

Supporting information

How Fast Can a Proton-Transfer Reaction Be Beyond the Solvent-Control Limit?

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Supporting Information Available:

- A. Vibration assisted tunneling theory
- B. MD simulations of oxygen atoms intermolecular vibrations in the proton wire of wt-GFP
- C. The ESPT geminate recombination model

A. Vibration assisted tunneling theory

A proton tunneling theory in solids based on intermolecular vibration was developed by Goldanskiĭ and coworkers¹ in the eighties of the previous century. When the tunneling probability is large, the limiting rate is the proton attempt frequency. We suggest that the attempt frequency is the intermolecular vibration frequency i.e. $\omega_Q=200\text{cm}^{-1}$, leading to $\tau_{PT}=10^{-13}\text{s}$ as the limit for ESPT processes. Another approach for finding the limiting rate for ESPT would be the TST theory. The preexponential factor of the reaction rate constant in the TST theory is $k_B T/\hbar \approx 10^{13}\text{s}^{-1}$. It is derived from breaking a chemical bond and providing the product a thermal energy $k_B T$. The thermal velocity of a proton (at room temperature) is $\sim 2\text{km/s}$. The proton needs to move about 1\AA along the $\text{O}-\bar{\text{H}}\cdots\text{O}$ intermolecular bond in order to form the product $\text{O}^-\cdots\text{H}-\text{O}$. The time it takes is $\sim 50\text{fs}$.

The tunneling rate is given by¹

$$k(T) = \nu \exp \left\{ -J(R_0) + \frac{1}{8} \sum_K \partial J / \partial Q_K \times \coth(\hbar \Omega_K / 4 K_B T) \right\} \quad (\text{S1})$$

with

$$J(R) = 2S(R) / \hbar = (2 / \hbar) \int \left\{ 2m_H [U(x, R) - E_H(R)] \right\}^{1/2} dx \quad (\text{S2})$$

where ν is a frequency prefactor of the order of magnitude 10^{14} s^{-1} , Ω_K the frequencies of inter-molecular vibrations, Q_K their dimensionless normal coordinates, K_B the Boltzmann constant, and T is the temperature. $E_H(R)$ and $U(x, R)$ are the total and the potential energy of the tunneling atom, respectively, depending on the distance R between reagents ($\text{O}^-\cdots\text{O}$). R_0 is the equilibrium distance. Function $J(R)$ is an integral, determining the transparency of the potential barrier of tunneling — it equals twice the quasi-classical action $S(R)$. For the hydrogen atom in the under-barrier interval between the turning points. At $T \rightarrow 0$ Eq. (S1) results in the quantum low-temperature limit of the reaction rate constant. At higher temperatures $T > \hbar \Omega_K / 4 K_B$ the intermolecular vibrations become classical and Eq. (S1) is simplified to $k(T) = \nu \exp \{-J(R_0) + \alpha T\}$ where α depends on the medium elastic properties.

B. MD simulations of oxygen atoms intermolecular vibrations in the proton wire of wt-GFP

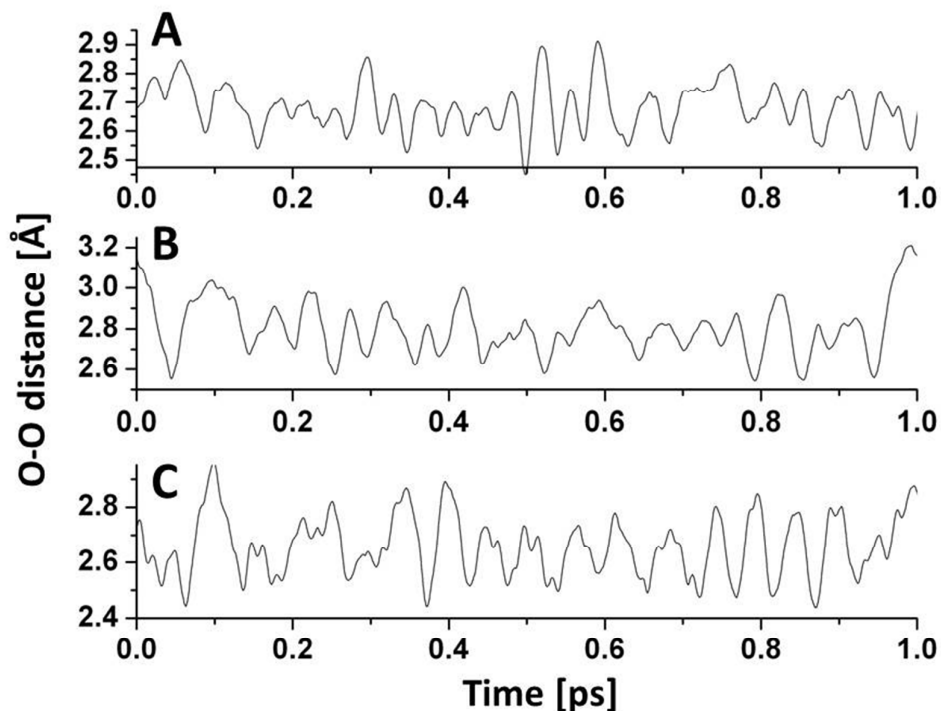
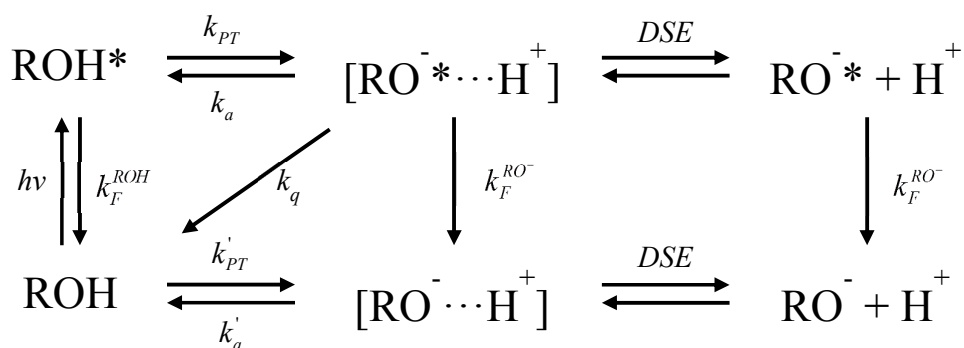


