

Electronic Supplementary Information for

Improved Analysis of Excited State Proton Transfer Kinetics by the Combination of Standard and Convolution Methods

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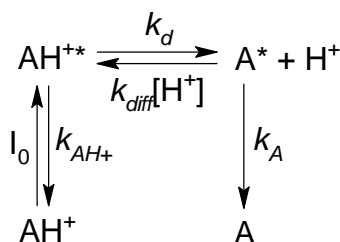
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ESPT of 7-hydroxy-4-methylflavylium in water: 2 species

Given the reversible reactions represented by Scheme 1S:

Scheme 1S.



the time evolution of the species can be represented by the following differential equation:

$$\frac{d}{dt} \begin{bmatrix} \text{AH}^{+*} \\ \text{A}^* \end{bmatrix} = \begin{bmatrix} -X_w & k_{diff}[\text{H}^+] \\ k_d & -Y_w \end{bmatrix} \times \begin{bmatrix} \text{AH}^{+*} \\ \text{A}^* \end{bmatrix} \quad (\text{S1})$$

where $X_w = k_{AH^+} + k_d$ and $Y_w = k_A + k_{diff}[\text{H}^+]$. The initial concentrations of AH^{+*} and A^* are $[\text{AH}^{+*}]_0$ and 0, respectively, and the time-dependent concentrations, $C_i(t)$, of the species in the excited state can be written in integrated form as $C_i(t) = P_i \otimes C_{i\delta}$ based on the concept of convolution (Reference 4 of the paper), where P_i is the rate of production of the species C_i and $C_{i\delta}$ is the respective delta response function. For the flavylium cation and the quinonoidal base the respective rates of production and delta responses are:

$$P_{\text{AH}^{+*}} = [\text{AH}^{+*}]_0 \delta(t) + k_{diff}[\text{H}^+][\text{A}^*] \quad (\text{S2})$$

$$P_{\text{A}^*} = k_d[\text{AH}^{+*}] \quad (\text{S3})$$

$$C_{\text{AH}^{+*}\delta} = [\text{AH}^{+*}]_0 \delta(t) = e^{-X_w t} \quad (\text{S4})$$

$$C_{\text{A}^*\delta} = [\text{A}^*] \delta(t) = e^{-Y_w t} \quad (\text{S5})$$

Thus, the temporal evolutions of the concentrations of AH^{+*} and A^* are:

$$[AH^{+*}] = [AH^{+*}]_0 e^{-X_w t} + k_{diff} [H^+] [A^*] \otimes e^{-X_w t} \quad (S6)$$

$$[A^*] = k_d [AH^{+*}] \otimes e^{-Y_w t} \quad (S7)$$

Equations S6 and S7 can be solved by Laplace transformation theory, $\mathcal{L}\{f(t)\} = \int_0^{\infty} e^{-st} f(t) dt$, and the solution for reversible first order reactions is described in reference 4. Here we are interested only in the temporal evolution of $[A^*]$ and do not need to solve equation S6 since $[AH^{+*}]$ will serve as the effective Instrument Response Function (in practical terms, $k_d[AH^{+*}]$ will operate as if it were a delta function). From the algebraic properties of convolution, the convolution of a delta function with some other function results in the function itself at the position of the delta function. Thus, the time evolution of the quinonoidal base using the signal of AH^{+*} as the IRF is:

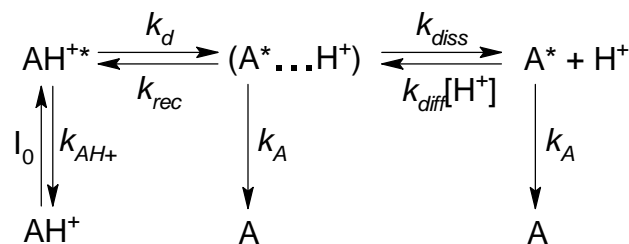
$$[A^*] = e^{-Y_w t} \quad (S8)$$

and the monoexponential lifetime obtained gives the two rate constants for the deactivation of the excited state of A^* , as experimentally observed for the ESPT of HMF in water.

