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Effect of a dispersion of electron transfer rates on steady-state catalytic electron transport in [NiFe]-hydrogenase and other enzymes.

Supplementary Information

Derivation of eq 5.

We note $F_{k_0}(t)$ the (cumulative) distribution function of k_0, i.e. the probability $P(k_0 < t)$ that k_0 takes a value lower than t, and $f_{k_0}(t)$ the density function of k_0 [that we loosely note $p(k_0)$ in the main text]. They are related to each other by $F_{k_0}(t) = \int_0^t f_{k_0}(u)du$.

$$F_{k_0}(t) = P\left(k_0^{(d=0)} \exp(-\beta d) < t\right) \tag{S1a}$$

$$= 1 - P\left(d < -\frac{1}{\beta}\ln\frac{t}{k_0^{(d=0)}}\right) \tag{S1b}$$

$$= 1 - F_d\left(-\frac{1}{\beta}\ln\frac{t}{k_0^{(d=0)}}\right) \tag{S1c}$$

Differentiation of eq S1c with respect to t gives:

$$f_{k_0}(t) = \frac{1}{\beta t}f_d\left(-\beta^{-1}\ln\frac{t}{k_0^{(d=0)}}\right) \tag{S2}$$

With

$$f_d\left(-\frac{1}{\beta}\ln\frac{t}{k_0^{(d=0)}}\right) = \begin{cases} 1/d_0 & \text{for } d \in [d_{\min}, d_{\max}] \\ 0 & \text{for any other value} \end{cases} \tag{S3}$$

and $d_{\max} = d_{\min} + d_0$, we get eq 5, with $k_0^{\min} = k_0^{\max}\exp(-\beta d_0)$:

$$f_{k_0}(t) = \begin{cases} 1/\beta d_0 t & \text{for } t \in [k_0^{\min}, k_0^{\max}] \\ 0 & \text{for any other value} \end{cases} \tag{S4}$$

Derivation of eq 6, and corresponding equation for a reductive wave.

For oxidative catalysis, the corrected current $i^\star$ is obtained by integrating eq 2 (derived in ref 5) across the distribution of k_0 values (eq 5), $i^\star = \int_{k_0^{\min}}^{k_0^{\max}} i(k_0) p(k_0) dk_0$ with $k_0^{\min} = k_0^{\max} \exp(-\beta d_0)$, and so:

$$\frac{i^\star}{i_{\text{ilim}}} = \int_{k_0^{\min}}^{k_0^{\max}} \frac{1}{1 + e_{\text{O/I}}^{-1}\left(1 + e_{\text{I/R}}^{-1}\right) + \frac{k_2}{u}\left\{e_{\text{I/R}}^{-1/2} + e_{\text{O/I}}^{-1/2}\left(1 + e_{\text{I/R}}^{-1}\right)\right\}} \frac{(\beta d_0)^{-1}}{u} du \qquad \text{(S5)}$$

Changing variables, we let

$$v^{\text{ox}} = \frac{k_2}{u}\left\{e_{\text{I/R}}^{-1/2} + e_{\text{O/I}}^{-1/2}\left(1 + e_{\text{I/R}}^{-1}\right)\right\} \qquad \text{(S6)}$$

so that

$$\frac{i^\star}{i_{\text{ilim}}} = -\frac{1}{\beta d_0}\int_{v_1^{\text{ox}}}^{v_2^{\text{ox}}} \frac{1}{a^{\text{ox}} + v^{\text{ox}}} \frac{1}{v^{\text{ox}}} dv^{\text{ox}} \qquad \text{(S7a)}$$

$$v_2^{\text{ox}} = \frac{k_2}{k_0^{\max}}\left\{e_{\text{I/R}}^{-1/2} + e_{\text{O/I}}^{-1/2}\left(1 + e_{\text{I/R}}^{-1}\right)\right\} \qquad \text{(S7b)}$$

$$v_1^{\text{ox}} = v_2^{\text{ox}}\exp(\beta d_0) \qquad \text{(S7c)}$$

with a^{ox} given by eq 6b. Integration, using $\int (a+v)^{-1}v^{-1}dv = a^{-1}\left[\ln(v) - \ln(a+v)\right]$, gives

$$\frac{i^\star}{i_{\text{ilim}}} = \frac{1}{\beta d_0}\frac{1}{a^{\text{ox}}}\left[-\ln v + \ln(a^{\text{ox}} + v)\right]_{v_2^{\text{ox}}\exp(\beta d_0)}^{v_2^{\text{ox}}} \qquad \text{(S8a)}$$

$$= \frac{1}{\beta d_0}\frac{1}{a^{\text{ox}}}\left(\beta d_0 + \ln\frac{a^{\text{ox}} + v_2^{\text{ox}}}{a^{\text{ox}} + v_2^{\text{ox}}\exp(\beta d_0)}\right) \qquad \text{(S8b)}$$

This is equivalent to eq 6 with $v_2^{\text{ox}} \equiv b_2^{\text{ox}}$.

When $k_2/k_0^{\max}$, and thus b_2, tends to zero, $i^\star/i_{\text{lim}}$ tends to $1/a^{\text{ox}}$ and the reversible limit is recovered. When βd_0 tends to zero, $i^\star/i_{\text{lim}}$ tends to[i] $(a^{\text{ox}} + b_2^{\text{ox}})^{-1}$ and the dispersion of ET rates is negligible.

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[i]This can be obtained from eq 6a with $\exp(\epsilon) \approx 1 + \epsilon$ and $\ln(1+\epsilon) \approx \epsilon$, so that

$$\ln\frac{a+b_2}{a+b_2\exp(\epsilon)} \approx -\ln\frac{a+b_2(1+\epsilon)}{a+b_2} \approx -\ln\left(1 + \frac{b_2}{1+b_2}\epsilon\right) \approx -\frac{b_2}{1+b_2} \quad \text{and} \quad \frac{1}{a}\left(1 - \frac{b_2}{1+b_2}\right) = \frac{1}{a+b_2}$$

For reductive catalysis, the ideal current equation is:[5]

$$i_{\text{lim}}/i - 1 = e_{\text{I/R}}\left(1 + e_{\text{O/I}}\right) + \frac{k_2}{k_0}\left\{e_{\text{O/I}}^{1/2} + e_{\text{I/R}}^{1/2}\left(1 + e_{\text{O/I}}\right)\right\} \tag{S9}$$

and once integrated over the values of k_0, the corrected current equation reads as eqs 6a and 8 but with

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\begin{aligned}
a^{\text{red}} &= 1 + e_{\text{I/R}}(1 + e_{\text{O/I}}) & \text{(S10a)} \\
b_2^{\text{red}} &= (k_2/k_0^{\text{max}})\left(e_{\text{O/I}}^{1/2} + e_{\text{I/R}}^{1/2}(1 + e_{\text{O/I}})\right) & \text{(S10b)}
\end{aligned}
$$