fluorescence (Figure 2). This indicates that upon excitation, **N*** undergoes ESPT to form **T*** directly

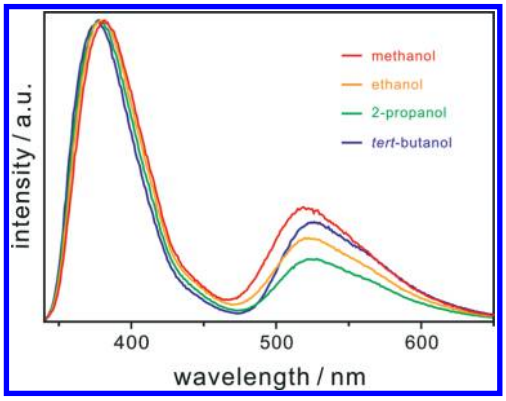

Figure 2. Maximum-normalized emission spectra, with excitation at 330 nm, of 0.1 mM 7HQ in indicated alcohols.

without accumulating any cationic or anionic intermediate species of 7HQ. Strong **N*** fluorescence suggests that a large fraction of 7HQ molecules exist as *trans*-**N** conformers at the moment of excitation, which cannot undergo ESPT (Scheme S1c of the Supporting Information). The time-resolved kinetic profiles of 7HQ support that nearly half of 7HQ molecules exist as *trans*-**N** conformers in the ground state (see below). Note that in a nonpolar aprotic solvent such as *n*-heptane, the emission spectrum of 7HQ shows a **N*** fluorescence band only, which is the mirror image of its lowest electronic absorption band.[20,21] Thus, the excited-state tautomerization of 7HQ is operative when protic solvent molecules mediate ESPT from the photoacidic enolic group to the photobasic imino group of 7HQ. As the solvent changes from *tert*-butanol to methanol, **N*** fluorescence shifts to the red by 3.8 nm (Figure 2), whereas **T*** fluorescence shifts to the blue by 4.9 nm (Figure S1 of the Supporting Information). The bathochromic shift of **N*** fluorescence is attributed to the larger dipole moment of **N*** than that of **N**; electronic rearrangement following excitation enhances both the enol acidity and the imine basicity of 7HQ enormously. Whereas **T** has zwitterionic character with a large charge separation, **T*** possesses more quinonoidal character.[38] Thus, the dipole moment of **T*** is much smaller than that of **T**, resulting in the hypsochromic solvatochromism of **T*** fluorescence.

The excitation spectrum of **T*** fluorescence monitored at 550 nm shows a single band at 330 nm, which is attributed to the absorption of **N**, in every employed alcohol (Figure 3). The

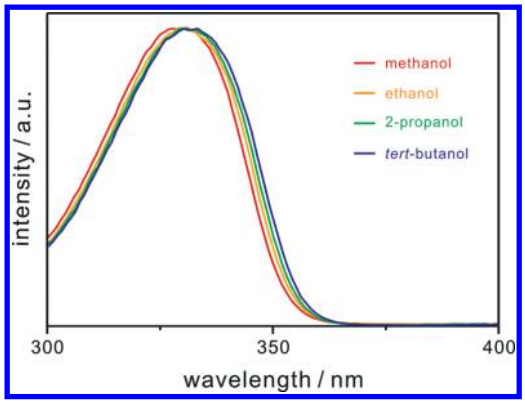

Figure 3. Maximum-normalized excitation spectra, monitored at 550 nm, of 0.1 mM 7HQ in indicated alcohols.

excitation spectra of 7HQ in bulk alcohols correspond well to its absorption spectra shown in Figure 1, designating that **T*** fluorescence arises only from the ESPT of **N**. This also supports that neither **T** nor any intermediate species of 7HQ exists in the ground state. It is noteworthy that the direction and the degree of the solvatochromism of the excitation spectra are the same as the respective ones of the absorption spectra.

