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“Cyclic Transmembrane Charge Transport Mediated by Pyrylium and Thiopyrylium Ions”, Rafail F. Khairutdinov and James K. Hurst, Department of Chemistry, Washington State University, Pullman, WA, USA 99164-4630

Derivation of Kinetic Equations for Transmembrane Diffusion of Neutral Pyrylium Radicals. All experiments reported were made under conditions where on average less than 0.6 TPP₉ or TPTPO radicals per vesicle were generated by the laser pulse. Under these conditions, the rate equations describing the radical decay are:

$$\frac{d[\text{Pyr}^\circ]_e}{dt} = -\tau_0^{-1}[\text{Pyr}^\circ]_e + \tau^{-1}\left(-[\text{Pyr}^\circ]_e + [\text{Pyr}^\circ]_i\right)$$  \hspace{1cm} (S1)

$$\frac{d[\text{Pyr}^\circ]_i}{dt} = -(nk_q + \tau_0^{-1})[\text{Pyr}^\circ]_i + \tau^{-1}\left(-[\text{Pyr}^\circ]_i + [\text{Pyr}^\circ]_e\right)$$  \hspace{1cm} (S2)

where the concentration subscripts i and e refer to the intravesicular and extravascular location of the radicals, $\tau_0$ is the characteristic time for decay of Pyr$^\circ$ in the absence of Co(bpy)$_3^{3+}$, $\tau$ is the characteristic time for transmembrane diffusion of Pyr$^\circ$, $k_q$ is the rate constant of (Pyr$^\circ$) oxidation by Co(bpy)$_3^{3+}$ and n is the number of Co(bpy)$_3^{3+}$ ions located within a particular vesicle. Equations S1 and S2 can be solved analytically to give for the total (intravesicular and extravascular) concentration of Pyr$^\circ$:

$$\frac{[\text{Pyr}^\circ](t)}{[\text{Pyr}^\circ](0)} = F(t, \tau_0, \tau, nk_q) = A_1(\tau_0, \tau, nk_q)e^{-\lambda_1 t} + A_2(\tau_0, \tau, nk_q)e^{-\lambda_2 t}$$  \hspace{1cm} (S3)

where $A_1(\tau_0, \tau, nk_q)$ and $A_2(\tau_0, \tau, nk_q)$ are constants and

$$\lambda_{1,2} = \frac{-2/\tau_0 + 2/\tau + nk_q}{2} \pm \sqrt{4/\tau^2 + n^2k_q^2}$$

within the population of vesicles follows the Poisson distribution, one obtains:

$$\frac{[\text{Pyr}^\circ](t)}{[\text{Pyr}^\circ](0)} = \sum_{n=0}^{\infty} \frac{m^n}{n!}\exp(-m)F(t, \tau_0, \tau, nk_q)$$  \hspace{1cm} (S4)

where $m = [\text{Co(bpy)}_3^{3+}]/[\text{ves}]$ is the average number of Co(bpy)$_3^{3+}$ ions per vesicle. The characteristic decay time is the first moment of the decay kinetics, so we have:

$$\tau' = \int_0^{\infty} \frac{[\text{Pyr}^\circ](t)}{[\text{Pyr}^\circ](0)} \, dt = \sum_{n=0}^{\infty} \frac{m^n}{n!} \int_0^{\infty} F(t, \tau_0, \tau, nk_q) \, dt$$  \hspace{1cm} (S5)

where $\tau'$ is the experimentally observed characteristic time for Pyr$^\circ$ decay.

If $k_q >> \tau^{-1}, \tau_0^{-1}$, it follows from Equation S5 that

$$\tau' = \frac{\tau_0}{\tau_0 + \tau}$$  \hspace{1cm} (S6)
and the characteristic decay time changes from $\tau_0$ in the absence of Co(bpy)$_3^{3+}$ to $\tau_0\tau/(\tau_0+\tau)$ at large Co(bpy)$_3^{3+}$ concentrations. When $\tau_0 \gg \tau$, $\tau' = \tau$, i.e., the rate of decay equals the rate of transmembrane diffusion of Pyr$^0$.

If $k_q << \tau^{-1}$, $\tau_0^{-1} << k_q << \tau^{-1}$, it follows from Equation S6 that $\tau' = \tau_0$, so that the characteristic decay time remains unchanged upon addition of Co(bpy)$_3^{3+}$.

Only the first limiting case, $k_q >> \tau^{-1}$, can account for the experimental data (Figure 11). Consequently, the experimental decay time measures the characteristic time for transmembrane diffusion of Pyr$^0$.

**Figure S1.** Kinetics of TPTP$^+$ hydrolysis in DHP vesicles. Reactions were monitored by changes in absorption at 400 nm in 40 mM acetate buffer, pH 11. Conditions: [TPTP$^+$]/[vesicle] = 160 (1) and [TPTP$^+$]/[vesicle] = 30 (2). Solid lines are best fits to a sum of two exponents with $\tau_1 = 13.5$ s and $\tau_2 = 353$ s (1) and to a single-exponential rate law with $\tau = 13.5$ s (2).

**Figure S2.** Emission spectra of TPTP$^+$. Conditions: in 40 mM acetate buffer, pH 5.0 (1), and bound to DHP vesicles at [TPTP$^+$]/[vesicle] = 30 (2) and [TPTP$^+$]/[vesicle] = 160 (3); $\lambda_{ex} = 400$ nm.