ESPT of 7-hydroxy-4-methylflavylium in water-dioxane mixtures and functionalized flavylium salts anchored in SDS micelles: 3 observable species involved in ESPT

Given Scheme 2S below:

Scheme 2S.



the corresponding kinetics obey the differential equation,

$$\frac{d}{dt} \begin{bmatrix} AH^{+*} \\ (A^* \cdots H^+) \\ A^* \end{bmatrix} = \begin{bmatrix} -X & k_{rec} & 0 \\ k_d & -Y & k_{diff}[H^+] \\ 0 & k_{diss} & -Z \end{bmatrix} \times \begin{bmatrix} AH^{+*} \\ (A^* \cdots H^+) \\ A^* \end{bmatrix} \quad (S9)$$

where $X = k_{AH^+} + k_d$, $Y = k_A + k_{rec} + k_{diss}$ and $Z = k_A + k_{diff}[H^+]$ represent the sums of the rate constants for all the decay processes of AH^{+*} and $(A^* \cdots H^+)$, respectively. Since all of the processes indicated in Scheme 2S are first (or pseudo-first) order, it is also possible in this case to write the time-dependent concentration $C_i(t)$ of the species directly in the integrated form, as done in the previous case. At pHs below 2, only the flavylium cation is present in solution and the initial concentrations of $[AH^{+*}]$, $(A^* \cdots H^+)$ and $[A^*]$ are $[AH^{+*}]_0$, 0 and 0, respectively. Thus, the Delta responses $C_{i\delta}$ can be written as:

$$[AH^{+*}]\delta(t) = e^{-Xt} \quad (S10)$$

$$[A^* \cdots H^+]\delta(t) = e^{-Yt} \quad (S11)$$

$$[A^*]\delta(t) = e^{-Zt} \quad (S12)$$

Because the initial concentrations $[A^* \cdots H^+]_0$ and $[A^*]_0$ are zero, the production rates P_i are:

$$P_{AH^{+*}} = [AH^{+*}]_0 \delta(t) + k_{rec} [A^* \cdots H^+] \quad (S13)$$

$$P_{A^* \cdots H^+} = [A^* \cdots H^+]_0 \delta(t) + k_d [AH^{+*}] + k_{diff} [H^+] [A^*]$$

$$P_{A^* \cdots H^+} = k_d [AH^{+*}] + k_{diff} [H^+] [A^*] \quad (S14)$$

$$P_{A^*} = [A^*]_0 \delta(t) + k_{diss} [A^* \cdots H^+]$$

$$P_{A^*} = k_{diss} [A^* \cdots H^+] \quad (S15)$$

Substituting the Delta responses and production rates of the species in the equation $C_i(t) = P_i \otimes C_{i\delta}$, the concentrations $C_i(t)$ are given by:

$$[AH^{+*}] = [AH^{+*}]_0 \delta(t) \otimes e^{-Xt} + k_{rec} [A^* \cdots H^+] \otimes e^{-Xt}$$

$$[AH^{+*}] = [AH^{+*}]_0 e^{-Xt} + k_{rec} [A^* \cdots H^+] \otimes e^{-Xt} \quad (S16)$$

$$[A^* \cdots H^+] = k_d [AH^{+*}] \otimes e^{-Yt} + k_{diff} [H^+] [A^*] \otimes e^{-Yt} \quad (S17)$$

$$[A^*] = k_{diss} [A^* \cdots H^+] \otimes e^{-Zt} \quad (S18)$$

Thus, taking the decay of AH^{+*} measured at 480 nm as the effective IRF that generates the decay at 620 nm, the overall product $[B^*]$ will be the sum of the concentrations of the geminate pair and the quinonoidal base, i.e., $[B^*] = [A^* \cdots H^+] + [A^*]$. From the properties of Laplace transforms, $\mathcal{L}\{f \otimes g\} = \mathcal{L}\{f\} \cdot \mathcal{L}\{g\}$ and from Laplace transform tables $\mathcal{L}\{e^{-at}\} = 1/(s+a)$. The Laplace transforms of S17 and S18 are, respectively:

$$\overline{[A^* \cdots H^+]} = \frac{k_d \overline{[AH^{+*}]}}{(s+Y)} + \frac{k_p [H^+] \overline{[A^*]}}{(s+Y)} \quad (S19)$$

$$\overline{[A^*]} = \frac{k_{diss} \overline{[A^* \cdots H^+]}}{(s+Z)} \quad (S20)$$

