Proton Transfer

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Excited-State Triple Proton Transfer of 7-Hydroxyquinoline along a Hydrogen-Bonded Alcohol Chain: Vibrationally Assisted Proton Tunneling**

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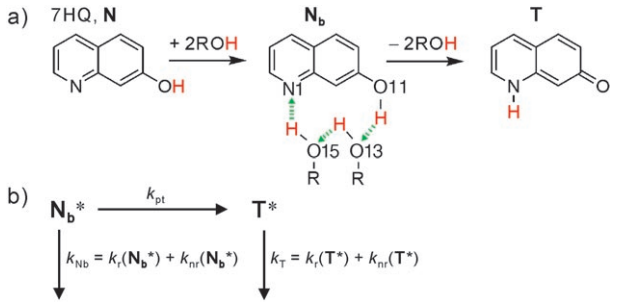
Proton transfer plays a key role in a variety of biological and chemical phenomena such as water autoionization, fast proton diffusion, acid–base neutralization, DNA mutagenesis, enzyme catalysis, and proton pumping through membrane protein channels.[1–5] Hydrogen-bonded (H-bonded) chains extending over a long distance have been thought to be particularly effective in mediating the translocation of protons by a Grotthus-type mechanism.[3] However, even in cases of relatively simple and well-characterized systems, the experimental elucidation of the molecular mechanism of proton transfer along H-bonded chains is difficult because the event is intrinsically transient.

Amphoteric aromatic molecules are especially interesting to study excited-state proton transfer (ESPT) because they can be experimental molecular models for biological proton-relay systems.[5–7] In this regard, 7-hydroxyquinoline (7HQ), which has two prototropic groups (photoacidic enol and photobasic imine), has been extensively explored.[1,8–13] Protic solvent molecules are indispensable for the tautomerization of 7HQ, because the two prototropic groups are too far apart to donate/accept a proton directly.[11,12] Leutwyler et al. showed that a Grotthus-type proton-relay process of excited 7HQ takes place along a H-bonded ammonia wire in the gas phase.[1] Varma et al. proposed the biphasic ESPT mechanism of Scheme 1a for the tautomerization of 7HQ in bulk alcohols.[11] The first step is attributed to solvent reorganization for a normal molecule (**N**) to form a cyclically H-bonded complex with two alcohol molecules (ROH), while the subsequent step is intrinsic proton transfer in the complex to produce a tautomeric molecule (**T**). The first, solvent-reorganization step is reported to determine the overall tautomerization dynamics of 7HQ in bulk alcohols.[11] Consequently, it is desirable to explore the proton-relay dynamics of the cyclically H-bonded 7HQ–$(ROH)_2$ complex ($\mathbf{N_b}$) directly without their being veiled by the rate-determining slow step of solvent reorganization to better understand the intrinsic dynamics of the ESPT of 7HQ. In this regard, the ESPT of $\mathbf{N_b}$, prepared by adding a small amount of alcohols in nonpolar solvents, has been investigated,[12] although it is not understood adequately yet. Here we report on an investigation of the intrinsic proton-relay dynamics of $\mathbf{N_b}$ with variation of alcohol, solvent, isotopes, and temperature, and show that triple proton transfer along the cyclically H-bonded chain occurs asymmetrically with tunneling as the rate-determining first step.



Scheme 1.

Figure 1a shows that the lowest absorption of 7HQ shifts to the red and loses the sharp vibronic structure with increasing concentration of ethanol in *n*-heptane. This implies that 7HQ molecules associate with ethanol molecules by H-bonding in *n*-heptane, as reported for *n*-hexane.[12] The addition of ethanol does not result in perceivable absorption around 410 nm, that is, proton-translocated **T** does not form in the ground state. The emission spectra of Figure 1a show that excitation of the complexes at 345 nm gives rise to prominent **T*** fluorescence at 530 nm and normal fluorescence at 360 nm.[11,12] This shows that ESPT of 7HQ is operative in *n*-heptane in the presence of ethanol. The increasing intensity of **T*** fluorescence with increasing $[C_2H_5OH]$ suggests that excitation produces **T*** from the complexes of 7HQ with ethanol.