Figure S1: The O-O distance between two adjacent oxygen atoms of the total four oxygen atoms in the proton wire of wt-GFP along the MD simulations of 1ps. Plot A shows the O(Cro)-O(Wat25) distance with an average distance of 2.68 Å, Plot B demonstrates the O(Wat25)-O(Ser205) distance with an average distance of 2.75 Å and Plot C illustrates the O(Ser205) sidechain-O2(Glu222) distance with an average distance of 2.65 Å.

C. The ESPT geminate recombination model

Scheme S1 shows a model that describes the photoprotolytic cycle of a photoacid.^{2,3}



Scheme S1: Photoprotolytic cycle of Photoacids. DSE stands for Debye-Smoluchowski equation, see text

The ESPT geminate recombination model accounts not only for the proton transfer to the solvent step, but also to the probability that the proton recombines with the excited state deprotonated molecule to reform an excited state photoacid. The proton geminate recombination step is seen as a nonexponential long-time fluorescence tail that obeys a power law $t^{-\alpha}$ decay. The decay law is sensitive to the proton diffusion space dimension.

Reversible and irreversible photoprotolytic cycles of photoacids

Excitation of a photoacid solution at pH lower than its ground-state pK_a , generates a vibrationally relaxed, electronically excited ROH molecule (denoted by ROH*) that initiates a photoprotolytic cycle (Scheme S1). Proton dissociation, with an intrinsic rate constant, k_{PT} , leads to the formation of an ion-pair $RO^{-*}\cdots H^+$ that subsequently forms an unpaired RO^{-*} and a solvated proton, which diffuses into the bulk of the solution. The proton and RO^{-*} may recombine via reversible (adiabatic) recombination with a rate constant, k_a , and reform the excited acid, ROH*. In general, back-protonation may also proceed by an irreversible (non-adiabatic) pathway, involving fluorescence quenching of the RO^{-*} by a proton with a rate constant, k_q , forming the ground-state ROH.

Removal of an ion-pair from the contact radius, a , to infinity is described by the transient numerical solution of the Debye-Smoluchowski equation (DSE)^{4,5}. The motion of the transferred proton in water near the photoacid depends strongly on the electrical potential existing between it and the deprotonated form. The diffusion-assisted geminate recombination of RO^{-*} with the proton can be quantitatively described with the use of a numerical solution of the DSE under the initial and boundary conditions of the photoprotolytic process. In addition, the fluorescence lifetimes of all excited species are considered, with $1/k_F^{ROH} = \tau_{ROH}$ for the acid, and $1/k_F^{RO^{-}} = \tau_{RO^{-}}$ for the conjugate base. Generally, $k_F^{RO^{-}}$ and k_F^{ROH} are much smaller than both the proton-reaction and the diffusion-controlled rate constants. The amplitude of the long-time fluorescence tail of ROH* depends on the intrinsic rate constants, k_a and k_{PT} , on the proton-diffusion coefficient, D_H^+ , and on the electrical potential between RO^{-*} and the proton.

Time resolved fluorescence data analysis using the geminate recombination model

HPTS is a negatively charged reversible mild photoacid with a $pK_{a,chem}^* \approx 0.7$ ($pK_{a,chem}^* = pK_a^* - \Delta pK_{a,elec}^* = 1.3 - 0.6$). Mild photoacids with $pK_{a,chem}^* > 0$ transfer a proton within the excited state lifetime to H_2O but not to alcohols like methanol and ethanol and other protic liquids. It is estimated that the ESPT rate constant k_{PT} of HPTS to methanol is about four orders of magnitude smaller than in H_2O . In H_2O $k_{PT} \approx 10^{10} s^{-1}$, ($\tau_{PT} \approx 100$ ps) and thus ESPT rate for methanol is about $\sim 10^6 s^{-1}$, smaller by a factor of 200 than the radiative rate $k_F \sim 2 \times 10^8 s^{-1}$.