In this case, the temporal evolutions of $[A^*\cdots H^+]$ and $[A^*]$ are not independent and equations S19 and S20 are coupled. The solution of S19 and S20 gives:

$$\overline{[A^*\cdots H^+]} = \frac{k_d \overline{[AH^{+*}]}(s+Z)}{(s+Y)(s+Z) - k_{diss}k_{diff}[H^+]} \quad (S21)$$

$$\overline{[A^*]} = \frac{k_{diss}k_d \overline{[AH^{+*}]}}{(s+Y)(s+Z) - k_{diss}k_{diff}[H^+]} \quad (S22)$$

Reorganizing the denominator in both equations leads to

$$\overline{[A^*\cdots H^+]} = \frac{k_d \overline{[AH^{+*}]}(s+Z)}{(s+\beta)(s+\gamma)} \quad (S23)$$

$$\overline{[A^*]} = \frac{k_{diss}k_d \overline{[AH^{+*}]}}{(s+\beta)(s+\gamma)} \quad (S24)$$

where $\beta = \frac{Y+Z - \sqrt{(Y-Z)^2 + 4k_{diss}k_{diff}[H^+]}}{2}$ and $\gamma = \frac{Y+Z + \sqrt{(Y-Z)^2 + 4k_{diss}k_{diff}[H^+]}}{2}$.

On the other hand, the inverse Laplace transform $\mathcal{L}^{-1}\left\{\frac{s+\alpha}{(s+a)(s+b)}\right\}$ is $\frac{(\alpha-a)}{b-a}e^{-at} - \frac{(\alpha-b)}{b-a}e^{-bt}$ and

the inverse of $\mathcal{L}^{-1}\left\{\frac{1}{(s+a)(s+b)}\right\}$ is $\frac{1}{b-a}e^{-at} - \frac{1}{b-a}e^{-bt}$. With these pieces of information, the

solutions of S23 and S24 are:

$$[A^*\cdots H^+] = k_d[AH^{+*}] \otimes \left\{ \frac{1}{\gamma-\beta} \left[(Z-\beta)e^{-\beta t} - (Z+\gamma)e^{-\gamma t} \right] \right\} \quad (S25)$$

$$[A^*] = k_d[AH^{+*}] \otimes \left[\frac{k_{diss}}{\gamma-\beta} (e^{-\beta t} - e^{-\gamma t}) \right] \quad (S26)$$

$$[B^*] = [A^*\cdots H^+] + [A^*] \quad (S27)$$

$$[B^*] = k_d[AH^{+*}] \otimes \left\{ \frac{1}{\gamma-\beta} \left[(Z-\beta+k_{diss})e^{-\beta t} + (\gamma-Z-k_{diss})e^{-\gamma t} \right] \right\} \quad (S28)$$

where the term $k_d[AH^{+*}]$ is the effective IRF. Equation S28 predicts a double-exponential decay with $\tau_1 = 1/\beta$ and $\tau_2 = 1/\gamma$ for a system of two reactions coupled in series, in agreement with the experimental results for HMF in aqueous-organic solvent mixtures and for functionalized flavylum salts anchored in SDS micelles.

Determining the individual rate constants

The differential Equation S9 (equivalent to equation 5 of the paper) predicts triple-exponential decays for all species, $X_i^* = \text{AH}^+^*$, $(\text{A}^*\cdots\text{H}^+)$ and A^* :

$$[X_i^*] = a_{i,1}e^{-\lambda_1 t} + a_{i,2}e^{-\lambda_2 t} + a_{i,3}e^{-\lambda_3 t} \quad (\text{S29})$$

The reciprocals of the three decay times, $\lambda_j = 1/\tau_j$, are the eigenvalues of the constant matrix \mathbf{k} , which can be expressed as a function of the diagonal reciprocal decay time matrix $\boldsymbol{\lambda}$, and the pre-exponential coefficient ($a_{i,j}$) matrix \mathbf{a} , as:^{17,S1}

$$\mathbf{k} = \mathbf{a}\boldsymbol{\lambda}\mathbf{a}^{-1} \quad (\text{S30})$$