Figures 1b and 1c indicate that a 7HQ molecule associates with two alcohol molecules in *n*-heptane to form $\mathbf{N_b}$ as shown in Equation (1).[12]

$$7HQ + 2\,ROH \overset{K}{\rightleftarrows} 7HQ{-}(ROH)_2 \qquad (1)$$

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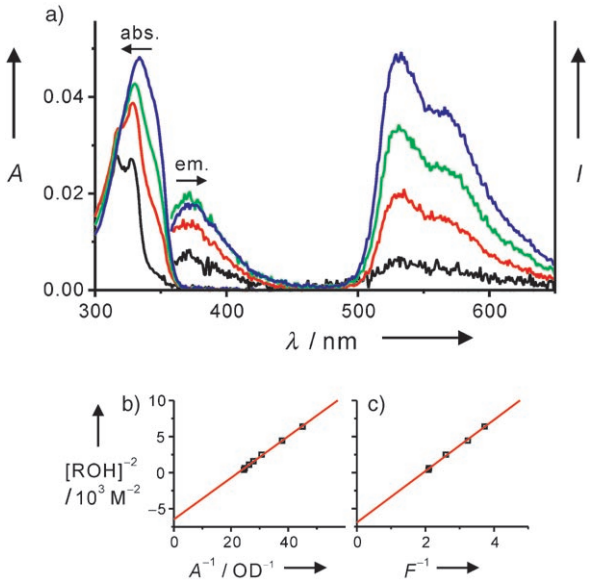

Figure 1. a) Absorption and emission spectra (with excitation at 345 nm) of 7HQ at ethanol concentrations of 5 (black), 10 (red), 15 (green), and 30 mM (blue) in *n*-heptane. b, c) Plots, with best linear fits (lines), of squared reciprocals of molar ethanol concentration [ROH] versus reciprocal absorbance A^{-1} at 345 nm (b) and reciprocal fluorescence intensity F^{-1} at 570 nm (c).

The complex-formation constant K in Equation (1) can be deduced by plotting $[ROH]^{-2} = cX - K$ linearly, where c is a constant and X is (absorbance)$^{-1}$ or (fluorescence)$^{-1}$.[13] The K value of 6500 M^{-2} obtained for absorbance numerically agrees with that of 6900 M^{-2} obtained for fluorescence. The good linearity of Figure 1c reveals that **T*** is formed from 7HQ–$(ROH)_2$ complexes on photoexcitation. We also confirmed, by measuring absorbance changes on gradually adding several other alcohols, that a 7HQ molecule associates with two alcohol molecules to form 7HQ–$(ROH)_2$ in *n*-heptane (see the Supporting Information). Table 1 shows that K decreases with increasing complexity of the alkyl chain and with decreasing Kamlet–Taft acidity α. Thus, the acidity of the alcohol is inferred to play an important role in the formation of H-bonded complexes. The magnitudes of α and Kamlet–Taft basicity β for H-bonding molecules provide explicit measures of the H-bond-donating and the H-bond-accepting abilities of the molecules, respectively.[15] The most stable ground-state structure of 7HQ–$(ROH)_2$ is reported to have the cyclic geometry of $\mathbf{N_b}$.[16] The H-bond involving the imino group is calculated to be 0.2 Å longer than that involving the enol group in the complex $\mathbf{N_b}$.[16] Thus, the H-bond strength of ROH···N is inferred to be relatively low and thus determine the formation of $\mathbf{N_b}$.

On excitation of a sample containing C_2H_5OH at 355 nm, normal fluorescence recorded at 420 nm shows a biphasic decay profile composed of 74 (97%) and 800 ps (3%), while **T*** fluorescence monitored at 550 nm rises in 75 ps and decays in 2.3 ns (Figure 2). On excitation of a sample containing C_2H_5OD, the rise time (710 ps) of **T*** fluorescence correlates

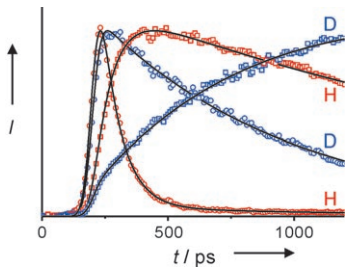

Figure 2. Fluorescence kinetic profiles (excitation at 355 nm and monitoring at 420 (circles) and 550 nm (squares)) of 7HQ in *n*-heptane with C_2H_5OH (H) and C_2H_5OD (D) concentrations of 30 mM. Lines are best-fit curves.

well with the fast decay time (710 ps) of normal fluorescence. The slow decay time of normal fluorescence and the lifetime of **T*** fluorescence are 1.7 and 6.2 ns, respectively. All the time constants mentioned above do not vary with ethanol concentration, although the fractional initial amplitudes of the two decay components do. This indicates that the collision-induced formation of $\mathbf{N_b}$ does not occur to conduct ESPT within the lifetime of **N***. Therefore, the fast-decay component is attributed to the decay of $\mathbf{N_b}$ coupled to ESPT, while the long decay time is assigned to the fluorescence lifetime of noncyclically H-bonded 7HQ complexes with ethanol.