The fluorescence kinetic profiles of 7HQ in bulk alcohols have been measured with variation of excitation wavelengths. Regardless of excitation wavelengths, the kinetic profiles of **N*** fluorescence monitored at 420 nm show double-exponential decay while those of **T*** fluorescence monitored at 550 nm show double-exponential rise and single-exponential decay (Figures 4 and 5 and Table S1 of the Supporting Information). The fast-decay time of **N*** fluorescence is attributed to the proton transfer of *cis*-**N***, while the slow-decay time of **N*** fluorescence is ascribed to the relaxation of *trans*-**N*** (Scheme

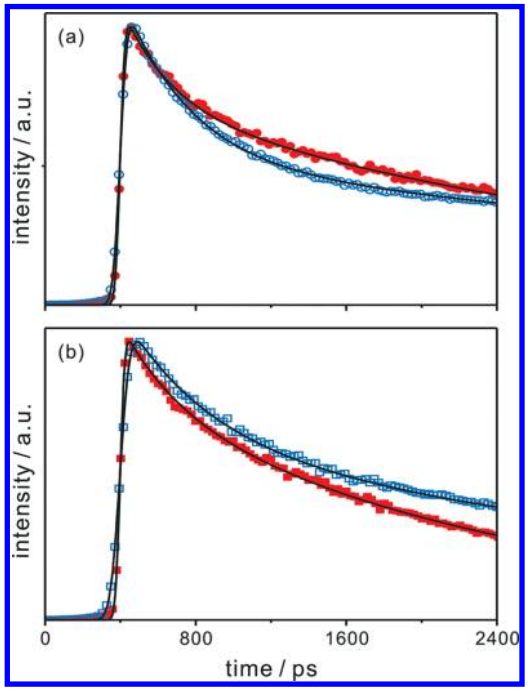

Figure 4. **N***-fluorescence kinetic profiles, with excitation at 315 nm (open) and 355 nm (closed), of 0.1 mM 7HQ in ethanol (a) and 2-propanol (b). Samples were monitored at 420 nm, and solid lines are the best-fitted curves to extract kinetic constants given in Table S1.

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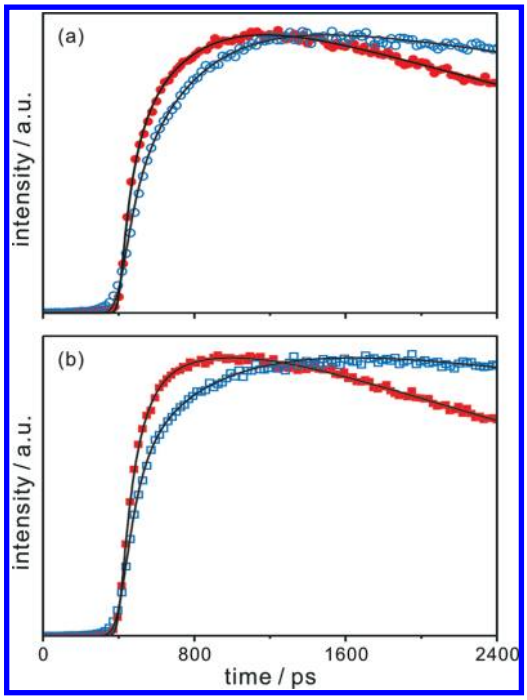

Figure 5. T*-fluorescence kinetic profiles, with excitation at 315 nm (open) and 355 nm (closed), of 0.1 mM 7HQ in ethanol (a) and 2-propanol (b). Samples were monitored at 550 nm, and solid lines are the best-fitted curves to extract kinetic constants given in Table S1.