HPTS RO^- is four times negatively charged and the Coulomb attraction $RO^{-*} \cdots H^+$ is very large. HPTS serves therefore as an example for the geminate recombination model since the ROH fluorescence relative tail intensity is very large and is easily measured even at long times of about 20 ns, about four times longer than the fluorescence decay time of both ROH and RO^- forms. The fluorescence long-time tail, when compensated by multiplying the signal by $\exp[t/\tau_F]$ for the finite excited-state lifetime decays as a power law $t^{-\alpha}$. The asymptotic long-time expression for the amplitude and the decay law is given by:

$$I_f^{ROH}(t) \sim \frac{\pi a^2 k_r \exp[-V(a)]}{2k_{PT}(\pi D)^{d/2}} t^{-d/2} \quad (1)$$

where a is the reaction-sphere radius, k_{PT} and k_r are the intrinsic ESPT and geminate recombination rates occurring on the reaction sphere, $-V(a) = R_D/a$ is the potential at the reaction sphere, D is the mutual diffusion coefficient between RO^- and H^+ and d is the diffusion-space dimension. This expression predicts a non-exponential fluorescence decay that fits a power law of $t^{-d/2}$. Equation 1 indicates that the amplitude of the long fluorescence depends on many parameters, but the decay law depends only on the dimension of the diffusion space.

We used in the past the spherically symmetric diffusion problem (SSDP) program of Krissinel and Agmon⁶ that was designed to solve the geminate recombination problem, in order to fit the time-resolved emission signals of HPTS and other photoacids in bulk water and in a confined volume. The parameters that govern the time-resolved emission of the ROH or RO^- signals are the ESPT rate constant k_{PT} and the intrinsic geminate recombination rate k_a . k_{PT} controls the initial ROH signal decay and thus it can be exclusively determined with minimum interference of all the other

parameters: D , a , d , R_D , k_F^{ROH} and $k_F^{RO^-}$, which are parameters that control the amplitude and shape of the intermediate and long times^{2,3}. The proton diffusion constant for bulk water is $9 \times 10^{-5} \text{ cm}^2/\text{s}$. We used this value for H_2O samples. For the reaction sphere radius a we used $a=6 \text{ \AA}$. The Coulomb attraction potential is defined by R_D , and for the dielectric constant of water, $\epsilon_{\text{H}_2\text{O}} = 78$, and HPTS RO^- charge of $-4e$, we receive that $R_D=28 \text{ \AA}$. It means that at 28 \AA the Coulomb potential and the thermal energy $k_B T$ are equal where T is room temperature. As seen in equation 1, R_D affects exponentially the amplitude of the ROH nonexponential fluorescence tail.

The excited state radiative lifetimes for both ROH and RO^- forms of HPTS are similar at $\tau_F \approx 5.4 \text{ ns}$. The excited state lifetime exponentially decreases both the ROH and RO^- signals. The intensity of the time-resolved emission signals of both ROH and RO^- forms at long times is determined by the radiative rate. In bulk water and D_2O the HPTS ROH fluorescence is considered as a textbook example for the reversible diffusion assisted proton geminate recombination model^{2,3}. The ROH signal in water and D_2O could be fitted in almost perfect agreement to the model to about four orders of magnitude of intensity and within a large time window of 0-20 ns extended to about four lifetimes. The bulk water parameters are $k_{PT}=10^{10} \text{ s}^{-1}$, $k_a=7.3 \text{ \AA/ns}$, $D=9 \times 10^{-5} \text{ cm}^2/\text{s}$, $d=3$, $a_0=6 \text{ \AA}$ and $\tau_F=5.4 \text{ ns}$. τ_F^{ROH} is measured by exciting HPTS in ethanol and $\tau_F^{RO^-}$ either by the long time slope of the TCSPC signal measured at $\lambda \geq 520 \text{ nm}$ or by direct excitation of HPTS RO^- form in a basic solution.

Table S1 provides the fitting parameters of the ROH fluorescence signals of HPTS in water/methanol mixtures. Note that the ESPT rate k_{PT} and the proton diffusion coefficient decrease as the methanol concentration increases.

Table S1: fitting parameters of the HPTS ROH fluorescence signal in water/methanol mixtures as a function of methanol fraction⁷

mol%	ϵ	R_D (Å)	D (Å ² /cm)	k_{PT}	k_a	pK_a^*
0	80	28.3	930	8.0	7.2	1.28
8.4	78.5	28.8	710	4.3	6.7	1.55
15.1	75	30.2	570	3.0	5.9	1.74
25	69	32.8	450	1.5	4.2	2.05
37	63	35.9	370	0.8	3.2	2.4
64	49	46.2	260	0.22	0.62	2.89

k_{PT} decreases by a factor of 40 in a water/methanol mixture of 64% mole percent methanol from its value at neat H₂O.

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