We have analyzed the observed kinetic constants of $\mathbf{N_b}$* and **T*** by employing the irreversible two-state model described in Scheme 1b, where k_r and k_{nr} denote the rate constants of radiative and nonradiative relaxation, respectively. Then we can derive Equations (2) and (3) to show the temporal behaviors of [$\mathbf{N_b}$*] and [**T***], respectively.

$$[\mathbf{N_b}^*] = [\mathbf{N_b}^*]_0\, e^{-(k_{Nb}+k_{pt})t} \quad (2)$$

$$[\mathbf{T}^*] = \left(\frac{[\mathbf{N_b}^*]_0\, k_{pt}}{k_{Nb}+k_{pt}-k_T}\right)\left[e^{-k_T t} - e^{-(k_{Nb}+k_{pt})t}\right] \quad (3)$$

The k_{Nb} values of 7HQ–$(C_2H_5OH)_2$ and 7DQ–$(C_2H_5OD)_2$ were assumed to be the same as the reciprocals of the slow decay times of normal fluorescence in samples containing C_2H_5OH and C_2H_5OD, respectively. Thus, k_{pt} values for 7HQ–$(C_2H_5OH)_2$ and 7DQ–$(C_2H_5OD)_2$ complexes were

Table 1: Dependence of K, k_{pt}, and KIE of $\mathbf{N_b}$ on alcohol and solvent.

Solvent[a]	Alcohol[b]	α[c]	β[c]	K [M^{-2}]	k_{pt}^{-1} [ps]	KIE
n-Heptane	2,2,2-trifluoroethanol	1.51	0	10400 ± 400	15 ± 5	3.0 ± 1.0
	methanol	0.93	0.62	9500 ± 400	62 ± 3	15.2 ± 0.9
	ethanol	0.83	0.77	6500 ± 300	82 ± 4	15.0 ± 0.8
	2-propanol	0.76	0.95	6100 ± 300	134 ± 6	12.2 ± 0.6
	2-methyl-2-propanol	0.68	1.01	4200 ± 400	214 ± 10	8.5 ± 0.4
n-Decane	ethanol	0.83	0.77	–[d]	85 ± 4	14.4 ± 0.8
	2-methyl-2-propanol	0.68	1.01	–[d]	212 ± 10	8.5 ± 0.4
n-Dodecane	ethanol	0.83	0.77	–[d]	93 ± 4	13.1 ± 0.7
	2-methyl-2-propanol	0.68	1.01	–[d]	252 ± 10	7.2 ± 0.3

[a] The viscosities of *n*-heptane, *n*-decane, and *n*-dodecane at 25 °C are 0.41, 0.92, and 1.45 cP, respectively.[14] [b] At 30 mM. [c] With bulk alcohols because the values of monomeric alcohols, which have similar trends to those of bulk alcohols, are not available in the literature for some of the employed alcohols.[15] [d] Not measured.

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deduced to be $(82\,\mathrm{ps})^{-1}$ and $(1220\,\mathrm{ps})^{-1}$, respectively. We compared a kinetic isotope effect (KIE) calculated as k_{pt}^{H}/k_{pt}^{D} with an alternative KIE value obtained from the quantum yields and the fluorescence lifetimes to check the validity of our kinetic analysis. The two values obtained with each employed alcohol in *n*-heptane coincide within our experimental errors (see the Supporting Information).