S1 of the Supporting Information). Itoh and co-workers have reported that 6-methyl-7HQ, corresponding to *cis*-**N**, undergoes ESPT, whereas 8-methyl-7HQ, corresponding to *trans*-**N**, does not undergo ESPT.[27] The coexistence of *cis* and *trans* conformers of **N** has been proposed by semiempirical calculations and jet-cooled molecular-beam experiments; **N** in the gas phase exists as either *cis* or *trans* although the *cis*-**N** is lower by 0.71 kcal/mol in energy than *trans*-**N**.[39−43] The energy barrier for the internal rotation of the hydroxyl group of 7HQ has been reported as high as 2.9 kcal/mol,[40] and it is expected to increase tremendously upon excitation due to the increment of quinonoidal character on the hydroxyl moiety of 7HQ. Furthermore, H bonding between a protic solvent molecule and the hydroxyl group would raise the energy barrier for the internal rotation of the hydroxyl group; the barrier for the internal rotation of the hydroxyl group in H-bonded phenol-water clusters has been reported to be 3.5 kcal/mol in S_0 and 13.5 kcal/mol in S_1.[43] In these regards, we infer that the *cis* and the *trans* rotamers of **N** cannot rotate internally to transform into each other within their excited-state lifetimes due to the high energy barrier of the internal rotation of the hydroxyl group in S_1. Therefore, we attribute the biphasic decay of **N*** fluorescence in bulk alcohols to the coexistence of *cis*-**N** and *trans*-**N** conformers; the fast decay arises from the ESPT of *cis*-**N*** while the slow decay does from the relaxation of *trans*-**N***.

We have assigned the two observed rise times of **T*** fluorescence (Figure 5 and Table S1 of the Supporting Information) to ESPT times for two following cases. The fast rise time (k_f^{-1}) is attributed to the intrinsic ESPT time of **Nc** (Scheme S1a of the Supporting Information); *cis*-**N** complexed cyclically with two alcohol molecules, that is, **Nc**, already at the moment of excitation can undergo ESPT rapidly via tunneling without going through solvent reorganization to form **Nc**.[20,22] The slow one (k_s^{-1}) is ascribed to solvent reorganization prior to intrinsic ESPT (Scheme S1b of the Supporting Information); noncyclic *cis*-**N** conformers such as 7HQ monomers, 1:1 7HQ-alcohol complexes, and noncyclically H-bonded 1:2 7HQ-alcohol complexes should undergo solvent reorganization to form **Nc**, which then can undergo intrinsic ESPT rapidly. Our observed solvent reorganization times of 190−620 ps are much longer than the typical solvent relaxation times of alcohols because the formation of **Nc** requires extra energy to break preexisting strong H bonds. As discussed already in the Introduction section, the rate constant of overall ESPT (k_{PT}) would be determined mostly by k_r when the solvent reorganization becomes the rate-determining step of ESPT (Scheme 1), and k_{PT} would be k_{pt} when **Nc** becomes excited (Scheme S1a of the Supporting Information). In these regards, we consider that k_f and k_s correspond to k_{pt} and k_r, respectively (Table 1). On the other hand, recall that **N*** fluorescence shows double-exponential decay, rather than triple-exponential decay, although **T*** fluorescence shows double-exponential rise. If three decay times were observed in **N*** fluorescence and the two fast times of **N*** fluorescence matched well with the respective ones of two rise times of **T*** fluorescence, it could be more obvious that k_f and k_s indicate k_{pt} and k_r, respectively. However, observed k_f and k_s values are too close to be distinguished kinetically in **N*** fluorescence, so that k_{pt} and k_r are convoluted together to give rise to the fast-decay component of **N*** fluorescence. Nonetheless, the result that two distinctive rise times of **T*** fluorescence have been observed is enough to show that two different ESPT pathways depending on the ground-state conformations of *cis*-**N** at the moment of excitation: **Nc** and noncyclic *cis*-**N** (Scheme S1 and Table S1 of the Supporting Information).

