Supporting Information

Excited-State Intermolecular Proton Transfer of Firefly Luciferin V. Proton Transfer to Fluoride Base

by

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Supporting Information Available

a. The Smoluchowski model.

The Smoluchowski Model

The Smoluchowski model is used to describe the diffusion-assisted irreversible reaction $A + B \rightarrow AB,$ where the concentration of B is in a great excess over A. In this study it is used to fit the time-resolved emission decay of the protonated and deprotonated forms of d-luciferin in a highly concentrated F^- aqueous solution.

We assumed that the F^- transport toward the NROH* is the rate limiting step. The mathematical and computational details of the Smoluchowski model are given elsewhere.[1] According to the Smoluchowski model, the survival probability of a single (static) donor, an excited NROH molecule (the A particle), due to its irreversible reaction with a $c = [Ac^-]$ (B is the Ac^- ion in the liquid) is given by[2]

$$S(t) = \exp\left(-c\int_0^t k(t')dt' \right) \tag{1}$$

where $k(t)$ is the time-dependent rate coefficient for the donor-acceptor pair

$$k(t) = k_a\, p(a,t) \tag{2}$$

whose intrinsic proton transfer rate constant is k_a. The pair (NROH*/Ac^-) density distribution, $p(r, t)$, is governed by a three-dimensional Smoluchowski equation (diffusion in a potential $U(r)$). When $U(r) = 0$, the above equations are analytically solvable for $k(t)$. Szabo[2] found an approximate expression for the time-dependent rate constant for the instances when $U(r) \neq 0$. When a potential is introduced, it behaves correctly at both t=0 and t=∞, i.e.,

$$k(0) = k_{PT} e^{-\beta U(a)}, \quad k(\infty) = [k(0)^{-1} + k_D^{-1}]^{-1} \tag{3}$$

where $$k_D = 4\pi\, D a_e \tag{4}$$

is the diffusion-controlled rate constant, and a_e is an effective radius that depends on the Coulomb pair attraction potential.

The mutual diffusion constant of d-luciferin and F^- is estimated to be around 1.10^{-5} cm^2/s for a dilute aqueous solution with a viscosity of 1 centipoise. In concentrated NaAc solutions of several molars the viscosity rises with the concentration, whereas the mutual diffusion constant decreases, since it scales inversely with the viscosity. The effective long-time reaction rate constant is given by:

$$k(\infty) = \left(k(0)^{-1} + k_D^{-1} \right)^{-1} \tag{5}$$

where k_0 and k_D are the intrinsic and diffusion-controlled rate constants, respectively.

If $k_0 \ll k_D$ then $k_\infty \ll k_D$, and the reaction is nearly diffusion-controlled. Since the diffusion constant is small, the pseudo-first order reaction rate constant is given by

$$k_D^{'} = 5 \times 10^9 \cdot c_B \, \mathrm{s}^{-1} \tag{6}$$

where c_B is the base concentration in molar units.

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1. Cohen, B.; Huppert, D.; Agmon, N. *J. Phys. Chem. A* **2001**, 105, 7165.

2. Szabo, A. *J. Phys. Chem.* **1989**, 93, 6929.