The proton-relay process in $\mathbf{N_b}$ may occur by transfer of three hydrogen atoms concertedly through a single transition state or of three protons stepwise with formation of intermediate complexes.[17] Proton-inventory experiments with variation of the degree of deuteration of protic hydrogen atoms in $\mathbf{N_b}$ for the determination of k_{pt} can give us a clue to this issue.[17–21] In isotopically mixed systems, eight different types of complexes can be present: HHH, HDH, HHD, HDD, DHH, DDH, DHD, and DDD, where the successive three letters denote protic hydrogen atoms attached to O11, O13, and O15 of $\mathbf{N_b}$, respectively. The overall rate constants ($k_{all} = k_{Nb} + k_{pt}$) of $\mathbf{N_b}$ of the above complexes are k_{all}^{HHH}, k_{all}^{HDH}, k_{all}^{HHD}, k_{all}^{HDD}, k_{all}^{DHH}, k_{all}^{DDH}, k_{all}^{DHD}, and k_{all}^{DDD}, respectively. If $X_D = [\text{protic D}]/([\text{protic H}] + [\text{protic D}])$ and $X_H = 1 - X_D$, then we can deduce Equations (4) and (5) for overall rates according to the protic hydrogen isotopes of the enol group of 7HQ.

$$\mathrm{d[7HQ]}/\mathrm{d}t = -\{X_H^2 k_{all}^{HHH} + X_H X_D (k_{all}^{HDH} + k_{all}^{HHD}) + X_D^2 k_{all}^{HDD}\}[\mathrm{7HQ}] \quad (4)$$

$$\mathrm{d[7DQ]}/\mathrm{d}t = -\{X_H^2 k_{all}^{DHH} + X_H X_D (k_{all}^{DDH} + k_{all}^{DHD}) + X_D^2 k_{all}^{DDD}\}[\mathrm{7DQ}] \quad (5)$$

Although isotopic fractionation constants were assumed to be unity, we note that their actual values are slightly different from unity.[21] The isotope distribution should be directly measured by an NMR technique.[21] However, we have roughly calculated the distribution using the OH stretching frequencies of the four involved species[22] because of the very low concentrations of $\mathbf{N_b}$ in our samples. The estimated equilibrium constant of $7HQ + CH_3OD \rightleftharpoons 7DQ + CH_3OH$ at 23 °C is 1.03.

Because the isotopic exchange of a protic hydrogen atom is much slower than ESPT, we expect the fluorescence of $\mathbf{N_b}$ to decay biexponentially according to Equation (6).

$$F(t) = X_H \exp(-k^H t) + X_D \exp(-k^D t) \quad (6)$$

Then, the experimentally observed parameters k^H and k^D in Equation (6) consist of the eight different k_{all} values according to Equations (7) and (8), respectively.

$$k^H = k_{all}^{HHH} + (k_{all}^{HHD} + k_{all}^{HDH} - 2k_{all}^{HHH}) X_D + (k_{all}^{HHH} + k_{all}^{HDD} - k_{all}^{HHD} - k_{all}^{HDH}) X_D^2 \quad (7)$$

$$k^D = k_{all}^{DHH} + (k_{all}^{DDH} + k_{all}^{DHD} - 2k_{all}^{DHH}) X_D + (k_{all}^{DHH} + k_{all}^{DDD} - k_{all}^{DDH} - k_{all}^{DHD}) X_D^2 \quad (8)$$

The quadratic correlations of k^H and k^D with X_D given in Figure 3 yield k_{all}^{HHH}, k_{all}^{HDD}, k_{all}^{DHH}, and k_{all}^{DDD} as $(80\,\mathrm{ps})^{-1}$, $(220\,\mathrm{ps})^{-1}$, $(250\,\mathrm{ps})^{-1}$, and $(720\,\mathrm{ps})^{-1}$, respectively. If ESPT occurs concertedly without tunneling effects then, according to the rule of the geometric mean, $k_{obs}^{HHH}/k_{obs}^{DHH} = k_{obs}^{DHH}/k_{obs}^{HDD} = k_{obs}^{HDD}/k_{obs}^{DDD} = (k_{obs}^{HHH}/k_{obs}^{DDD})^{1/3}$ should hold.[17–21] However, $k_{obs}^{HHH}/k_{obs}^{DHH}$, $k_{obs}^{DHH}/k_{obs}^{HDD}$, $k_{obs}^{HDD}/k_{obs}^{DDD}$, and $(k_{obs}^{HHH}/k_{obs}^{DDD})^{1/3}$ are observed to be 3.1 ± 0.1, 0.86 ± 0.15, 3.3 ± 0.8, and 2.1 ± 0.3, respectively. These values indicate that the rule of the geometric mean is not valid in the ESPT of $\mathbf{N_b}$, which implies that the three protons move asymmetrically or that tunneling is involved in the rate-limiting step.