However, Equation S30 cannot be solved analytically in the present case because the pre-exponential coefficients ($a_{i,j}$) of the “matrix of concentrations” \mathbf{a} cannot be equated to the experimental coefficients of the “matrix of fluorescence intensities” \mathbf{A} ,¹⁷ because there are 3 kinetically discernible species but only 2 are spectroscopically observable. Thus, the matrix \mathbf{A} is a 2×3 matrix with $A_{2,j} = a_{2,j} + a_{3,j}$ (assuming that the radiative rate constants of the free base A^* and the geminate pair $\text{A}^*\cdots\text{H}^+$ are equal). However, the analysis can be substantially improved by independently measuring the lifetime of the base ($1/k_{\text{A}} = 1.46 \times 10^{-10}$ s) in solutions with $\text{pH} > 9$ and the lifetime of the acid in the absence of the excited state proton transfer process ($1/k_{\text{AH}^+} = 3.13 \times 10^{-9}$ s), taken to be equal to the lifetime of the parent compound 7-methoxy-4-methyl-flavylium ion (MMF). Since the 9 pieces of experimental information (3 decay times, 3 pre-exponential coefficients at 480 nm and 3 pre-exponential coefficients at 620 nm, listed in Table 1S) are sufficient to evaluate the remaining 4 unknowns, \mathbf{k} can be estimated by minimization of the deviations between the calculated and experimental decay times and pre-exponential coefficients.^{17,9}

The analysis of the results for the water:dioxane mixture with $x_{\text{Dx}} = 0.18$, based on Scheme 2S (equivalent to Scheme 3 of the paper), provides the individual values of k_{d} , k_{rec} , k_{diss} and k_{diff} (shown in Figure 1S) and separates the rate constants involved in the proton transfer processes (deprotonation and recombination) from the diffusional ones (pair dissociation and diffusion-controlled encounter).

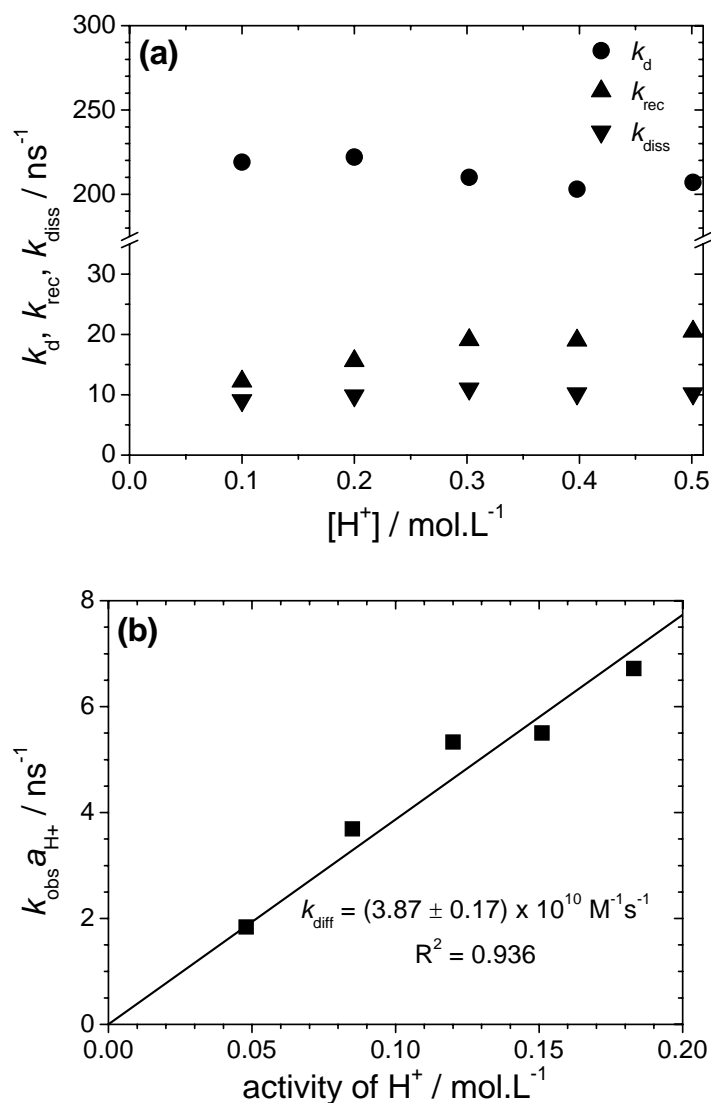


Figure 1S. (a) Deprotonation, recombination and dissociation rate constants (k_d , k_{rec} , k_{diss}) as a function of $[\text{H}^+]$; (b) rate constants for diffusion-controlled formation of the geminate pair ($k_{diff}a_{\text{H}^+}$) in water-1,4-dioxane ($x_{\text{Dx}} = 0.18$), as a function of the activity of H^+ .