We have already reported the intrinsic ESPT of **Nc** in isolated systems;[20,22] in nonpolar aprotic media of *n*-alkanes, most 7HQ molecules associate with two alcohol molecules to form **Nc** stably in the ground state, so that the intrinsic ESPT dynamics of 7HQ along a H-bonded alcohol chain can be investigated directly without interference by solvent reorganization. In previous papers,[20−22] it has been reported that the ESPT of **Nc** is initiated by the proton donation of the adjacent alcohol molecule to the imino group of 7HQ via tunneling, which is the rate-determining step of the intrinsic ESPT of **Nc**, and completed by subsequent rapid proton relay from the enolic group of 7HQ to the deprotonated alkoxide moiety (Scheme S1a of the Supporting Information). The ESPT of **Nc** takes place in an asymmetrically concerted manner, rather than in a stepwise manner; although the imine-protonated 7HQ forms transiently at the rate-determining step, it is not accumulated during ESPT.[20−22] It has been reported that the ESPT of **Nc** isolated in *n*-alkanes becomes faster with the increasing proton-donating ability (α) of the alcohol.[20−22] Similarly, in bulk alcohols, the intrinsic ESPT of **Nc** (k_{pt}), corresponding to k_f, becomes more rapid as the α value of the alcohol increases (Table 1). Meanwhile, solvent reorganization to form **Nc** occurring prior to intrinsic ESPT would be affected by the viscosity (η) of the alcohol. Solvent reorganization (k_r), corresponding to k_s, becomes slower with the increasing η value of the alcohol (Table 1); solvent fluctuation, which plays a key role in solvent reorganization, is reduced in a viscous solvent. Moreover, the structural complexity of alcohols also influences on solvent reorganization; solvent reorganization becomes slower in secondary or tertiary alcohols than in primary alcohols (Table 1).

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It is noteworthy that k_{pt} of 7HQ·(alcohol)$_2$ is substantially larger in a bulk alcoholic solvent than in *n*-heptane.[20] The rate constant of the ESPT of **Nc** is affected considerably by the polarity of the medium solvent. We have previously reported that the ESPT energy barrier of 7HQ decreases with the increasing polarity of the medium solvent;[31] the intrinsic ESPT of 7HQ·(ethanol)$_2$ becomes faster in the more polar medium due to the lower energy barrier of ESPT.[31] Moreover, we have previously shown that the intrinsic ESPT rate of 7HQ·(H$_2$O)$_2$ is larger in diethyl ether (ε = 4.27 at 20 °C) than in dipropyl ether (ε = 3.38 at 20 °C); ether molecules associate with water molecules of cyclic 7HQ·(H$_2$O)$_2$ complexes via H bonds, and at the rate-determining step, a more polar diethyl ether molecule helps a water molecule to accept a proton from the enolic group of 7HQ more facilely.[19] Similarly, the ESPT of 7HQ·(alcohol)$_2$ is faster in a polar alcoholic solvent than in nonpolar *n*-heptane (Table 1); for example, the ESPT times of 7HQ·(ethanol)$_2$ and 7HQ·(2-propanol)$_2$ in bulk alcohols are observed to be 62 and 79 ps, respectively, while the respective ones in *n*-heptane are reported to be 82 and 134 ps.[20] The ratio of the ESPT rate constant in a bulk alcohol to the rate constant in *n*-heptane increases gradually as the polarity of the alcohol decreases: 1.1 in methanol, 1.3 in ethanol, 1.7 in 2-propanol, and 2.3 in *tert*-butanol. In *n*-heptane which is a nonpolar medium, the rate constant is determined mostly by the proton-donating ability of the complexed alcohol because the rate-determining step is the proton donation of the adjacent alcohol molecule to the imino group of 7HQ. However, in bulk alcohols which are polar media, the secondary solvation molecules surrounding the cyclic complex of 7HQ·(alcohol)$_2$ are also alcohol molecules. Accordingly, the polar medium solvent can help ESPT to take place facilely, resulting in the larger rate constant of ESPT in the more polar medium. Such polarity effect on the rate constant of ESPT would be larger in *tert*-butanol than in methanol because the proton-donating ability of methanol is strong enough to donate a proton to 7HQ facilely while the proton-donating ability of *tert*-butanol is so weak to donate a proton for itself.

As shown in Table S1 of the Supporting Information, for the rise kinetics of **T*** fluorescence in each alcohol, initial amplitude percentages vary with the excitation wavelength whereas time constants do not. In every alcohol, the fast-rise component of **T*** fluorescence with excitation at 355 nm has a larger initial amplitude percentage than that of **T*** fluorescence with excitation at 315 nm does. The absorption maximum of 7-HQ shifts to the red largely as 7HQ molecules form H bonds with alcohol molecules.[20,22] Thus, doubly H-bonded 7HQ·(alcohol)$_2$ complexes are excited more selectively at 355 nm to make the amplitude percentage of the fast-rise component in **T*** fluorescence larger. This supports our suggestion that the ESPT pathways of 7HQ are determined by ground-state conformations at the moment of excitation. On the other hand, in *tert*-butanol, the initial amplitude percentage of the fast-rise component remains almost invariant regardless of the excitation wavelength. Due to the structural complexity of a tertiary alcohol, solvent reorganization to form **Nc** would be reduced extremely in *tert*-butanol. Thus, a significantly reduced fraction of noncyclic *cis*-**N** conformers can undergo ESPT through solvent reorganization in *tert*-butanol.