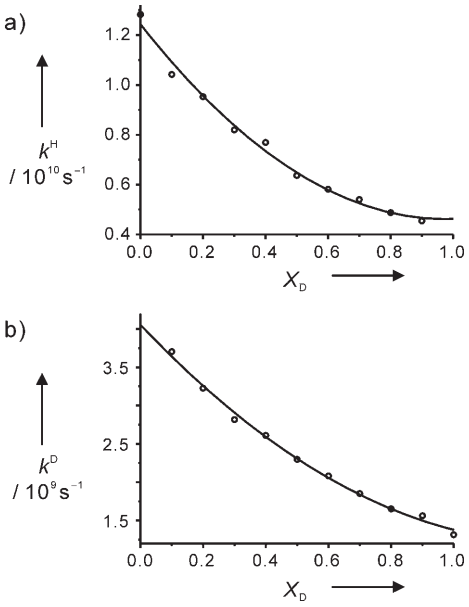
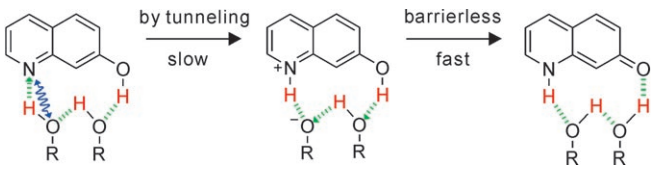


Figure 3. Plots of k^H (a) and k^D (b) with variation of X_D for 7HQ in *n*-heptane with $[C_2H_5OH]$ of 50 mM. Solid lines are best quadratic fittings to obtain k_{all}^{HHH}, k_{all}^{HDD}, k_{all}^{DHH}, and k_{all}^{DDD} as $(80 \pm 1\,\mathrm{ps})^{-1}$, $(220 \pm 37\,\mathrm{ps})^{-1}$, $(250 \pm 4\,\mathrm{ps})^{-1}$, and $(720 \pm 120\,\mathrm{ps})^{-1}$, respectively.

Alcohol-dependent kinetic measurements show that k_{pt} of $\mathbf{N_b}$ tends to increase with increasing α (Table 1). Because $\mathbf{N_b}$ formed with 2,2,2-trifluoroethanol, which has $\beta = 0$ and the highest α value, shows the highest k_{pt} value, β is not considered to affect k_{pt} noticeably. The structure of a cyclically H-bonded 7HQ–$(CH_3OH)_2$ complex at the excited state has been calculated to show that the N···HO H-bond is substantially longer than any of the other two H-bonds in the complex.[16] The dependence of k_{pt} on α indicates that ESPT becomes more exoergic with stronger acidity of the alcohol. This suggests that the H-bond-donating ability of an alcohol in the coordinate of N···HO is crucial for the dynamics of ESPT. Keeping in mind that the decay time of $\mathbf{N_b}^*$ and the rise time of $\mathbf{T}^*$ coincide and that k_{pt} depends on alcohol acidity, we propose that ESPT of $\mathbf{N_b}$ is initiated by the slow deprotonation of the alcohol molecule H-bonded to the nitrogen atom of 7HQ to form a zwitterionic intermediate complex (Scheme 2).[12c] The ESPT is then completed by rapid proton relay



Scheme 2.

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from the enol group of the 7HQ cation to the transient alkoxide anion through the neutral alcohol molecule.

The potential-energy surface from ab initio calculations showed that there are no metastable intermediate complexes.[16] The intermediate complex of Scheme 2 is too unstable to be kinetically significant, because both the alkoxide moiety and the 7HQ cation are energetically very unfavorable. Therefore, we infer that the observed rate constant of ESPT is mainly determined by the initial single proton transfer of the N···HO coordinate.