The deprotonation constant k_d (average value of $2.1 \pm 0.1 \times 10^{11} \text{ s}^{-1}$) is smaller than that observed for HMF in water⁹ ($2.5 \pm 0.4 \times 10^{11} \text{ s}^{-1}$) and reflects the decrease in dielectric constant of the solution rather than a disruption of the hydrogen-bonding network, because water clusters are still present in the mixtures at $x_{\text{Dx}} = 0.18$.^{S2,S3} The behavior of the recombination rate constant k_{rec} explains why the geminate pair is detected in $\text{H}_2\text{O}:\text{Dx}$ mixtures and not in water. In water, k_{rec} is negligible (expected⁹ to be smaller than $2 \times 10^9 \text{ s}^{-1}$) and the geminate pair is not detected because the efficiency of pair

recombination [$k_{\text{rec}}/(k_{\text{rec}} + k_{\text{diss}})$] is much too small. On the other hand, the addition of cosolvent increases k_{rec} to *ca.* $1.7 \pm 0.3 \times 10^{10} \text{ s}^{-1}$ at $x_{\text{Dx}} = 0.18$, making it of the same order of magnitude as k_{diss} ($1.0 \pm 0.1 \times 10^{10} \text{ s}^{-1}$), resulting in a pair recombination efficiency of 0.6.

The dissociation constant of the geminate pair, k_{diss} , depends on the viscosity η of the solution and can be estimated^{S4} from the diffusion coefficient of the species D_i , given by $D_i = k_{\text{B}}T/(6\pi\eta R_i f_i)$, where

$$f_i = \left[1.5 \frac{R_{\text{H}_2\text{O}}}{R_i} + \left(1 + \frac{R_{\text{H}_2\text{O}}}{R_i} \right)^{-1} \right]^{-1}.$$

In this equation, k_{B} is the Boltzmann constant and R_i is the van der Waals radius of the species, calculated with the program GEPOL.^{S5} Assuming that the binding energy of the encounter complex is zero and taking $R_{\text{H}_2\text{O}} = 1.4 \text{ \AA}$, $R_{\text{H}_3\text{O}_2^+} + R_{\text{HMF}} = 5.9 \text{ \AA}$ and $\eta = 2.19 \text{ cP}$ (interpolated from data at $T = 25 \text{ }^\circ\text{C}$ in reference S6), one obtains $k_{\text{diss}} = 3(D_{\text{H}_3\text{O}_2^+} + D_{\text{HMF}})/(R_{\text{H}_3\text{O}_2^+} + R_{\text{HMF}})^2 = 1.1 \times 10^{10} \text{ s}^{-1}$, which is in good agreement with the experimental value.

Table 1S. Decay times ($\tau_j \pm 10\%$) and pre-exponential coefficients ($A_{i,j}$) of HMF in water:1,4-dioxane solutions ($x_{\text{Dx}} = 0.18$) at $T = 25 \text{ }^\circ\text{C}$ obtained from global analysis of the decays collected at 480 nm (emission of AH^{+*} , $i = 1$) and at 620 nm (emission of A^* , $i = 2$), with excitation at 434 nm. The reduced chi-squared (χ_i^2) of the global analyses is also presented.

$[\text{H}^+]/$ $\text{mol}\cdot\text{L}^{-1}$	$\tau_1 /$ ps	$\tau_2 /$ ps	$\tau_3 /$ ps	$A_{1,1}$	$A_{1,2}$	$A_{1,3}$	$A_{2,1}$	$A_{2,2}$	$A_{2,3}$	χ_1^2	χ_2^2
0.50	168	48.8	4.40	0.03	0.07	0.90	1.00	-0.08	-0.92	1.03	1.00
0.40	170	49.0	4.50	0.03	0.06	0.91	1.00	-0.07	-0.93	1.06	1.10
0.30	169	47.5	4.35	0.03	0.06	0.91	1.00	-0.08	-0.92	0.93	1.01
0.20	158	53.3	4.35	0.02	0.06	0.92	1.00	-0.09	-0.91	1.02	1.03
0.10	157	57.8	4.35	0.01	0.05	0.94	1.00	-0.07	-0.93	0.95	1.08
1.0×10^{-9}	146	-	-	-	-	-	1.00	-	-	-	1.06

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