In contrast to proton transfer which shows two rise components of **T*** fluorescence arising from the ground-state conformations of **Nc** and noncyclic *cis*-**N**, only one rise component of **T*** fluorescence has been observed in the excited-state triple deuteron transfer of 7DQ, and the rise time of **T*** fluorescence matches well with the fast-decay time of the **N*** fluorescence of 7DQ (Table S2 of the Supporting Information). The intrinsic proton transfer of **Nc** is well-known to occur via tunneling, passing through the energy barrier, and the kinetic isotope effect (KIE) for the ESPT of **Nc** has been reported to be enormously large; for example, KIE for the ESPT of 7HQ·(ethanol)$_2$ in *n*-heptane has been observed to be 15.[20] A deuteron is twice as heavy as a proton, and the energy barrier of deuteron transfer is higher than that of proton trasnfer due to the lower zero-point energy of 7DQ·(ROD)$_2$. Thus, it is hard for a deuteron to pass through the energy barrier of deuteron transfer via tunneling, so that deuteron transfer becomes much slower than proton transfer. Accordingly, in contrast to proton transfer, two components have not been separated in deuteron transfer because the **T*** rise time of 7DQ is slower than the solvent reorganization time measured from the 7HQ kinetic profile in the same alcohol. Note that intrinsic proton transfer via tunneling is isotopically sensitive whereas solvent reorganization to form **Nc** is isotopically insensitive; the coordinates of solvent reorganization and intrinsic proton transfer are orthogonal to each other in the potential hypersurface. Considering that solvent reorganization would be independent of isotopic substitution, we suggest that the retarded rise time of the **T*** fluorescence of 7DQ is attributed to intrinsic deuteron transfer via tunneling, which is the rate-determining step of overall deuteron transfer, rather than solvent reorganization. Thus, KIE values for the ESPT of 7HQ in methanol, ethanol, 2-propanol have been found to be 7, 10, and 10, respectively.

4. CONCLUSIONS

The conformation-specific ESPT pathways of 7HQ in bulk alcohols have been observed directly. There are two possible conformers of 7HQ according to the configuration of its hydroxyl group, which are *trans* and *cis*. On one hand, *trans*-7HQ cannot undergo proton transfer even in the excited state because the internal rotation of the hydroxyl group to form *cis*-7HQ hardly occurs within the excited-state lifetime of 7HQ. On the other hand, some *cis*-7HQ conformers exist as cyclically H-bonded complexes of 7HQ·(alcohol)$_2$ (**Nc**) already at the moment of excitation, and **Nc** can undergo proton transfer rapidly via tunneling upon absorption of a photon. However, the other *cis*-7HQ conformers, which remain as 7HQ monomers, 1:1 7HQ-alcohol complexes, or noncyclically H-bonded 1:2 7HQ-alcohol complexes, need to associate with alcohol molecules to form **Nc** by solvent reorganization before undergoing intrinsic ESPT, and the solvent reorganization becomes the rate-determining step of their overall ESPT. The rate constant of intrinsic ESPT has been observed to be determined mostly by the proton-donating ability of the alcohol while the rate constant of solvent reorganization has been found to be dependent mainly on the viscosity of the alcohol. In contrast to proton transfer where intrinsic ESPT and solvent reorganization have been observed separately in time-resolved kinetic profiles, intrinsic deuteron transfer is rate-limiting. The kinetic isotope effects of ESPT in bulk alcoholic solvents have found be significantly smaller than those in isolated systems.

■ ASSOCIATED CONTENT

Supporting Information

Conformation-specific ESPT pathways, fluorescence kinetic constants, and maximum-normalized **T*** emission spectra. This

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material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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