The KIE value of k_{pt} observed in 7HQ–$(C_2H_5OH)_2$ complexes in *n*-heptane at room temperature is 15.0 (Figure 2 and Table 1). Recall that our proton-inventory results deviate from the rule of the geometric mean and that single proton transfer through the H-bond of N···HO determines k_{pt}. The large KIE in the single proton transfer implies that the rate-determining step is mainly a tunneling process. The KIE values with diverse alcohols are also listed in Table 1. The less acidic alcohol makes the ESPT reaction less exothermic and more symmetric energetically to increase the contribution of tunneling and reduce the rate constant.[20,23] Thus, $\mathbf{N_b}$ with methanol ($\alpha = 0.93$) has a KIE five times greater than that of $\mathbf{N_b}$ with 2,2,2-trifluoroethanol ($\alpha = 1.51$). However, KIE tends to decrease with decreasing α if α decreases gradually and the molecular size increases rapidly. We consider that the effect of mobility reduction on KIE prevails over that of decreasing α in the above case. This hints that heavy-atom motions, which are isotopically insensitive, as well as short heavy-atom distances, are essential in tunneling. The intrinsic proton relay governed by tunneling requires optimized bond angles and short H-bond lengths in addition to the cyclic H-bonded structure. The reorganization of the H-bond bridge for $\mathbf{N_b}$ to form such a precursor configuration optimal for tunneling is not sensitive to isotope effects and consists mostly of heavy-atom motions. Configurational optimization and intrinsic tunneling occur in two orthogonal reaction coordinates of the potential hypersurface, and solvent fluctuations are suggested to play a crucial role in optimization. In the regime where hydrogen-atom motions including tunneling limit the rate exclusively, KIE is predicted to be independent of solvent viscosity and much greater than unity. Alternatively, when heavy-atom reorganization assists quantum tunneling, KIE depends on viscosity. The heavy-atom reorganization that is required to reach the optimal configuration for pretunneling becomes slow with increasing viscosity. Thus, the tunneling contribution and KIE tend to be small with increasing viscosity.[24] Table 1 shows that KIE and k_{pt} decrease with the increasing solvent viscosity. The dependence of k_{pt} on viscosity suggests that the rate of the overall proton-transfer reaction at high viscosity is also affected to some extent by the configurational-optimization rate of $\mathbf{N_b}^*$, and this supports the above idea that solvent fluctuations enhance tunneling in the ESPT of $\mathbf{N_b}$. The overall proton transfer of 7HQ in neat methanol is reported to occur on a timescale of 200 ps with KIE of 1.4.[12b] The rate is low and the KIE is small because large-amplitude solvent reorganization to form $\mathbf{N_b}$ is known to be the rate-determining step.[11]

The Arrhenius plots of k_{pt} in Figure 4 show that the KIE is independent of temperature within our experimental errors,

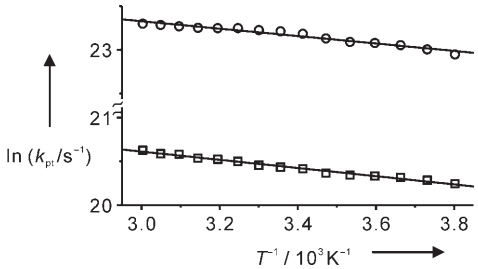

Figure 4. Arrhenius plots of k_{pt} in *n*-heptane with [C_2H_5OH] (circles) and [C_2H_5OD] (squares) of 30 mM. Activation energies (preexponential factors) extracted for C_2H_5OH and C_2H_5OD are 0.84 ± 0.05 kcal mol^{-1} ($(4.8 \pm 0.4) \times 10^{10}$ s^{-1}) and 0.93 ± 0.03 kcal mol^{-1} ($(3.7 \pm 0.2) \times 10^{9}$ s^{-1}), respectively.

although k_{pt} is slightly dependent on temperature. When the tunneling contribution is large, the ratio of preexponential factors $A(H)/A(D)$ is much less than unity in general. However, if tunneling becomes extremely effective for both H and D, then the ratio becomes much greater than unity. The deduced activation energies E_a of 7HQ–$(C_2H_5OH)_2$ and 7DQ–$(C_2H_5OD)_2$ are quite small (0.84 and 0.93 kcal mol^{-1}, respectively). This supports the suggestion that tunneling determines the ESPT rate. The fact that the two E_a values are very close to each other indicates that the KIE of 15.0 ± 0.8 is mostly determined by the $A(H)/A(D)$ ratio of 13.0 ± 1.3. This suggests that the rate-determining process for the ESPT of $\mathbf{N_b}$ takes place with extensive tunneling contribution in the reaction coordinate of N···HO. Temperature independence of the KIE has also been reported in enzymatic proton transfers[25] and solvent-mediated proton transfers.[11,20] Temperature-independent and large KIEs in enzymes have been explained with a model employing vibrationally enhanced proton tunneling.[26–28]

The temperature dependence of the rate constant arises from the temperature dependence of the population of the states that allow the proton to tunnel through the barrier. The observed small values of E_a are inferred to originate from the activation energy required to form a pretunneling configuration with heavy-atom motions. We have observed that the fast-decaying component of normal fluorescence disappears abruptly below the glass temperature of the solvent (Figure 5). This supports the idea that solvent fluctuations assist tunneling in the proton relay of 7HQ along a H-bonded alcohol chain. A similar conclusion was reached for temper-

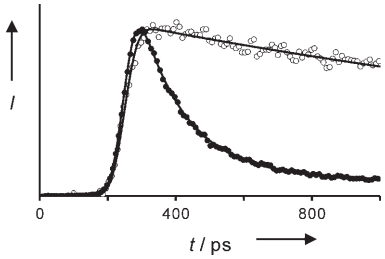

Figure 5. Normal-fluorescence kinetic profiles of 7HQ in *n*-heptane with [C_2H_5OH] of 20 mM measured at 180 (open circles) and 200 K (filled circles). The sample was excited at 355 nm and monitored at 420 nm.

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ature-dependent rate constants and temperature-independent KIE in the ground-state reverse proton transfer of 7HQ in neat alcohols.[11]

The picture of the ESPT mechanism in the cyclically H-bonded complex of 7HQ–$(ROH)_2$ is in line with the novel idea of Leutwyler et al. that photoexcited 7HQ–$(NH_3)_3$ in the gas phase requires the additional excitation of ammonia-wire vibrations to undergo proton transfer, and this reveals the crucial role of the coordinated solvent in proton tunneling.[1] Note that 7HQ–$(CH_3OH)_2$ in the gas phase does not undergo ESPT although 7HQ–$(CH_3OH)_3$ does.[22] The ESPT activity only in the 7HQ–$(CH_3OH)_3$ cluster has been attributed to shortened heavy-atom distances between the prototropic groups of 7HQ and nearby H-bonded methanol molecules. The efficiency of proton tunneling is closely related to the distances of heavy atoms in the reaction coordinates. The slight reorganization of $\mathbf{N_b}$ in condensed phases to form the pretunneling configuration having optimal bond angles and short H-bond lengths can be achieved by the assistance of solvent fluctuations.

In summary, the triple proton transfer of cyclically H-bonded 7HQ–$(ROH)_2$ complexes formed in nonpolar *n*-alkanes occurs asymmetrically on a timescale of 10–200 ps with unusually large, temperature-independent, and viscosity-dependent KIEs near room temperature. The ESPT is triggered by proton transfer from the alcohol molecule to the imino group and completed by rapid proton transfer from the enol group to the transient alkoxide moiety. Thus, intrinsic proton relay is governed by single proton tunneling to the nitrogen atom, although heavy-atom motions, depicted as a wavy arrow in Scheme 2, assist the H-bonded complex of $\mathbf{N_b}$ in reaching the optimal precursor configuration. Tunneling in our system is conceptually identical to vibrationally assisted tunneling observed in enzymatic proton transfer. Solvent fluctuations replace low-frequency protein motions in our system. The detailed dynamics of ESPT in $\mathbf{N_b}$ requires multidimensional reaction coordinates to be described properly and thus poses great theoretical challenges.

Experimental Section

7HQ (99%) from Acros, alcohols, and *n*-alkanes (anhydrous) were used as purchased. The protic hydrogen atoms of 7HQ and ROH were exchanged with ^{1}H (H) and ^{2}H (D) atoms for proton-inventory experiments by dissolving 7HQ in nonpolar solvents containing RO^1H and RO^2H (isotopic purity $\geq$99.5%), respectively. The concentrations of 7HQ were kept at 1×10^{-5} M in our samples. Absorption spectra were obtained with a UV/Vis spectrophotometer (Scinco, S-3100), and emission spectra with a home-built fluorimeter.[20] An actively/passively mode-locked 25 ps Nd:YAG laser (Quantel, YG 701) and a 10 ps streak camera (Hamamatsu, C2830) attached to a CCD detector (Princeton Instruments, RTE128H) were employed to monitor fluorescence kinetics.[20] Samples were excited with third-harmonic pulses (355 nm) of the laser. Unless specified otherwise, static and kinetic measurements were carried out at 23 °C.

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